Anaerobic Digestion in Sustainable Biomass Chains

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Thesis

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A todos los seres con quienes comparto
el increible misterio de vivir,
unidos desde el corazón

Contents

Abstract

This thesis evaluates the potential contribution of anaerobic digestion (AD) to the sustainability of biomass chains. Results provide insights in the technological potential to recover energy and valuable by-products from energy crops and residues, and evaluate biomass cascades involving AD technology for their feasibility and desirability. Embedding AD in biomass chains addresses current constraints towards increased use of biomass for energy production considering land competition and environmental pollution. In this context, so far the major advantages of AD to improve energy efficiency and closing material cycles have received, thus far, limited attention. As part of the experimental research an Oxitop® protocol was refined for screening plant material suitable for anaerobic digestion based on their energy content. Environmental factors influencing the test outcome are the use of NaOH pellets for CO_2 scavenging, substrate pretreatment, microbial culture, and type of buffer. The use of NaOH pellets and substrate pretreatments were most influential on the results. By means of the developed Oxitop® protocol the relationship between plant ligno-cellulosic composition and the Biochemical Methane Potential (BMP) and first-order hydrolysis constant (k_h) was researched. The Acid Detergent Fibre (ADF) and the Neutral Detergent Fibre (NDF) as analyzed by the van Soest method were proposed as suitable plant characterization techniques for predicting BMP and k_h, respectively. The model proposed was further used to predict the biodegradability of 114 European plant samples identifying interesting crops and crop residues suitable for anaerobic digestion. Batch experiments on digestate quality during codigestion of maize silage and manure showed an increase of 20-26% and 0-36% in solublised NH_4^+ and PO_4^{3-}, respectively, after 2 months of digestion. The largest fraction of the inorganic nutrients was found in the liquid fraction of the digestate, i.e. 80-92% NH_4^+ and 65-74% PO_4^{3-}. Increase in manure content in the mixture showed a positive effect in the methane production rate. Digestion time and increased proportion of maize silage in the mixture positively influenced the availability of PO_4^{3-}. The added value of AD within different biomass cascades was evaluated by means of a sustainability framework developed for the purpose. The sensitivity analysis of the energy balance of an AD facility showed that the most important energy loss when a high value substrate such as energy maize is employed are heat losses induced by restricted reuse possibilities within the cascade. In contrast, when low energy substrates such as manure are used, indirect energy inputs embedded in infrastructure become significant. The developed sustainability framework was applied for the Colombian case. Results show that production of bio-ethanol from cassava is only sustainable from an energy and greenhouse gas (GHG) perspective when energy recovery from the process residues, using AD, is part of the process. The exact outcome of the evaluation largely depends on variables like substrate drying, type of fuel used, reuse possibilities for the digestate and type of applied AD system. During the study of other Colombian biofuel cascades the contribution of by-products was shown to be crucial, constituting 41-68% of the sum of all energy flows. For oil palm, sugarcane, panelacane and cassava, the estimated energy contribution of the by-products to the different biofuel systems fluctuate between 51-158, 122-290, 71-170, and 36-71 $GJ.ha^{-1}yr^{-1}$, respectively. AD had also a positive impact on nutrient recovery and water savings in the studied chains. The energy, nutrient and water benefits were set in perspective by giving an indication on the economic benefits and land savings potentially attainable under Colombian conditions.

Chapter 1

General Introduction

1 INTRODUCTION

For an expanding population living on a single planet, improving resource-use efficiency is not only a must but a fascinating challenge for human creativity. As of 2005 humanity's total ecological footprint was estimated at 1.3 planet Earths. As Wackernagel and Rees estate: "*human beings are in need of intelectually and emotionally accepting the fact that we are materially dependent on nature and that nature's productive capacity is limited*" (De Swaan Arons et al. 2004). The same authors calculated that a drastic 4-10 fold reduction in material and energy intensity per unit of economic output is required for global sustainability.

The combined effect of population growth and consumption trends mean that more resources, i.e. energy, land, water, nutrients will be demanded. According to UN estimations, at a medium growth rate, the 2050 world population will surpass 9 billion, which means a 37% increase as compared to the current 6.7 billion. This is an increase equivalent to the total size of the world population in 1950 (UN 2007b). In addition, and as a result of an increase in economic affluence, diets are expected to change towards higher meat consumption claiming more natural resources (Penning De Vries et al. 1997).

Similarly, energy consumption per capita is also expected to increase (Sheffield 1998). Current anthropogenic energy flow accounts for 440 EJ yr^{-1} and it is projected that will triple by 2050 (Niele 2005). Nowadays fossil fuels constitute approximately 80% of the energy consumed by humanity. Their finite quality and perceived short-term scarcity, aggravated by existing geopolitical tension, has induced energy instability and high prices fluctuation in the last years. Energy security risks to countries heavily dependant on external energy resources and also to those depending on their own finite energy sources are also a consequence of the existing tension (Dufey 2006).

A clean energy portfolio, which would make use of renewable and local/regional available resources is appealing as part of new strategies directed towards increased energy self-sufficiency and diversification. Amongst the most prominent renewable energy options in place are solar, eolic, geothermal, hydropower, and bioenergy. Solar energy is the largest of the renewable energy sources and appears as the easiest and cleanest means of tapping renewable energy. Solar technologies, however, have been criticized for their limitations both in energy storage and large-scale power generation, as well as for the energy requirements and pollution risks related to their fabrication (Abbasi and Abbasi 2000). Similarly, other renewable energy options show advantages and limitations both intrinsic to the technology and to their applicability in different contexts. As a result, most likely the future energy supply will comprise a diverse range of alternatives depending on technological potentials, regional possibilities, and type of end use demand.

Bioenergy is the name given to energy that originates from biological materials. Biomass resources used for energy production include agricultural and forestry residues, municipal solid wastes, and aquatic crops used for energy purposes. As a means of harvesting solar energy, plants are inefficient, being able to photosynthesize only 1-3% of solar radiation. Still, producing energy from crops and agro residues is attractive for many reasons:

(i) Bioenergy is a renewable form of energy as long as vegetation is carefully managed;
(ii) Bioenergy can be regarded as more easily accessible than fossil energy sources and may be exploited using less capital-intensive technologies;
(iii) Bioenergy provides a setting for industries to be brought into rural areas, which in turn can potentially create jobs and return money into rural systems and give the opportunity for local, regional, and national energy self-sufficiency across the globe;
(iv) In many cases, use of biomass can contribute to solve environmental problems, related for example to the inadequate management of waste, or undesirable biomass growth caused by eutrophication;
(v) Decrease in greenhouse gas (GHG) emissions coming from the use of fossil fuels can be a gain as they are replaced by carbon neutral biofuels. The savings in GHG emissions could become an appealing economic incentive, particularly to less economically developed countries, as encouraged by the Clean Development Mechanism. However, this holds true only as long as the harvesting of solar energy via biomass is not performed at the expense of fossil fuel expenditure.

Estimations on the contribution of crops to global energy supply vary widely depending on the assumptions made on the use of inputs in agriculture, the human diet and population growth. Scenarios exemplifying the influence of the different assumptions were explored by Wolf et al (2003). Worldwide large gaps in agricultural yield exist due to erratic rainfall, low soil fertility and especially lack of access to agricultural inputs such as improved seeds, fertiliser, pesticides and mechanisation and such situation is not expected to be solved in the short term (Rabbinge et al. 2008). Therefore, cautious rather than overoptimistic scenarios are preferred. In addition, extension of energy crops into currently uncultivated areas is highly questionable due to possible conflicts with nature conservation, competitive land use and high investments required. At a global level, the maximum production of biomass for energy in current agricultural area has thus been calculated to be 162 EJ yr^{-1} under prevailing suboptimal irrigation conditions and low external inputs (Wolf et al. 2003).

Other biomass materials of potential interest for energy generation are harvest residues, with an estimated global availability of about 3.8 billion ton. However, other uses are also being given to these organic streams, such as animal feed or soil conservation (Lal 2004; Nonhebel 2007) and hence they are not freely available in large quantities (Fischer and Schrattenholzer 2001).

Taking the above concerns into consideration, the present governmental and private enthusiasm related to the perceived bioenergy potential is rather frightening. In the last decade an unprecedented increase in the production of biofuels has taken place as a consequence of legislation enforcing their production. In the EU, the target is 5.75% biofuels for transportation in 2010, and 10% in 2020, which is equivalent to 20% in the share for renewable energy by 2020. Worldwide, the production of bioethanol almost doubled from 2000 to 2005 while biodiesel has expanded four times (van Dam et al. 2008).

Whereas today the amount of land used to produce biofuel feedstock occupies only 1% of world's cropland, in order to attain current targets on biofuels it is estimated that between 56-166 million hectares of land are required of the total 1500 million currently in use globally (Gallagher 2008). In parallel, demand of biomass of plant origin for food is expected to more than double by 2050 (Koning et al. 2008). The combined effect of the rising population, changing diets and demand for biofuels is estimated to increase demand for cropland in between 17% and 44% by 2020, biofuel production estimated to represent 11-83% of the additional global agricultural land requirement forecast (Gallagher 2008). Meanwhile, resource limits to satisfy food needs are already evident at regional level as shown for several countries in South-East Asia and Africa (Groot et al. 1998; Penning De Vries et al. 1997).

The previous considerations beg the question: Should bioenergy have a place at all within the spectrum of renewable energy alternatives? Considering the aforementioned facts (Wolf et al. 2003), potential does indeed exist. By year 2050 production of bioenergy from energy crops could cover 13% of the world energy supply, i.e. 162 EJ yr^{-1}÷ (440*3) EJ yr^{-1}. Still, the answer this question goes beyond the calculated potential. It demands a deeper debate regarding the way we want to allocate and optimize the use of existing limited resources.

Harvesting of bioenergy via energy crops maybe desirable under the appropriate socioeconomic circumstances and provided environment is taken care of. However, bioenergy still seems inefficient when considering its limited capacity to harvest solar energy and the inputs needed for its cultivation. On the other hand, important possibilities remain from incrementing efficiency in the use of already underutilized or misused resources. As Niele (2005) states: *"50-90 percent of the mass of industrialized-country environment flows goes up into the atmosphere…Waste products of economic activities are, for the most part, increasing…Today's economies act as a linear system: materials and energy are taken from the natural environment, put to a brief useful life, and then become waste in the atmosphere, on land, or in water"*. Thus, it is evident that the question regarding the place of bioenergy within renewable energy alternatives can be better approached in the context of maximising resource use efficiency via the design of sustainable biomass cascades that holistically address the various demands for biomass resources.

Technological considerations to attain this goal come now into discussion. Choices need to be made for the appropriate arrangement of suitable technologies adapted to fulfill the demands for food, feed, products and energy. As opposed to current linear use of resources, closed-loop technologies have a very special place within the array of possibilities for efficient biomass use. Closed-loop technologies can upgrade non-defined mixed resources, frequently mis-called "waste", into a reusable form of defined resources. In this way savings in direct and indirect resources are possible, i.e. water, nutrients, energy, land.

Anaerobic digestion (AD) is one of the technologies delivering a positive net energy output and allowing for closing energy, water, and nutrient cycles at different scales, thereby resembling the "no-waste policy" intrinsic to nature.

The process of transforming organic matter into methane takes place naturally in ecosystems. AD technology makes use of this feature for the conversion of different biomass resources to methane and a valuable stabilized organic by-product, i.e. digestate. Small scale decentralized technologies such as the Chinese dome digester and the Indian floating dome are centuries old. In the industrialized world, AD has been majorly employed to treat wastewater and wet residues. Major technological applications of AD have been the treatment of sewage-derived sludges and since the eighties, the treatment of industrial waste water (Lier van and Lubberding

2002; van Lier 2008). Other applications of the technology are the stabilization of (semi) solid wastes and slurries, crop residues and municipal solid waste (Mata-Alvarez et al. 2000).

Already in the eighties the possible energy contribution from crops and manure for producing biogas was recognized. However, economically, electricity from other sources was still cheaper and this kept the concept from penetrating the market (Baier and Delavy 2005; DeBruyn and Don 2004). Recently, the potential of AD has been rediscovered as having a central role in delivering higher outputs from finite biomass resources. During the last years, and as the result of specific governmental incentives, the construction of bioreactors for biogas production having energy crops as (co) substrate has become a reality in countries like Germany, Austria, and Sweden. In Germany, for example, it is estimated that in 1997 only 450 AD plants were functioning while 1800 were producing biogas in 2002 (Weiland 2003). Three years later, in 2005, the number of plants had duplicated from those present in 2002 reaching almost 4,000 units.

AD is considered a very flexible technology, accepting a wide range of different types of substrates, and implementation scales varying from very small to very big. In addition, the gaseous energy carrier can be easily converted to another energy form depending on local requirements. AD can be used to convert agricultural (by) products or energy crops into methane but it can also be part of different biomass arrangements, giving an adding value to residues in a rational way. The resulting methane can be directly used or can be upgraded to a higher quality gas suitable as vehicular fuel or for injection to the grid. Alternatively, it can be converted into electricity and heat in a combined heat and power (CHP) unit, or to heat or steam solely.

For the production of biofuels, AD is less demanding in resources such as water, nutrients, and fossil energy as compared to the more popular biofuel options like biodiesel or bioethanol. In a research studying possible self-sufficiency at farm level in Sweden, the use of biogas was favored as compared to the other two options in terms of its low relative need for arable land, concomitantly resulting in smaller soil emissions to air and water. Another advantage of AD is its potential to recycle plant nutrients (Fredriksson et al. 2006). Concerns regarding the technology are the fact that the fuel produced is a low energy density gas and not a liquid like biodiesel or bioethanol, implying that higher storage volumes are required. Another constraint are the possible emissions of GHG gases if technological units are not managed adequately (Baldassano and Soriano 2000). Nonetheless, as recently shown by Tilche and Galatola (2008), biogas may considerably contribute to GHG emission reductions in particular if used as a biofuel. The potential contribution of anaerobic digestion to GHG reduction as computed for 27 EU countries on the basis of their 2005 Kyoto declarations is in the order of magnitude of $3.9 \times 10^9 m^3$ CH_4 yr^{-1}. The sum of bio-methane from landfills and from sewage sludge corresponding to about 380 PJ yr^{-1}, and if considering also energy crops biogas has the potential of covering almost 50% of the 10% biofuel target of all automotive transport fuels for 2020, without implying a change in land use.

Taking into account the challenges of the current global resource crisis, this thesis strives to shed light on the potential contribution of AD to increase sustainability of biomass chains. Firstly, and considering the high availability of different plant materials to digest anaerobically the selection of those delivering maximum amount of methane and a favorable production rate is addressed. Therefore, within this thesis simplified methods are studied to assess the resource quality of biomass products in terms of both methane amount and digestate quality. Secondly, the contribution of anaerobic digestion technology to biomass cascades is analyzed from a theoretical and applied perspective using a sustainability framework designed for this purpose. Colombia has been selected as a case study area to apply the framework in order to gain further insight into the possibilities of anaerobic digestion for tropical developing countries. In Latin America, anaerobic digestion technology is gaining recognition for the treatment of waste and wastewater streams including municipal and industrial wastewater (Seghezzo 2004). In addition, Latin America is one of the regions where food security is not intrinsically impeded by resource scarcity (Koning et al. 2008). Tropical developing countries are also recognized to be favoured over temperate regions for the production of biofuels due to their more favourable agro-climatic conditions. Since 2001, a legal framework has encouraged biofuel production in Colombia. This legislative strategy aimed to increase self-sufficiency in fuel provision and diversify outlets for agricultural products. The aforementioned features of the Colombian case make the focus of this thesis an interesting challenge, and not in the least because it happens to be the author's home country.

In the following sections the main notions and challenges relevant to this thesis topic are presented. The concepts of anaerobic digestion, resource cascading and sustainable development, as well as background information about Colombian reality, are discussed. Thereafter the methodological approach as well as the scope and organization of this thesis are presented.

2 ANAEROBIC DIGESTION, AN APPEALING OPTION FOR BIOENERGY PRODUCTION

Anaerobic digestion is a technologically simple process, with a low to zero energy requirement that is used to convert organic material from a wide range of wastewater types, solid wastes and other types of biomass into methane. In the process, microorganisms derive energy and growth by metabolizing organic material in an oxygen-free environment resulting in the production of methane (CH_4), carbon dioxide (CO_2) and minimal quantities of other reduced gases like H_2. As an additional output also a residual solid and/or liquid by-product is obtained, which corresponds to the input material not converted into gas, the newly grown bacterial mass residues and the mineralized fraction including valuable nutrients.

The AD process can be subdivided in four phases according to the characteristic microorganisms and important conversions taking place: hydrolysis, acidogenesis, acetogenesis and methanogenesis (Figure 1.1). A complex culture of different microorganisms is part of the AD process allowing the transformation of the original substrate into methane gas and other by-products. In the hydrolysis step, complex suspended compounds and colloidal matter are converted into their monomeric or dimeric components, such as aminoacids, single sugars and long chain fatty acids (LCFA). Acidogenic bacteria excrete enzymes for hydrolysis and convert soluble organics into volatile fatty acids and alcohols. Acetogenic bacteria then convert volatile fatty acids and alcohols into acetic acid or hydrogen and carbon dioxide. Methanogenic bacteria use acetic acid, hydrogen and carbon dioxide to produce methane.

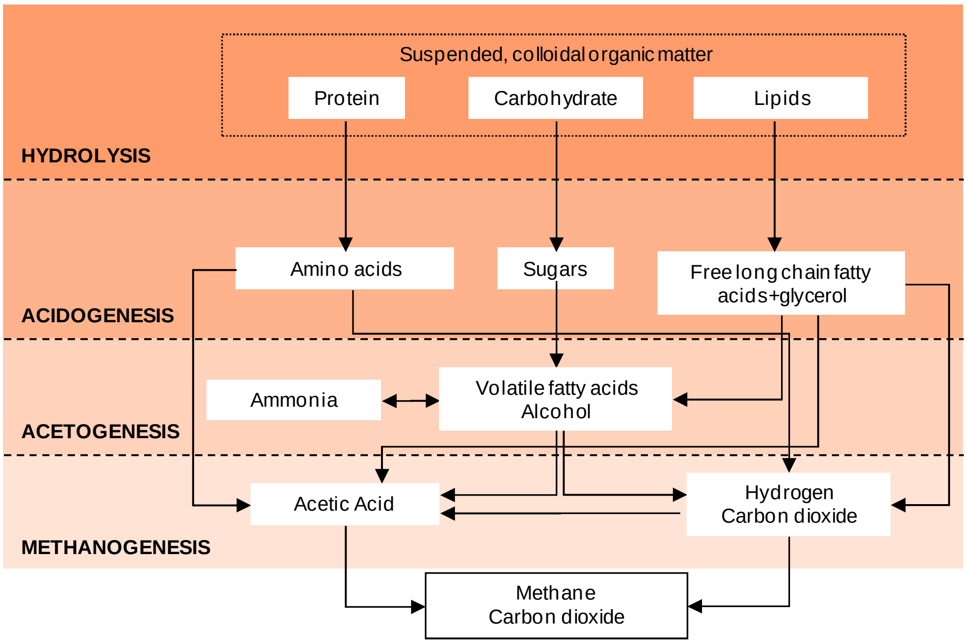


Figure 1.1 Simplified schematic representation of the anaerobic degradation process

As a means of realizing the bio-energy potential in organic materials, AD offers significant advantages over other technological options, such as:

(i) It is a single step process, which removes the need for secondary processing as is required for bio-ethanol and bio-diesel production;

(ii) AD is a flexible, non-sterile technology that can process wet or dry feeds and does not require pure or defined cultures;

(iii) It is a compact system easy to operate;

(iv) As a hydrocarbon fuel, biologically produced methane (CH_4) has almost identical characteristics to natural gas, which allows it to be used for different purposes. It can be used on-site as an energy source for heating, i.e. crop drying or processing, animal pens, farm buildings, or as fuel for tractors and other machinery. It can also be utilized for direct combustion or co-generation or as a gas source that could be added to the grid and transported for direct consumption or electricity production elsewhere. In the medium term biogas can also be used for feeding fuel cells;

(v) Bio-energy production through AD is particularly promising because of its low energy requirement and its contribution to diminish greenhouse gases emissions (Mata-Alvarez et al. 2000);

(vi) An additional interesting characteristic of the AD process is the residual semi-solid and/or liquid by-product i.e. digestate. The digestate has attractive characteristics for reuse in agriculture, as it is a stabilized product, rich in nutrients and mostly free of pathogens if manure or septage is not used as raw material.

AD performance varies according to the type of input material to be digested and to the technological configuration and operation of the AD unit. In both areas research challenges remain. This thesis is mainly concerned with the challenges related to the first issue, i.e. substrate selection for anaerobic digestion.

Both, the composition of the material itself and the test configuration for determining the methane potential will influence the screening process for the most suitable substrates in terms of energy. Further, considering the maximization of resource use efficiency complementarities among crops and residues are of interest both in terms of energy and digestate quality. These topics are studied in detail in Chapters 3, 4 and 5 of this thesis, following they are briefly introduced.

2.1 Influence of the experimental set-up in the determination of AD potential of plant material

To evaluate the effectiveness of anaerobic digestion of complex substrates two values are experimentally assessed: (1) the 'Biological Methane Potential' or degree of biodegradation and (2) the first order hydrolysis constant (k_h).

The extent and rate of degradation reported for biomass materials depend on the design of the tests used to assess their properties. Different experimental set-ups, i.e. batch or continuous, can be applied for their determination. In general the biological approach to determine anaerobic biodegradation or methane potentials leads to substantial uncertainty in the determination (Angelidaki and Sanders 2004). Several operational conditions have been reported to influence the outcomes of the described tests including: retention time; pH; temperature; type of hydrolyzing biomass; concentration of hydrolyzing biomass i.e. inoculum to substrate ratio; water addition; nutrient addition i.e. media (Angelidaki and Sanders 2004; Gunaseelan 1997; Rozzi and Remigi 2004b). The equipment used and the applied laboratory and analytical procedures also exert an influence in the outcomes (Muller et al. 2004; Rozzi and Remigi 2004b). Colleran and Pender (2002) highlighted the need to harmonize anaerobic biodegradation, activity and inhibition assays, especially in what refers to the standardization of the test inoculum, the test medium, the test conditions and the duration of the biodegradability tests.

Given that the diversity of lignocellulosic materials that can be converted into methane is immense, an accurate and simple method is needed to screen for those materials more appealing for digestion. In this thesis the revision and simplification of the BMP test is prioritized as well as the comparison of different test set-ups in the assessment of biodegradability and hydrolysis constant.

2.2 Influence of plant composition in its anaerobic conversion potential

The more than 250 thousand higher plants species in the world and the variations imposed by genotypes, cultivation methods, plant growth stage and plant parts, contribute to the diversity of materials potentially available for anaerobic digestion (Deren et al. 1991; Gunaseelan 1997; Lehtomaki 2006; Saint-Joly et al. 2000). Knowledge on the anaerobic biodegradability of such potential substrates is needed in order to screen for the most suitable ones to be part of sustainable agro-industrial ecosystems.

The time length and possible interferences of laboratory tests makes it desirable to find more straightforward relationships that simplify the screening process of suitable plant material for AD. In relation to their different chemical composition, different types of crop materials and residues will show different anaerobic biodegradability. Factors reported as influencing the degree of degradation achieved via AD are: relative lignin content; relative hemicelluloses content; mannose content (among hemicelluloses); relative cellulose content; proportion of structural and non-structural carbohydrates; cellulose cristallinity; degree of association between lignin and carbohydrates; the wood-to-bark ratio and the presence of toxic components (Gunaseelan 1997; Jimenez et al. 1990; Lehtomaki et al. 2003). These factors will also show variation among the same crop species according to different cultivation methods, plant parts, harvest time/plant age/growth stage, and genotypes (Deren et al. 1991; Gunaseelan 1997; Lehtomaki et al. 2003).

Previous research has attempted to define mathematical equations for estimating anaerobic biodegradability based on lignocellulosic substrate composition. One of the main attempts to get a straight forward relation between biomass composition and its methane potential was performed by Chandler et al (1980). They proposed that the sample lignin content was a useful parameter to predict the volatile solids destruction attained during anaerobic digestion of biomass. However, in latter studies such relation was not directly found for other materials, and it was proposed that other factors apart from lignin like the cellulose form should be considered in the assessment (Buffiere et al. 2006; Tong et al. 1990). As substrates other than crop material have been used (Chandler et al. 1980; Eleazer et al. 1997; Tong et al. 1990), differences in composition, i.e. presence of toxic compounds, proportion of structural and non-structural components, are expected and could potentially influence the computed outcome. Furthermore, the different studies vary in their methods for assessing BMP and characterizing plant material, which might very well explain their different outcome. Therefore, the question remains if a relationship can be found between the biodegradability of plant material and its physic-chemical composition.

2.3 Energy crops and/or residues for bioenergy production

Energy crop AD units can always be (co-)supplied with negative-value organic matter such as agricultural wastes, manure, waste streams from agro-industries, and/or biomass that is derived from stand aside lands including road sides, parks, natural resorts, etc. Combining wastes not only allows for more flexible utilization of the reactor volume according to resource availability, but it also allows for better treatability of wastes difficult to treat alone such as high protein or fatty wastes (Lier van et al. 2001). In Germany for example more than 90% of farm-based biogas plants use co-digestion to achieve higher efficiencies and add further stability to the process due to the addition of macro/micro nutrients and the enrichment of the microbial flora (Rintala 2005; Weiland 2005). During continuous co-digestion experiments having energy crops and manure as substrates, Lehtomaki (2005) found a 54% increase in the methane potential of a reactor fed with manure and grass (70:30) versus one treating only manure. Still for other crops the ratio was not so much significant. Recirculation of co-digestion effluent can also lead to higher inputs of water and nutrients into the agricultural system reduing the need for external inputs. Both energy quantity and the digested effluent quality are influenced by substrate composition and digestion time, therefore it remains a challenge to better define the trade-offs in terms of energy and digestate output of different crop residues mixtures. In general, the most appropriate combinations are yet to be defined. Obviously the choice on the substrate to use implies considerations at the technological, agricultural and environmental level, the quality of the end product and the opportunities for recirculation within the farming system. For example, when added to an AD unit, low value residues are turned into energy whereas existing environmental problems are ameliorated; on the other hand they diminish the net energy output per unit reactor volume. Trade-offs at this level are then of interest to better determine the extent to which AD can contribute to efficient and environmentally sound resource use.

3 RESOURCE CASCADING AND AD

Biomass cascading is an important concept to consider when striving for efficient biomass utilization. Resource cascading is defined as the sequential exploitation of the full potential of a resource during its use, and is one of the ways of improving efficiency of raw materials use. The principles of renewable resource cascading are:

(i) Appropriate application, i.e., resource application on the basis of its typical properties and the highest quality level that is possible.

(ii) Lifetime extension, i.e., increase of the lifetime of products and accumulated lifetime of all applications.

(iii) Quality-conservation or minimization of quality-loss in the next step in the cascade (Fraanje 1997).

Bioenergy is one of the possibilities for exploiting valuable biomass characteristics. Nonetheless, while considering the biomass-cascading concept it is clear that energy should be regarded only as one of the possibilities for the exploitation of useful biomass properties in a chain. In this way the role of bio-energy production could be better addressed following an integrated approach that leads to an effective utilization of the available biomass for food and non-food as well as energy production.

Bioenergy cascades can have many forms. Different types of biomass can be produced using different agricultural systems, while also diverse processes can be used to transform biomass in valuable energy and by-products with different applications (Figure 1.2).

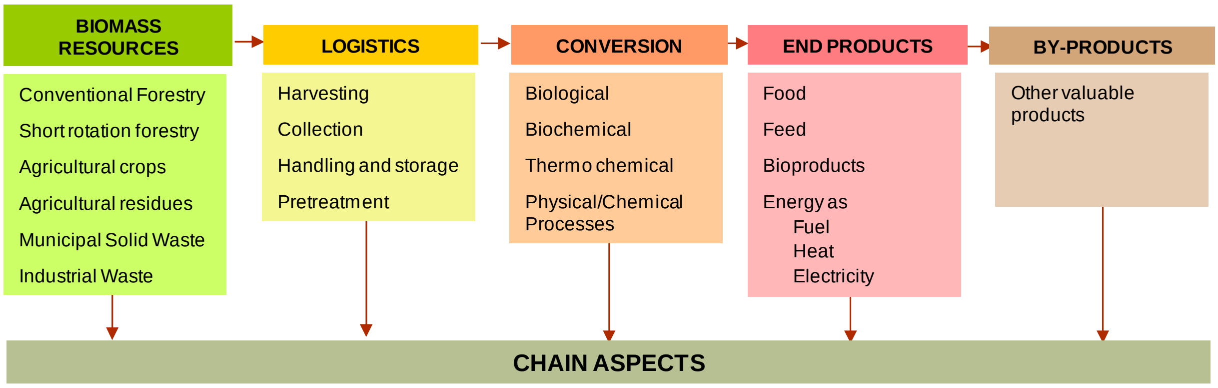


Figure 1.2 Bioenergy production elements (Adapted from different sources)

Current conditions of residues availability, environmental nuisances associated with them, the demands from the climate change agenda and the world transition towards a biobased economy are triggering new opportunities for anaerobic digestion (Ahring and Westermann 2004; Holbein and Layzell 2004; Mata-Alvarez et al. 2000; van Dam et al. 2005; Verstraete et al. 2004). AD is called to increase its contribution in two possible ways. Firstly, AD could be used to directly convert crops into methane as it has been recognized that the technology is competitive in efficiencies and costs to processes yielding other biomass energy forms including heat, synthesis gases and ethanol (Chynoweth et al. 2001). Secondly, new residues, raw materials for AD will be generated by other bioprocesses in the form of either diluted waste streams with important organic load or complex solid or semi-solid materials. Here the flexibility and simplicity of the AD process can add to the economical and environmental sustainability of the entire chain by decreasing waste via the production of extra energy in the form of methane. In addition, AD contributes to closing nutrient and carbon cycles at farm level by means of the reuse of the residual digestate as soil amendment (Figure 1.3).

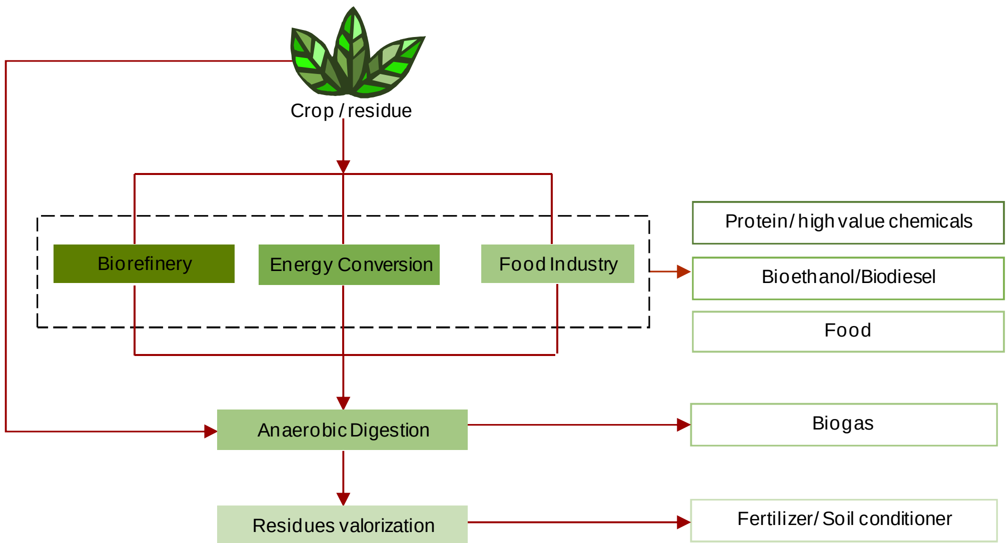


Figure 1.3 Possibilities for biomass cascade configurations having anaerobic digestion as a key element

Examples are in place where the contribution of the AD technology to biomass cascades is shown. Van Haandel (2005) showed how by digesting the vinasse and bagasse resulting from the production of ethanol from sugarcane in Brazil, 8,750 kWh are produced in addition to the 5,000 liters ethanol produced from the original total 65-75 ton wet sugarcane. In this way AD generates 23% energy of the whole chain. The added value of AD to a grass biorefinery concept has also been demonstrated in Switzerland (Baier and Delavy 2005). In this case AD adds value to the biomass chain by generating 500 kWh ton^{-1} grass in addition to the 0.4 ton ton^{-1} fibres, and the 0.12 ton ton^{-1} proteins, originally produced from the initial biomass.
Most of the technological research performed in the bioenergy field focuses on one stage of the process and the inner system possibilities for optimization of the process efficiency. However research is needed for the optimization of the full chain considering the demands from the outer system. The question here is how boundaries and cascade conditions influence the role that AD can add to different biomass chains.

4 THE SUSTAINABLE DEVELOPMENT CONCEPT GUIDING THE QUEST

The concept of sustainable development is defined by the Brundtland commission in the report Our Common Future (UN 1987) as *"the development that meets the needs of the present without compromising the ability of future generations to meet their own needs"*.
This definition of sustainable development is open to various interpretations. They largely depend on how the needs of present and future generations, and the earth's carrying capacity to supply them are defined. Such questions can not be fully answered by scientific analysis hence normative choices need to be made. Thus, policy development is guided by a certain interpretation of sustainability and by a perception of the risks associated with projected trends in societal environmental developments. In 'Sustained Risks: a Lasting Phenomenon', the Scientific Council for Government Policy (WRR, 1995) examines the various ways in which the concept of sustainable development can be manageably translated into policy terms. This report argues that it is impossible to work with an objectively fixed elaboration of sustainable development. In order to elaborate the concept of sustainability as a genuinely operative policy concept, normative choices are necessary in relation to the identified risks and uncertainties which need to be made explicit. Therefore the WRR study proposes four action perspectives (utilising, managing, saving, conserving) that differ in (i) the degree to which they avoid or accept environmental and societal risks, (ii) the degree to which they connect to adaptations in ways of production or consumption patterns, or (iii) the degree to which they trust in technology or in laws and regulations.
Working from such perspectives allows to look into the future and to develop scenarios about sustainable development that include different opinions in society. In this context, the contribution of science can be then seen as the development of sustainability frameworks devoted to give input to the decision making process.
Three domains are usually employed for the operationalization of the sustainability concept, the so-called 3Ps: People, Planet and Profit. People concerns with the societal implications of human actions. Planet concerns the environmental ones including effects in different

compartments, soil, water, air, biodiversity, energy. Profit refers to the economical consequences of the evaluated intervention, i.e. income generation. According to the specific problematic to be analyzed, criteria and indicators are defined in the mentioned domains.

Within this research, sustainability is considered for the evaluation of the role of AD in biomass cascades. The guiding line that the sustainable development concept provides in this case is that technological processes should be designed to fit the characteristics of their surrounding environment in a way that maximization of compatibility is achieved.

Within the framework of the WRR previously introduced, the scientific work presented in this thesis can be described as an effort to quantify the sustainability benefits that can be brought about by trusting in a specific technology, i.e. anaerobic digestion, as it shapes the way bioenergy production is performed, bringing a shift from energy plantations to resource cascading. The findings are contextualized into Colombian reality by showing the implications in increased in resource use efficiency created by such technological intervention. In the discussion insights are given into how present laws and regulations, and consumption patterns in Colombia shape the possibilities of AD.

Anaerobic digestion has been identified as a sustainable technology from a waste management perspective. If compared to other alternatives like composting and landfilling, the sum of its advantages will outweigh other options: lower greenhouse gas emissions, positive energy balance, removal of CO_2 and the possibility of carbon and nutrients incorporation into the soil in a stabilized form (Mata-Alvarez et al. 2000). However, there are still questions regarding the possibility of having methane losses when handling the biogas and they need to be considered in the evaluation. Methane losses from storage of the digestate, the biogas upgrading and the fuel utilization contribute to greenhouse gas emissions (Baldassano and Soriano 2000). Two recent system analysis studies also shed light on environmental performance of anaerobic digestion systems. When comparing different anaerobic digestion systems in terms of their fuel-cycle emissions based on six different raw materials, Borjesson and Berglund (2006) concluded that the emissions will be greatly affected by the properties of the raw material being digested, the energy efficiency of the biogas production and the status of the end-use technology. The same authors in a different study assessed the energy balances of different biogas systems using different raw materials(Berglund and Borjesson 2006). They concluded as well, that large variations in energy efficiencies could be found in the systems studied. These variations depend on the properties of the raw material under study, system design and allocation method.

Given that anaerobic digestion produces a valuable energy carrier from biomass, frameworks for assessing the sustainability of bioenergy interventions are of relevance. Operationalizing the sustainability concept specifically for evaluating biomass use for energy purposes is an important effort which since recently has been undertaken at international level. Whereas sustainability as an objective and measurable end status for the bioenergy industry cannot be established, sustainable development in the domain of bioenergy can be enhanced by design, implementation, monitoring and constant adaptation of robust, comprehensive and mandatory sustainability indicators.

Table 1.1 provides an overview of the areas of concern found relevant for the sustainability certification/evaluation of bioenergy systems.

Due to the amount of sustainabiity criteria and indicators, their selection and priorization is of main importance. Hence it is needed that the arguments justifying choices are made explicit.

Given the political character of sustainability definitions, building consensus among stakeholders on the selection and definition of such indicators is a complex task. In their review of certification initiatives at the national, international, private, governmental and non-governmental level, van Dam et al (2008) recognize that differences in priorities among criteria, strictness and level of detail are a main challenge. The situation is accentuated as a result of the numerous stakeholders involved, for example Lewandowski and Faaij (2006) identified about 45 organization/systems at world level directly or indirectly give input to the development of certification systems for bioenergy production.

Table 1.1 Overview of the areas of concern for the sustainability assessment/ certification of bioenergy systems.

Study	**Areas of concern**			
	Environmental	**Economic**	**Social**	**Institutional**
Cramer Report (Cramer 2006)	Greenhouse gas balance; Carbon balance; Energy balance; Biodiversity protection; Soil quality; Water depletion and quality; Air quality;	Local economic prosperity;	Local social well-being; Human/property/use rights; Competition with food and other applications;	Governance
Lewandowski & Faaij (2006)	Protection of the atmosphere; Preservation of existing sensitive ecosystems; conservation of biodiversity; conservation and improvement of soil fertility/ avoidance of soil erosion; conservation of ground and surface water; combating deforestation; combating desertification and drought; landscape view; conservation of non-renewable resources; waste management; environmental additionality;	Viability of the business; Long term perspective; Strength and diversification of local economy; reliability of resources; yields; no blocking of other desirable developments; improvement of conditions at local level	Labour conditions; protection of human safety and health; Rights of children, women, indigenous people and discrimination; Access to resource ensuring adequate quality of life; Food and energy supply safety; Capacity building; Combating poverty; Democratic participation; Land ownership; Community (institutional) well being; Fair trade conditions; acceptance; improvement of conditions at local level	Compliance with laws and international agreements; traceability; strengthening the role of non-governmental organizations
Smeets et al (2008)	Water use, water pollution, biodiversity, soil erosion, fertilizer use, genetically modified organisms, sugarcane burning, greenhouse gas emission and energy balance	Competition with food production, employment, income distribution, land tenure, wages, worker conditions and worker rights, child labour, social responsibility and benefits, competitiveness		

Beyond the stakeholders involved, selection of criteria and indicators needs to be performed not only in relation to their relevance but also in view of their operationability and verifiability. Not all aspects that need to be addressed for the sustainability assessment of bioenergy can be adequately measured as required by a certification system. In some cases, management rules rather than specific targets are better verifiable and useful as in the case of ecological indicators (Lewandowski and Faaij 2006). For social indicators, the definition of key terms such as equity, need to be specified and incorporated in normative decisions for them to be of use. The necessity of developing new methodologies for the assessment of GHG and energy balances and change in land use has been highlighted (van Dam et al. 2008) as well as those appropriate for the assessment of impacts on employment, biodiversity and food security (Smeets et al. 2008). Such difference in the nature of certain sustainability criteria also influences their legal feasibility for certification purposes. For example, when analyzing the obstacles in the implementation of the Cramer criteria taking into account European law and WTO treaties, whereas environmental criteria were found possible to be enforced although requiring time for their actual implementation, the principles regarding social wellbeing and economic prosperity were found to be unworkable in practice (van Dam et al. 2008). The complexity in the operationalization of the sustainability concept for bioenergy has lead to the necessity of assessing sustainability on a case by case basis. Currently NGOs and international organizations developing guidelines and certification standards have opted for having methodologies tested in the field (van Dam et al. 2008).

Since AD sustainability impact is related to the conditions of the biomass cascade and the surrounding environment where it is embedded, frameworks devoted to such analysis are also of interest. Dornburg (2004) developed a methodology to quantitatively evaluate the efficiency of multi-functional biomass systems, parameters included are savings of non-renewable energy consumption, greenhouse gas (GHG) emissions, land use, and total costs of the systems compared. Among the results, the author shows that economic attractiveness of multi-product crops depends strongly on crop yields, material market prices and crop production costs while GHG emissions are strongly influenced by the specific GHG emission reduction of material use, reference energy systems and the emissions coming from crop production. Because of the different performance of multi-crop systems in relation to this set of criteria, they conclude that a case by case evaluation is necessary as multi-product use cannot be regarded a-priory as an option increasing the performance of bioenergy systems.

From the previous it is clear that although anaerobic digestion technology as such does possess attributes regarded as essential for sustainability, different factors concerning the system design and the context conditions will define the contribution of anaerobic digestion to the sustainability biomass cascades. Hence a decision-making framework having sustainable development as an inspiration needs to be developed.

5 COLOMBIA AS A CASE STUDY AREA AND CASSAVA AS A CASE STUDY CROP

The possibility of creating energy and other products out of biomass in a competitive way might improve the economic conditions of farmers in developed and developing countries (Ahring and Westermann 2004). Tropical developing countries in Latin America are perceived as having good potential to produce bioenergy as they possess large land areas, good crop production conditions in terms of sun hours and low temperature fluctuation, and cheaper production costs compared to Europe (Faaij et al. 2002; Verstraete et al. 2004). At the same time as previously shown (See 1.1) concerns are in place regading the use of biomass for energy.

Colombia can be seen as a country exemplifying such a panorama, having a wide range of opportunities for biomass use as an energy source and rasing concers due to the rapid developments taking place in bioenergy production. The already existing expertise in the production of crops with an interesting energy potential like sugar cane, oil palm and cassava, the availability of crop residues, the existence of isolated rural areas not connected to the energy grid, the recent trends in the national energy policy and the necessity of making the rural sector a viable one in a situation of instability and unemployment, have raised interest in bioenergy production from crops and agro residues as an appealing option.

Recently, renewable energy options are gaining relevance at the National level. Although their contribution is still limited, energy generation projects via wind power, bioethanol and biodiesel are a reality. Various universities and research centers have undertaken action in the field of biodiesel driven by the expectation of importing diesel in the short term, which will make this a viable option in economic terms and also because of the incentives given to oil palm growing. Bioethanol is also receiving major attention and much more specific incentives. Law 693 of September 19 2001, states that gasoline used in urban centers with populations higher than 500,000 inhabitants must contain oxygenated compounds like carburant alcohols in the quantity and quality stated by the National Ministry of Mining and Energy (UPME 2003). The norm is already implemented and currently 70% of the gasoline in Colombia is oxygenated, at a 10% volume mixture of bioethanol to gasoline. Bioethanol is currently being produced from sugarcane, panelacane and cassava. Since 2008 biodiesel is also being produced and is currently blended with diesel at a 5% volume mixture. As a result of the previous, increase in land use for biofuel feedstock is taking place and simultaneously concerns related to competing claims on resources are raised.

Biogas has a marginal contribution nowadays and it is not mentioned in the current biofuel policy. However, the technology as such is not unknown, as it has played a major role in wastewater treatment projects and in on-farm applications especially for the treatment and reuse of manure. Lately it is also receiving major attention in the field of municipal solid waste management. Opportunities exist for taking further advantage of anaerobic processes as its application up to now has mainly focused in the treatment of pollution sources with a very limited use of the biogas produced as well and of the solid and liquid effluents.

There is a lack of knowledge regarding the possibilities that AD offers as part of different biomass cascades in Colombia. Setting the grounds on the numerous opportunities anaerobic digestion offers is therefore necessary in order to raise awareness.

Cassava has been selected as a case study crop due to its promising character as an energy crop, the lower amount of research available in comparison with e.g. sugarcane, and the interesting socio-economic factors that surround its production and transformation. Cassava is one of the main agricultural crops in Colombia. In 2005, the production of cassava in Colombia amounted to 2 megatons, which is about 8% of the total agricultural production of the country, corresponding to 180,600 ha of arable land or 6% of the available area. Cassava in Colombia is cultivated under various climates and soils and has traditionally been planted by small farmers at plots less than 10 ha of cassava per farm, mostly intercropped with maize, beans and yams. More recently, larger plantations of more than 10 ha of cassava per farm have been started in response to a boost in demand from cassava processors. This demand is driven by the Colombian government, which in the mid-1980s recognized the potential of cassava and began a programme involving a range of research and development institutions and farmers' groups to improve the efficiency of cassava production, develop new cassava based products and processing methods, and expand markets.

The use of cassava for bioethanol production is becoming a popular option in Asian and African countries. In Colombia its production at big scale is being promoted by the National government. The production of bioethanol as biofuel and the supplementation of the chain with anaerobic processing of by-products (vinasses, bagasse, trash), and of complementary substrates produced on-farm like animal manures, is desirable considering that a bioethanol production facility produces a considerable amount of liquid and solid by-products. Furthermore, opportunities exist for decentralized, cheaper and socially advantageous bioenergy production from cassava considering that biofuel and electricity needs are not satisfied in many areas of the country. The incorporation of an anaerobic digestion facility into the chain at different scales could deliver additional benefits like the reincorporation of nutrients and residual carbon into the land, the flexible end-use of the biogas and the avoidance of negative value by-products generation, and the delivery of valuable biogas for farmers to use in different applications.

6 MOTIVATION AND PURPOSE OF THIS THESIS

The world's transition towards a biobased economy and the renewed interest in biomass as a source of renewable energy create a panorama of new opportunities for AD. AD major advantages as a technology able to add value to biomass chains by allowing improving energy efficiency and closing material cycles have, so far, received a limited protagonism and deserve to be further explored.

Accounting for variability in technological options and context conditions is of importance when considering the possible role of anaerobic digestion in biomass cascades. The contribution of AD can vary according to the different substrates that can be used, different end uses for the biogas and digestate, and different scales. Furthermore, the feasibility of the cascades configured can vary according to context characteristics. Therefore, in order to fully exploit the potential of AD it is important to clearly define the niches in which AD is not only feasible but also desirable.

A lack of methodology in this respect is evident as well as the existence of knowledge gaps regarding technological potential and context restrictions.

With respect to the technological potential, comparable data available on the AD potential, i.e. biogas production and digestate characteristics of different biomass materials is limited. In addition, current procedures for assessing biogas production in terms of quantity, quality and rates are not standardized, whereas many current the procedures are costly and time demanding. Due to the immense variation of biomass that can be converted to methane, an accurate and simple method to assess their methane potential and screen for those more appealing, is needed. A systematic understanding of the relation between input and output of the process would be most valuable since it would allow for a quick screening of plant species attractive for their methane potential and digestate properties, the latter being of importance for either agricultural reuse purposes or for other uses of the digested fibres.

On the other hand, the context as defined by local conditions as well as by the restrictions imposed by the market and policy framework will narrow down the spectrum of feasible and desirable cascade configurations involving anaerobic digestion. Hence, other factors need to be considered in addition to the methane potential of biomass, like the land use and availability, food security, driving forces behind the energy demand, potential biomass production and the availability of other substrates for codigestion, i.e. manure, municipal solid waste, and/or other agro-residues. Colombia as a case study offers interesting challenges to explore possibilities for AD given the current bioenergy legislation.

Building from the presented concerns the main goal of this thesis is *to assess the contribution of anaerobic digestion to the sustainability of biomass chains, by gaining insight in the technological potential of anaerobic digestion to recover energy and valuable by-products from energy crops and agroresidues, and evaluating biomass cascades involving AD technology for their feasibility and desirability*.

7 SCOPE AND ORGANIZATION OF THIS THESIS

This thesis research has been built as an integration of experimental research and systems analysis studies as shown in Figure 1.4. The experimental phase has been oriented towards two goals, i.e. (i) to develop simple methods for screening plant material suitable for anaerobic digestion, and (ii) to gain insight on the trade-offs in terms of energy and digestate output during (co)digestion of crop and residues. Such aspects are covered in Chapters 3, 4 and 5 of this thesis. In Chapter 3 an OxiTop® protocol is developed for screening plant material suitable for anaerobic digestion. The chapter starts by recognizing the advantages and limitations of the OxiTop® system and, in the quest of the system optimization revisits the influence of different variables in the BMP test, i.e. addition of NaOH pellets, particle size reduction, microbial culture and type and molarity of the buffer employed. Guidelines and recommendations are provided for the utilization of the OxiTop® system for screening biomass for anaerobic digestion based on their energy content. In Chapter 4 the relationship between plant ligno-cellulosic composition and the BMP and first-order hydrolysis constants is researched by means of the developed OxiTop® protocol. Empiric models are developed and statistically tested for their validity. They are then compared with conceptual models that propose intrinsic biodegradability properties to individual fiber components. Following, empirical and conceptual approaches are compared based on their predictive ability. The model chosen is then contested with data from previous studies, and used to predict the biodegradability of 114 European plant samples, further identifying interesting crops for sustainable crop rotations.

In Chapter 5 the influence of retention time and substrate mixtures in methane production and digestate quality is researched during codigestion of maize silage-manure mixtures. The increase in nutrient availability is researched in the liquid and solid fraction of the digestate. The results are set in perspective by performing calculations on the energy value of digestate and manure for a farming system producing maize silage.

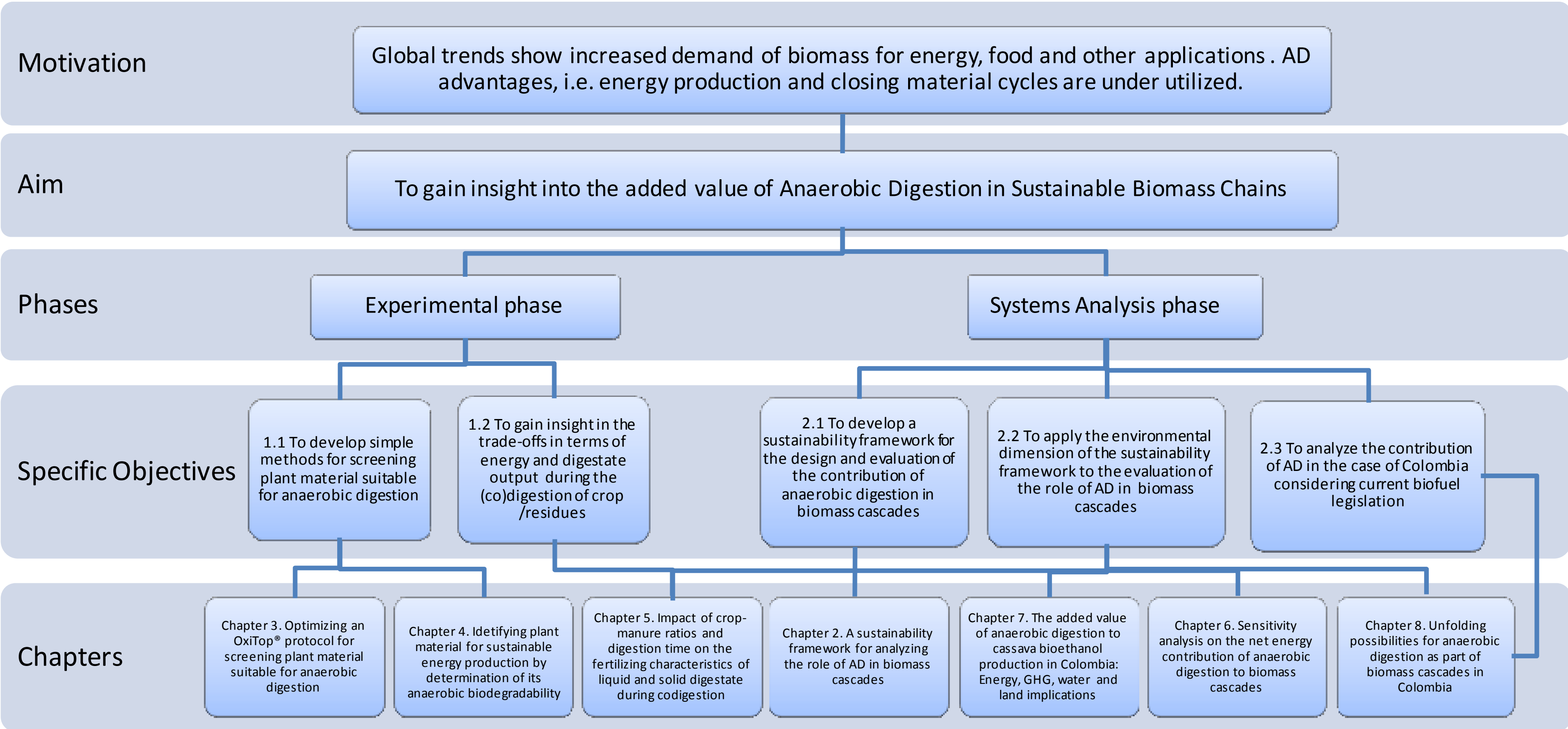
In the second part of the thesis the focus has been on exploring the added value of AD within different biomass cascades guided by the sustainable development concept. The objectives in this case were (i) to develop a sustainability framework for the design and evaluation of the contribution of anaerobic digestion to biomass cascades; (ii) to apply the environmental dimension of this framework to the evaluation of the role of AD in alternative biomass cascades; and (iii) to analyze the contribution of AD in the case of Colombia considering current biofuel legislation.

In Chapter 2 of this thesis a categorization of the role of AD in biomass cascades is performed and described based on the cascade chain theory. Following a sustainability framework is proposed for evaluating the role of AD in biomass cascades considering the 3P domains: People, Planet, Profit. The environmental dimension of the developed framework is further elaborated and developed into a model that allows assessing the contribution of AD in energy and land terms. In Chapter 6 of the thesis a sensitivity analysis of the energy balance of an AD facility is conducted as an extension of the model generally described in Chapter 2. The implications of the cascade conditions in the configuration and net energy output of the AD process are theoretically discussed. Conditions considered in the analysis are surrounding environment, input characteristics, type of energy demand and type of digestate demand. As a means to exemplify the sensitivity of AD systems three scenarios combining boundary conditions and system demands are applied to three alternative substrates, i.e. maize silage, manure and sugarcane vinasse.

Chapter 7 of the thesis goes beyond theoretical calculations by applying the developed sustainability framework to the assessment of the added value of AD to cassava bioethanol cascades in Colombia. Systems configurations are chosen based on current trends and possibilities and results depict how differences in location, farming systems, biofuel technology and presence of AD affect the energy, GHG, water and nutrient balances and land use.

Following the detailed analysis of Chapter 7, in Chapter 8 the overall contribution of AD is set in perspective by analyzing the possibilities that this technology could offer in Colombia in view of the present bioenergy legislation promoting the production of biofuels from sugarcane, panelacane, cassava and oil palm. General calculations are performed to show the potential benefits from AD for alternative cascades. The energy benefits are set in perspective by giving an indication on the land savings potentially attainable and the impact of the current economic framework. Finally, in Chapter 9 the results of this thesis are summarized and discussed following three categories of analysis, i.e. scientific achievement, methodological impacts and societal consequences.

Figure 1.4 Approach and organization of this PhD thesis



Chapter 2

A sustainability framework for analyzing the role of AD in biomass cascades

Abstract

In this chapter a framework for the design and evaluation of the role of anaerobic digestion in biomass cascades is developed. The chapter starts by proposing a typology of biomass cascades based on the roles that AD can serve, i.e. multifunctional, protagonist or contributive. Thereafter the typology is described following the four dimensional model of the cascade chain theory by Sirkin and ten Houten, i.e. resource quality, utilization time, consumption rate and savageability. Possibilities for optimization of the role of AD wirhin biomass cascades are also discussed considering the principles for optimal resource utilization proposed by the same theory. Based on the multidimensional character of the sustainable development concept, a sustainability framework is proposed suggesting environmental, social and economic objectives, criteria and indicators. The environmental dimension of the framework is further elaborated and operationalized by means of an energy model.

Pabon-Pereira CP, Slingerland M, van Lier JB, Rabbinge R

1 INTRODUCTION

Resource cascading defined as the sequential exploitation of the full potential of a resource on its path towards equilibrium, is a strategy to improve efficiency of materials use (Fraanje 1997; Sirkin and Ten Houten 1994). Anaerobic digestion (AD) is a technology that can play an important role in increasing sustainability of biomass cascades by transforming different organic flows into useful products and ultimately usable energy and by allowing the recirculation of nutrients and water contributing to the closing of material cycles. Whereas the flexibility of the technology can be regarded as its main positive attribute, it is also its main challenge when its contribution towards sustainability is to be assessed, as biogas systems can take many forms and the differences among possible systems make them complex to study (Borjesson and Berglund 2007).

In this chapter, first the possible value of AD in biomass chains is described and elaborated based in the cascade chain theory. Following, a sustainability framework is defined for assessing the impact of AD in biomass cascades. The framework is built upon the multidimensional character of sustainability, proposing environmental, social and economic objectives, criteria and indicators. Thereafter the environmental dimension of the framework is further elaborated by proposing a model for its operationalization.

2 UNDERSTANDING THE ROLE OF AD IN BIOMASS CASCADES

2.1 Typology of AD biomass cascades

Biomass systems can have many forms, the biomass following different routes during its production and utilization time. The differences among possible systems make them complex to study. The feasibility of a multifunctional biomass system is defined by the main application of biomass(Dornburg 2004). Among the many applications of biomass are the production of food, feed, construction materials, bioenergy and other biochemicals.

The production of methane and digestate through AD is only one of the many possible biomass applications and the role of AD needs to be set into context. AD can have a more or less protagonist role as part of a cascade and accordingly conditions imposed by the context can be more or less restrictive. Restrictions can be for example only those set by the overall boundary conditions where biomass is produced or, added to the previous, those imposed by existing industrial systems transforming biomass resources. The two levels impose different degrees of freedom or inventive scope in what refers to the configuration of biomass cascades. Accordingly, the role of AD can be approached either from a *multifunctional perspective*, a *protagonist perspective* or a *contributive perspective*. In the *multifunctional perspective*, the role of AD is that of being part of a biomass system envisaged towards the maximization of its environmental, social and economic outcomes where no restrictions are imposed by existing transformative production processes. In the *protagonist case*, restrictions are as well not imposed by existing transformative production processes but in this case, AD is the main process in the chain, like in the case of energy crop cultivation for energy production. In the *contributive perspective*, AD is incorporated within existing cascades, its added value being defined as a function of the complementary features it can establish with the existing processes. These processes will influence both the quantity and quality of the by-products and the possibilities for reuse of the energy and digestate after the AD process. In this sense, the configuration of the other applications producing and transforming the original biomass imposes restrictions, which limit the sustainability outcome of the entire system and the specific contribution of AD to the chain (Figure 2.1).

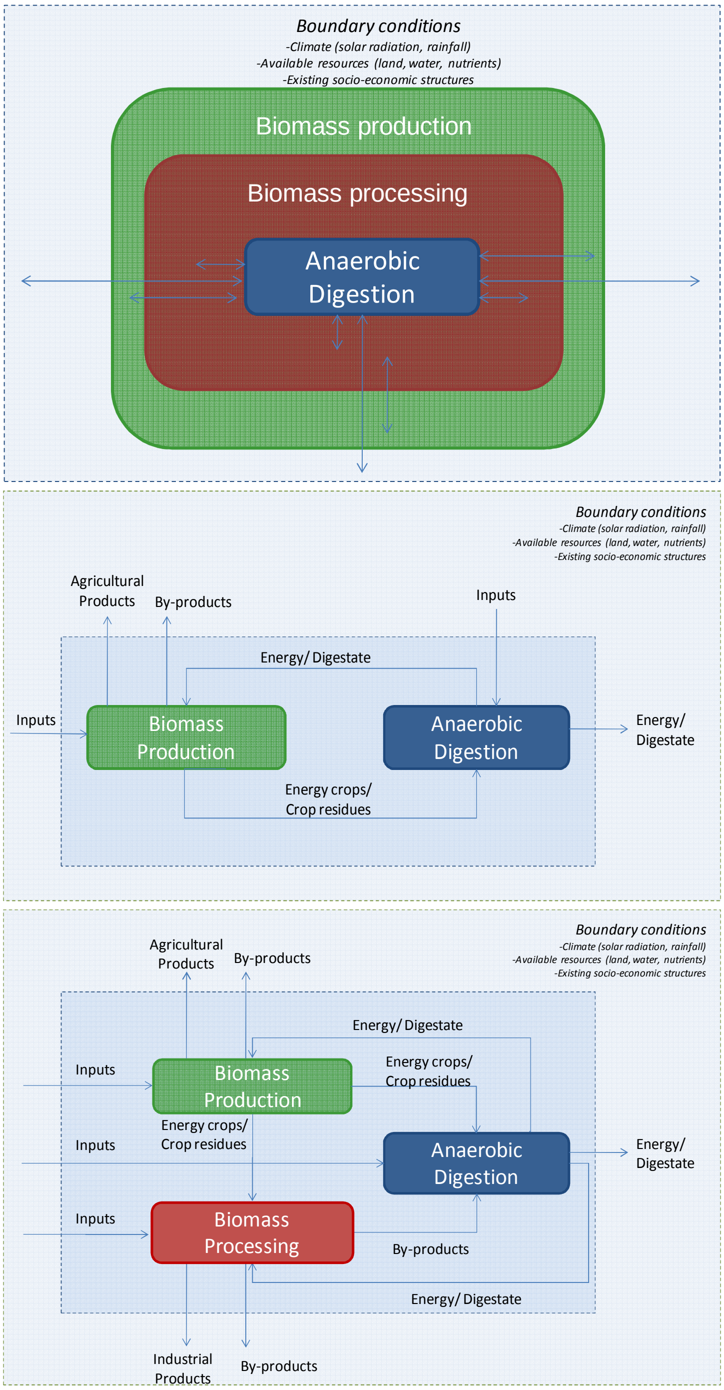


Figure 2.1 Multifunctional (top), protagonist (middle) and contributive perspective (bottom) for defining the role of AD in biomass chains.

Sirkin and Ten Houten (1994) proposed the concept of "cascade chain" expanding the definition of resource cascading into an operational framework for determining the efficiency and appropriateness of a given resource exploitation within a given context. Their model uses four dimensions for defining or describing a cascade: resource quality, utilization time, consumption rate and salvageability (Figure 2.2).

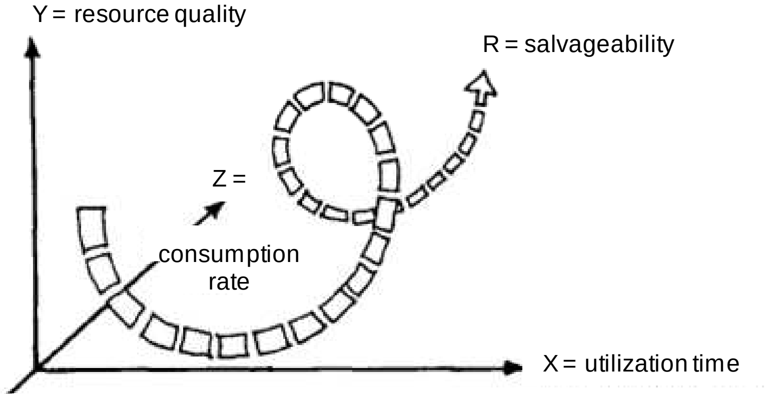


Figure 2.2 The four-dimensional cascade model as comprised of four dimensions after (Sirkin and Ten Houten 1994)

Resource quality refers to the extent to which a given resource is fitted to the task being performed. *Utilization time* refers to the time span over which the resource is used in the cascade. *Consumption rate* refers to the rate in resource flow and is a fundamental dimension in relation to sustainability as it relates to resource availability for coming generations. Finally, *salvageability* refers to the degree to which the resource quality of a material can be recirculated to the same chain or alternative cascade chains. The four-dimensions defined in the cascade chain model are used to describe the differences in the role of AD from the three defined perspectives as shown in Table 2.1.

Table 2.1 Three types of AD cascades described based on the four-dimensions following the cascade chain theory

Perspective / Dimension	Multifunctional	Protagonist	Contribution
Resource quality	Best fitted following the maximization of the environmental sustainability criteria	Best fitted for AD following the maximization of the energy output	Available from the agricultural and industrial processes already in place
Utilization time	Maximized by the appropriate use of the different fractions of the biomass	Defined by the AD process	Prolonged by the introduction of AD for the treatment of by-products
Consumption rate	Adjusted to fit the renewability of the resources employed	Adjusted to fit the energy demand	Fixed according to the main use of the biomass
Salvageability	Optimal as AD potential for closing cycles is fully exploited	Allowed by the incorporation of the digestate in the field	Defined by the other industrial processes involved

2.2 Applying the principles of the cascade chain theory for optimizing biomass cascades

The second element of the cascade chain theory considers four principles for achieving optimal resource utilization, allowing moving from the description of a cascade into the optimization of the design process and the comparison of alternative utilization routes for a given resource. The principles are: appropriate fit, augmentation, consecutive relinking and balancing resource metabolism.

Appropriate fit principle. This principle concerns the harmonization of resource quality to task demands. In relation to this principle the resource quality required for AD should be defined in operational terms as well as the trade-offs in terms of efficiency and productivity in dependence to the quality of the used resources.
It is inappropriate to exploit high quality resources for tasks that could be performed with lower quality ones. Here the question arises on whether it is desirable to use high quality resources such as energy crops as raw materials for biofuel production, i.e. protagonist perspective, when the same task can be performed by resources available in the form of residues, i.e. contribution perspective. The possible inappropriateness of the protagonist perspective becomes even more relevant when realizing that much of the ecological impact of bioenergy systems is induced by raw material production, mainly by the use of fossil fuels in cultivation, harvesting and transportation as well as in fertilizer production (Krotscheck et al. 2000). This aspect has been ratified in the study by Berglund and Borjesson (2006) were it was found that the energy input into biogas systems overall corresponds to 20-40% of the energy content of the biogas produced.
The principle of appropriate fit also implies that uses of biomass resources like food, feed, fertilizer, products from the biorefinery industry, and even other bio-fuels, which are competing for the same resources need to be considered and given priority according to the context conditions. The high quality biomass can be used for producing different products in a biorefinery approach that allows for maximization of sustainability, i.e. multifunctional perspective. If considering only environmental criteria the crucial question is which product or combination of them maximizes resource utilization, resource use efficiency and minimizes pollution. Still, recalling the social and economic sustainability dimensions the most efficient process might not be the most desirable, i.e. biogas production from maize is expected to be more energy efficient as for example dairy production from maize but the production of milk might be preferable if other energy sources are in place.

Augmentation and consecutive relinking. These two principles are related to the prolongation of the utilization time of a resource. In the case of augmentation, the prolongation is carried out within the same cascade, whereas in consecutive relinking the life span of a material is prolonged via other cascades. In both cases the effort required for this prolongation of the utilization time should be considered, as it should never outweigh the net utility of the exploitation. In the case of AD, the environmental benefits of producing methane and recirculating resources should outweigh the efforts, i.e. the transport of digestate required to allow the recirculation of water and nutrients and other energy requirements from the system.

Balancing resource metabolism. This principle addresses the issue of resource scarcity and as such is in direct relation to the resource utilization criteria. There should be a balance in resource exploitation with its regeneration capacity. In the contribution perspective, the consumption rate of AD is to be adjusted to the residue production rate of the main/previous process (es) and in this sense the sustainability of the complete cascade chain in relation to this criterion would be related to the consumption rate of the main process (es) and not to that of AD itself.
In the protagonist perspective, as AD is the main process in the chain, attention should be given to the fact that the process does not exhaust soil reserves of carbon and nutrients, preventing that the consumption rate of the coupled processes do not exceed the carrying capacity of the specific context where it is embedded. The recirculation of nutrient, water and organic matter in the digestate gains again importance.

3 THE THREE DIMENSIONAL SUSTAINABILITY FRAMEWORK

The sustainability of technological systems is better addressed as the interaction between technological and context characteristics (Pabon Pereira 2004). The function a technology performs is therefore specific to the system it is embedded in.
Ideally, technological processes should be designed to fit the characteristics of its surrounding environment in a way that maximization of compatibility is achieved. Following the design process methodology, technological design entails several steps, the first of which is the definition of objectives and constraints imposed by the context. Thereafter those objectives are transformed into functions and working principles which at the end are embodied by specific technological configurations. The process itself is a cyclic one in which the analysis, synthesis, simulation and evaluation of alternative systems is repeated until an optimal solution is attained given the context and technological restrictions (Hamelers et al. 2005).
In the same way the sustainability framework to be presented departs from the definition of the sustainability objectives to be attained, thereafter operationalized into criteria and indicators. The framework can be used either for the iterative design process or for the evaluation of biomass cascades already in place.
Sustainable development is a process of change striving to attain environmental, economic and social objectives. The operationalization of these objectives is however a complex subjective process as many possible effects can be expected from bioenergy projects, and many criteria and indicators are applicable. Illustrating this issue, in a recent review study covering the types of indicators and possible verification systems applied by different certification organizations relevant for biomass production and trading for energy purposes (Lewandowski and Faaij 2006), a list of 127 criteria was compiled. Other recent studies have also extensively compiled relevant indicators for bioenergy assessment (Cramer 2006; Smeets et al. 2008; van Dam et al. 2008).

Our framework proposes eight criteria covering the three mentioned dimensions as shown in Figure 2.3. While the criteria chosen are applicable to the overall evaluation of sustainability of biomass cascades and biofuel production (see Chapter 1), they have been chosen as those specifically relevant to the role of AD considering the specific features of this technology.

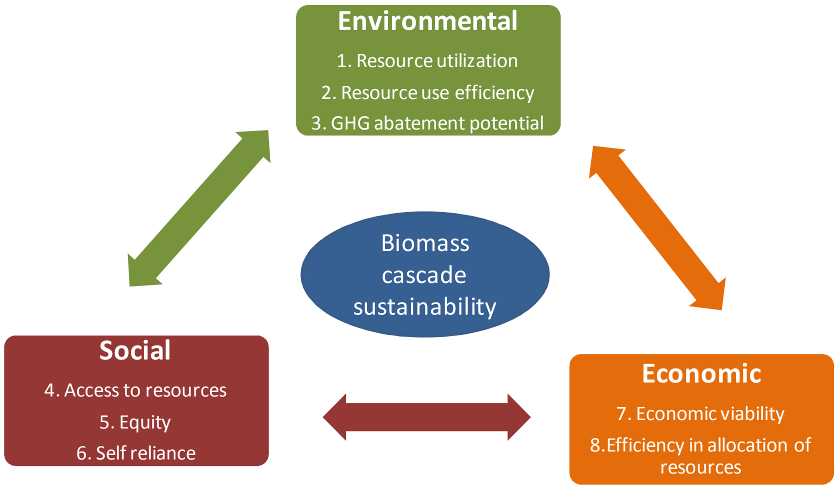


Figure 2.3 Sustainability dimensions and criteria for assessing the role of AD in biomass cascades

In Table 2.2 the framework is further detailed showing sustainability operationalization as going from the general objectives of maximization of environmental, social and economic performance, towards the definition of specific objectives, in which the eight criteria proposed and the indicators to be assessed are embedded.

Table 2.2 Sustainability objectives, criteria and indicators for the design and evaluation of AD biomass cascades

Objective	Specific objective	Criteria	Indicators
Maximize environmental performance	Minimize resource losses and depletion	Resource utilization	Energy balance Water balance Nutrient balance Land use
	Maximize resource use	Resource use efficiency	Energy efficiency Water efficiency Nutrient efficiency
	Minimize environmental pollution	GHG abatement	GHG balance
		Organic and inorganic pollution abatement	Concentration organic / inorganic pollutants in soil, water, air.
Maximize social benefits	Improve living conditions	Resource access (food, energy, water, nutrients)	Household expenditure in food, energy, water, fertilizer. Stability of the provision
	Recognize& enhance the existing social structure	Equity	Distribution of costs and benefits
		Self-reliance	Autonomy in the access to energy, water, fertilizers
Maximize economic viability	Recover the investment and generate profits	Private economic viability	Private Cost Benefit-Analysis
		Public economic viability	Public Cost-Benefit Analysis

3.1 Maximize environmental performance

Biogas systems normally lead to environmental improvements offering as main advantages as compared to bioethanol or biodiesel, the relative low need for arable land, with concomitant lower emissions to soil and water and the potential to recycle plant nutrients (Berglund 2006; Frederiksson et al. 2006). Although AD is regarded as a net energy producing process, variations in net energy outcomes and energy efficiencies are an intrinsic characteristic of the system and are mainly related to the properties of the raw materials, the system design and the allocation methods chosen (Berglund and Borjesson 2006; Salter and Banks 2008). Further, since biogas is produced from organic material, the origin of these materials can be related to the land needed to produce them. When biogas is produced from energy crops all land used for crop production is to be assigned to the system. However when AD is used to transform crop residues or industrial by-products, correct allocation of land is needed to distinguish among the different processes benefiting from its production. Under current pressure coming from population increase and increased ecosystem degradation, competition on land for food, feed and energy is of upmost importance. When biogas is produced from a biomass resource having a different possible use, the displacement of those other products need to be quantified as extra land needed to fulfil that purpose (Gallagher 2008; Nonhebel 2007).

From the perspective of pollution, the effect of AD can be perceived as positive when the technology makes a useful contribution to the use of a waste stream; however there are also risks associated contributing to problems like greenhouse gas emissions, acidification, eutrophication and photochemical disruption potential. The pollution risks in the case of biogas systems are related to both the production and final use of energy carriers and to changes in agricultural systems. The analysis of pollution risks should consider emissions of carbon dioxide (CO_2), carbon oxide (CO), nitrogen oxides (NO_x), sulphur dioxide (SO_2), hydrocarbons, methane (CH_4), particles, ammonia (NH_3), Nitrous oxide (N_2O) and Nitrate (NO_3^-). In the case of fuel-cycle emissions great variation was found among systems analyzed depending on the properties of the raw material digested, the energy efficiency of the biogas production and the status of the end-use technology (Borjesson and Berglund 2006). Overall evaluation of pollution risks is affected mostly by the raw materials digested, the energy service provided and the reference system replaced (Borjesson and Berglund 2007).

Among pollution risks GHG emissions deserve special attention. The main advantage of AD as a net generator of energy in turn draws significant advantages in terms of GHG emissions as highlighted for both municipal solid waste treatment (Baldassano and Soriano 2000) and wastewater treatment (Greenfield and Batstone 2004). However, a possible risk exists in the handling of the biogas which has an important global warming potential. Methane can be lost either in the gas storage facility or dissolved in the effluent. In general, 5-20% of the formed biogas can be generated in the storage tanks (Borjesson and Berglund 2006). On the other hand, methane dissolved in the effluent can be a major contributor of GHG emissions especially for low strength wastewaters, the cross over point being above 300-700 mg l^{-1} BOD in the influent (Cakir and Sternstrom 2005). Comparison among different biogas systems has shown that differences in the overall GHG balance come from the type of raw material digested, the energy efficiency of the biogas installation and the end-use technology (Borjesson and Berglund 2007). When extending the system beyond the anaerobic digestion facility, accounting for emissions coming from the cultivation, handling, transport of inputs and digestate and digestate application is required. Sources of GHG emissions during cultivation are mainly coming from fossil fuel use, use of fertilizers and land use change.

In this framework three environmental objectives are defined (Table 2.2). In the first two objectives resources of interest for analyzing the role of AD in biomass cascades are energy, nutrients, water and land. Organic matter recirculation is also of interest but has not been addressed within the scope of this thesis. Regarding the third objective concerned with the minimization of pollution, although all mentioned impacts are of importance within the scope of our framework the global warming potential as related to the measurement of the impact of AD in the GHG balance of biomass systems is given priority.

3.2 Maximize social benefits

Technology is a driver of social change as people are the actual creators and users. The improvement of existing living conditions as well and the enhancement of existing social structures are sustainability objectives possibly impacted by the introduction of biogas facilities.

Anaerobic digestion has been successfully introduced in many countries as a means to give access to energy and add value to otherwise nuisance resources(Aklaku et al. 2006; Bi and Haight 2007; Day et al. 1990; Zeeman and Lettinga 1999). The cases of China, India and Nepal are very well documented ones. In India for example 2.7 million family type biogas plants exist using cow manure as main substrate and producing 18 PJ yr^{-1}(Ravindranath et al. 2005). Such energy is used for cooking purposes replacing wood and the direct burning of manure as fuels. In both cases access to energy is enhanced and economic savings are produced whereas health conditions are improved as methane use avoids the release of unwanted particulate emissions coming from the direct burning of wood or residues.

Equity is another crucial consideration that can be impacted by the introduction of biogas facilities. The flexibility in scale of the AD can bring positive equity impacts as it allows for the better distribution of the social benefits and costs of the technology. At a higher scale however the impacts should be carefully addressed, as policies redirecting the use of land or biomass resources used for food or feed towards energy production can negatively impact the most vulnerable sectors of society.

Further, existing social capital can be strengthened when participation of users in the design, implementation and management of AD facilities are given priority. Communal facilities for the anaerobic treatment of manure, market residues or other wastes are interesting examples of the positive impact of appropriate technological interventions (Bi and Haight 2007; Day et al. 1990; Maunoir et al. 2007; Yepsen 2008).

The relation between technology and society is reciprocal and continuous hence appropriate and continuous methodologies are to be developed to accompany the social change that is triggered by the introduction of technological appliances. In the case of anaerobic digestion challenges in this area are in place, as the efforts to introduce the technology have shown to be dissimilar in their level of adoption, i.e. whereas in China and India the technology is widespread in Latin America many reactors installed in the 80’s are not in operation.

3.3 Maximize economic viability

From an economic perspective both the private and public economic viability of the system are to be assessed. In the first the quantification of private cost and benefits is of interest, whereas in the second the internalization of the system externalities like air and water pollution is to be added to the analysis.

The costs of biogas systems and the distribution among the different operations vary according to the type of input material used, the scale of the facility, the desired end use of the products and the sophistication of the system (Svensson et al. 2006).

While producing energy crops for biogas production entails costs related to the agricultural activities, in the case of materials with a negative environmental value such as wastewater or manure, only the investment and operational costs of the facility are to be considered (see Chapter 5). Chynoweth presented the cost distribution of the production of Napiergrass (*Pennisetum Purpureum*) for biogas in the United States. For a 10,000 GJ per year facility costs were distributed as follows: 32% anaerobic conversion, 26% crop production, 20% harvesting and storage, 14% gas cleaning, 7% transport and 2% digestate recycling. From the previous it follows that costs of biomass production can account for almost 50% of the total production costs (Chynoweth 2004).

Regarding the scale factor, economies of scale are traditionally claimed for chemical plants following an exponential factor of 0.6, while in the case of processes including the handling of solids 0.85 has been proposed (Amigun and von Blottnitz 2007). Nonetheless in an evaluation of 21 household and community AD facilities across 8 countries in Africa, diseconomies of scale were found to be the case with a cost capacity factor of 1.2 (Amigun and von Blottnitz 2007).

Quantifying benefits of AD plants should include issues like the substitution of energy, the avoidance of costs related to fertilizer use, the hygiene and odour reduction and the protection of the environment. Although these benefits are of direct impact in the quality of life, the way in which they are actually monetarized under different contexts defines the ultimate economic viability of plant. In this sense the different areas of application, i.e. individual household units, community plants, large scale commercial plants and industrial plants, already define different conditions to take into consideration.

In the case of household facilities, the Chinese case shows that while a simple biogas pit is economical due to its low investment, it does require a lot of maintenance and renewal and its management is costly (Marchaim 1992). At community level, key factors for the profitability of an AD system are the possibilities for selling the solid digestate, the possibility of getting savings in levies or fine paid to local authorities, the valorisation of the liquid digestate as fertilizer and the possibilities for monetarizing indirect benefits like increased health conditions due to the replacement of other fuels like wood, crop residues and charcoal (Day et al. 1990). The disadvantages of the maintenance are less prominent but the economics of a centralized facility are less positive due to the higher investment costs. In the economic analysis of village facilities the time and costs associated with the collection of the biomass material and the end use of the gas should be considered (Marchaim 1992).

An additional incentive to be incorporated in economic calculations is the possible benefits to be obtained from the Clean Development Mechanism (CDM). The CDM allows emission-reduction (or emission removal) projects in developing countries to earn certified emission reduction (CER) credits, each equivalent to one ton of CO_2. These CERs can be traded and sold, and used by industrialized countries to meet a part of their emission reduction targets under the Kyoto Protocol. The projects must qualify through a rigorous and public registration and issuance process designed to ensure real, measurable and verifiable emission reductions that are additional to what would have occurred without the project. The previous involves extra costs and a certain degree of expertise which may negatively influence the gaining of the actual benefits.

4 OPERATIONALIZING THE ENVIRONMENTAL SUSTAINABILITY DIMENSION FOR ADDRESSING THE ROLE OF AD IN BIOMASS CASCADES

The environmental criteria in the sustainability framework presented are built upon the acceptance of two notions defining the interaction of humans into their natural environment. First, is the fact that natural resources are limited and as such need to be wisely used. Second, is the notion that the use of resources by humans can create negative effects in the environment, i.e. pollution, which needs to be avoided or at least remediated. Following these two notions, three specific objectives for maximizing the environmental performance of biomass systems are: the minimization of resource depletion, the maximization of resource use and the minimization of pollution (see Table 2.2). The notion of resource use is directly linked to the first two objectives but it is approached from two different angles in each of them. The resource depletion objective emphasizes the net amount of a resource being used with respect to its abundance. In this sense the analysis of net resource use can be further elaborated by assigning abundance factors to the resources analyzed. This issue has been addressed in De Swaan Arons et al (2004) but is not within the scope of this study. In the case of resource use efficiency the emphasis is placed on how competent is the system in maximizing the use of the resource and minimizing its losses.

The third environmental objective of the framework covers the possible pollution effects of a biomass cascade which can also be expressed as the externalities that are created or avoided while using biomass (De Swaan Arons et al. 2004). The operationalization of the mentioned criteria into indicators is presented in Table 2.3.

Table 2.3 Operationalization of the environmental objective as proposed in this study

Criteria	Indicators		Units
Resource Utilization	Energy balance Water balance Nitrogen balance Phosphorus balance	$E_{balance} = E_{out} - E_{in}$ $W_{balance} = W_{out} - W_{in}$ $N_{balance} = N_{out} - N_{in}$ $P_{balance} = P_{out} - P_{in}$	[GJ yr^{-1}] [tonH_2O yr^{-1}] [kgN yr^{-1}] [kgP yr^{-1}]
	Land use		[ha yr^{-1}]
Resource use efficiency	Net Energy Ratio Net Water Ratio Net Nitrogen Ratio Net Phosphorus Ratio	$NER = (E_{out} - E_{in})/E_{in}$ $NWR = (W_{out} - W_{in})/W_{in}$ $NNR = (N_{out} - N_{in})/N_{in}$ $NPR = (P_{out} - P_{in})/P_{in}$	[$GJ_{out\text{-}in}$ GJ_{in}^{-1}] [$tonH_2O_{out\text{-}in}$ $tonH_2O_{in}^{-1}$] [$N_{out\text{-}in}$ N_{in}^{-1}] [$P_{out\text{-}in}$ P_{in}^{-1}]
GHG abatement potential	GHG balance	$GHG_{balance} = GHG_{bioprod} + GHG_{ind.proc} + GHG_{landuse} - GHG_{avoided}$	[ton $CO_{2\,eq}$ yr^{-1}]

4.1 Measurement units

The choice for the proper measuring units for environmental criteria is important when studying biomass cascades.

As shown in table 2.3, in our study net resource utilization, is expressed as net balances per unit time, i.e. [GJ yr^{-1}] or [tonN yr^{-1}]. Similarly net GHG abatement potential is expressed as [ton CO_{2eq} yr^{-1}]. On the other hand, resource use efficiency, measuring the competence of the cascade to make use of finite resources, is expressed as fractions of net output over total input, i.e. [$GJ_{out\text{-}in}$ GJ_{in}^{-1}].

Apart from the mentioned units, other units are employed to allow for comparison of different cascades on same grounds. Brehmer (2008a) showed that expressing energy savings per unit biorefinery chemical mixture [GJ ton^{-1} chemical] or per unit land use [GJ ha^{-1}] provides with useful insights when classifying biorefinery cropping systems. Similarly, Dornburg(2004) concluded that in the assessment of energy savings and GHG emission reduction of biobased polymers expressing results per unit of agricultural land or per unit polymer produced lead to different ranking of options. Dornburg (4) preferred land use as a comparison unit due to its direct reference to the proper use of this finite resource, as it is considered to be the main issue limiting implementation of biomass systems.

Because of the previous, apart from the units used in Table 2.3, balances can be expressed per unit product, per unit energy or per unit land, those measurements being complementary and useful when comparing different systems. Expressing them in monetary is also a useful option when comparing economic implications of alternative systems.

In the following item, the use of energy as a measurement unit is introduced as an approach which latter on is applied in Chapters 6 and 8 of this thesis. In chapter 9 the usefulness and limitations of such approach is revisited and discussed.

4.2 An energy model for analyzing the environmental contribution of AD to biomass cascades

Energy can be chosen as a unit to analyze the role of AD within biomass chains not only because energy can be regarding as the most significant and visible outcome of an AD unit, but also because it allows to translate other flows related to the benefits of AD, i.e. different type of nutrients and water, into equivalent units and produce single unit outcomes. In addition, and in view of the concerns related to the amount of land being used for bioenergy production and the competing claims, energy savings can be easily translated back to equivalent land units, allowing to make conclusions at a higher and more meaningful level. Similarly, using energy units allows for comparison with other biofuel production options.

In the analysis of different biogas systems the reference system is of major importance (Borjesson and Berglund 2007). Therefore in our approach for the operationalization of environmental sustainability criteria, the impact of AD to a cascade departs from the definition of the original system, followed by that of the system with AD. The difference among the two systems expresses the contribution of AD to the cascade. In the following section the *contributive perspective* introduced in section 2.1 is used to exemplify the proposed approach, similar approaches are valid for the other two perspectives, i.e. *multifunctional* and *protagonist* perspectives.

Figure 2.4 shows the situation in a system before AD is introduced. As can be seen major flows are inputs to biomass and industrial processes, and outputs in the form of products and by-products.

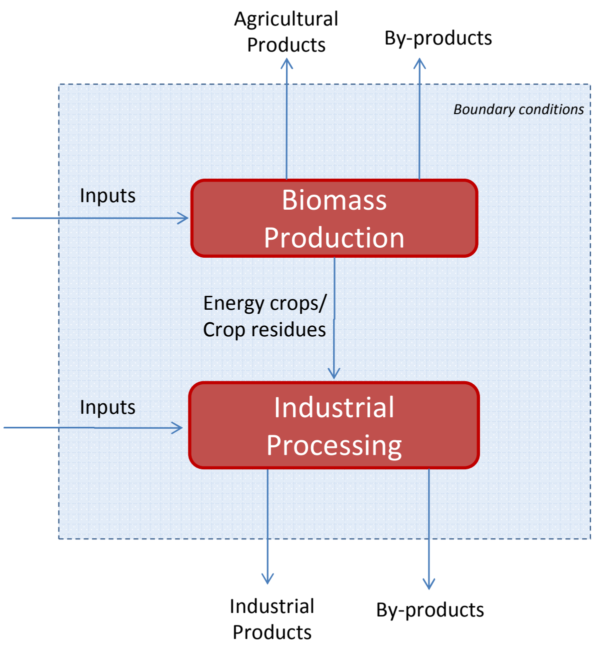


Figure 2.4 Biomass chain before AD

Equation 2.1 expresses the situation of a system before AD as the difference between energy outputs, in products and by-products, and energy inputs.

$$E_{bal1}\left[\frac{GJ}{yr}\right] = \left(E_{biom\ product} + E_{ind\ \ product} + E_{by-prod\ biom\ prod} + E_{by-prod\ ind\ \ prod}\right) - \left(E_{Input\ biom} + E_{Input\ ind}\right) \quad (2.1)$$

Once AD has been introduced into a system the flows in the system change as shown in Figure 2.5. Products and by-products from the agricultural and industrial system can be directed to the AD process which in turn will transform them into energy and digestate, i.e. water and nutrients, coming back into the same chain or leaving the system into other systems. The new energy balance can then be expressed as in Equation 2.2.

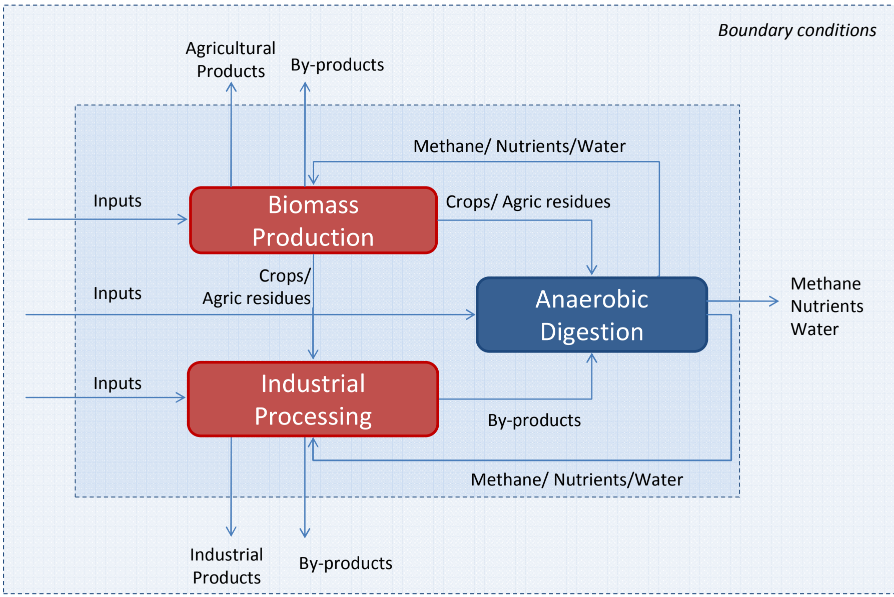


Figure 2.5 Biomass chain after AD

$$E_{bal2}\left[\frac{GJ}{yr}\right] = \left(E_{biom.product2} + E_{ind.product2} + E_{by-prod.bioprod2} + E_{by-prod.ind2}\right) - \left(E_{Inputs.bio2} + E_{Inputs.2}\right) + \left(E_{ext.outputAD} + E_{ext.inputAD}\right) \qquad (2.2)$$

The difference between equations 2.1 and 2.2, expressed in equation 2.3 expresses the contribution of AD to a biomass chain.

$$\Delta E_{bal}\left[\frac{GJ}{yr}\right] = \left(\Delta E_{biom\ prod} + \Delta E_{ind\ prod} + \Delta E_{by-prod.bio\ prod} + \Delta E_{by-prod.ind\ prod}\right) - \left(\Delta E_{Inputs.bioprod} + \Delta E_{Inputs.ind}\right) + \left(E_{ext.outputAD} + E_{ext.inputAD}\right) \qquad (2.3)$$

In Equation 2.3, the role of AD in a chain is embodied in the differences in inputs and outputs to the system before and after the technology has been introduced as well as in the new flows leaving the system from the AD unit.

5 Final comments

In this chapter the possible roles of AD within a chain have been described following the design methodology and the cascade chain theory. Further, a sustainability framework has been proposed for addressing the role of AD in biomass cascades covering environmental, social and economic dimensions. The environmental dimension has been additionally elaborated by developing a model for quantifying the environmental implications of AD in energy units. The choice for assessing the role of AD in energy units is made considering that it allows for expressing different types of units in a single one which later on can be translated into land equivalents. Further it allows for comparing AD systems with other biofuel options.

Different aspects of the framework are applied and elaborated in the following chapters of this thesis. In Chapter 5, the *protagonist* approach is contested by analyzing the role of by-products in the digestion of energy crops, i.e. manure and maize silage, having energy and nutrients as focus of the analysis. In Chapter 6, a sensitivity analysis of the AD unit is performed in order to understand how the restrictions imposed by the existing cascade in terms of type of input and energy and digestate demand, affect the overall configuration and energy efficiency achieved by the AD configuration. In Chapter 7, the environmental indicators proposed are used for the evaluation of the role of AD in different cassava bio ethanol cascades in Colombia. Finally, in Chapter 8, the energy model proposed is applied in the theoretical evaluation of selected AD biomass cascades for Colombia, the implications in the social and economic sustainability dimensions are also discussed.

Chapter 3

Optimizing an OxiTop® protocol for screening plant material suitable for anaerobic digestion

Abstract

In the search for simpler and accurate methods for the determination of the Biochemical Methane Potential (BMP) of plant material, a protocol was developed for the appropriate use of the OxiTop® system. Differences of up to 44% in the outcome of the test were found when manipulating different variables. The use of NaOH pellets affected the stability of the test negatively influencing methane production. The increased biodegradability of comminuted samples was found to be related to the proportion of lignin in the fibre content. When varying inoculum type and S/I ratio, the final BMP value achieved was in agreement with the observed changes in pH and volatile fatty acid concentration. Finally, evidence was found that phosphate buffer exceeding 20mM exerts a clear toxicity effect when using suspended inoculum. Guidelines and recommendations are given for the preparation, follow-up and calculations related to the use of the OxiTop® system for screening plant material based on their anaerobic biodegradability.

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Submitted to Bioresource Technology

1 INTRODUCTION

Production of biogas and valuable digestate from materials of plant origin through anaerobic digestion (AD) is an interesting alternative to add value to different biomass chains, to minimize environmental problems related to inadequate management of residues, and to provide an alternative use to land for energy purposes. Given that the diversity of lignocellulosic materials that can be converted to methane is immense, an accurate and simple method is needed to screen for those materials more appealing for digestion.

The Biochemical Methane Potential (BMP) test is used to assess the maximum anaerobic biodegradability from a sample which is incubated in a chemically defined medium, by monitoring its cumulative methane production (Owen et al. 1979). The BMP test has been used for decades, however, recently various authors are calling new attention on the need to further simplify and optimize the procedure (Angelidaki and Sanders 2004; Colleran and Pender 2002; Muller et al. 2004; Rozzi and Remigi 2004a). Colleran and Pender (2002) highlighted the need to harmonize anaerobic biodegradation, activity and inhibition assays, especially in what refers to the standardization of the test inoculum, the test medium, the test conditions and the duration of the biodegradability tests. Angelidaki and Sanders (2004) emphasized the pre-treatment of the sample, the type and amount of inoculum and the gas measuring technique. Others have mentioned pH, temperature, type and concentration of hydrolysing biomass, water addition, nutrient addition, the equipment used, and applied laboratory analytical procedures (Angelidaki and Sanders 2004; Gunaseelan 1997; Rozzi and Remigi 2004a).

Within the EU Project-Cropgen, in which the potential of European crops and agro-residues for methane production was studied, the revision and simplification of the BMP test was prioritized. To do so a BMP protocol adapted for the use of the OxiTop® pressure monitoring system (WTW, Giessen, GERMANY) was developed.

The OxiTop® system is a pressure monitoring device originally developed for BOD measurements. The system comprises the measuring heads and a controller, and uses an infrared interface for data transfer (Figure 3.1). The OxiTop® measuring head contains a pressure sensor and a data memory able to store up to 360 data sets depending on the running time, while one controller is able to manage up to 100 measuring heads. Advantages of the system are the possibility of carrying out many measurements in parallel and the minimization of human interference in the test, as pressure data is collected automatically by the controller at time intervals defined by the user. The data can be graphically displayed on the controller at any time and can be downloaded to the computer in excel format for analyzing the results.

Despite the listed advantages, the OxiTop® system has as major limitation the pressure limit of the measuring head, i.e. 0.30 atm. Such limitation causes restrictions on the amount of sample that can be used in the experiment, which in turn pose challenges for achieving sufficient representativeness in samples from non-homogeneous material such as crops and agro-residues. In addition, the produced overpressure consists of both CH_4 and CO_2, requiring gas analysis of the head space for assessing the COD balance in the test vials. Therefore, within the CROPGEN project, priority was given to overcome this limitation by studying the use of

NaOH pellets for CO_2 capture and the impact of the combined use of different pre-treatment/storage methods for plant samples. In addition, factors affecting the stability of the test such as inoculum type, inoculum concentration and the use of buffering systems were prioritized in view of increasing accuracy and simplifying the test by avoiding continuous control of factors such as pH and VFA.

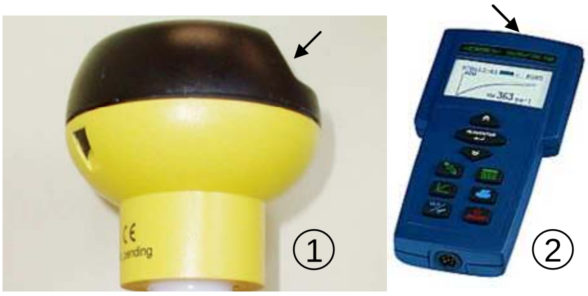


Figure 3.1 OxiTop® measuring system: 1.OxiTop head to be mounted on the batch bottles; 2.The controller used to obtain the data from the Oxitop heads using the infrared interface pointed out by the arrows.

Rudrum (2005) used the OxiTop® system with NaOH pellets addition as CO2 absorbent for composting stability measurements. In anaerobic measurements such combination has not been reported while many advantages can be expected as it would permit the doubling of sample amount and allow for test simplification as the need for headspace gas analyses could be avoided.

Although the ideal is to test substrates in a physical form close to reality, in laboratory tests different pretreatments are used in order to achieve sample representativeness and to cope with the restrictions imposed by the decay of the substrates and available experimental set-up. Using 1 cm particle size samples could be suitable for plant material expected to be homogenous in nature such as grasses or tubers. However, for non-homogeneous samples the use of pretreatments might be advisable. Increases in biodegradation, ranging from 9% up to 48%, have been reported for different materials and different degrees of comminution, i.e. particle size ranges (Chynoweth and Jerger 1985; Palmowski and Muller 2000; Perez Lopez et al. 2005; Sharma et al. 1988). Chynoweth (1993) mentioned that samples treated in the 1 mm to 10 mm range will not significantly expose more surface area and thus exhibit similar kinetics and biodegradability. However, Sharma et al (1988) reported interference for smaller particle sizes, whereas the assessed BMP varies according to fiber composition. Storing the samples by freezing or drying has as main advantage the possibility of having a test reproducible in time for the specific sample under evaluation. However, both freezing and drying can potentially exert changes on the physical and chemical properties of the material. Freezing adversely affects the texture of nearly all plant tissues, due to cellular dehydration and the accumulation of ice in the intercellular spaces (Thomashow 1998). This can increase the bioavailability of the substrate, possibly affecting its degradation rate and BMP. Oven drying has been reported to alter the chemical composition of plant samples by inducing the loss of energy containing volatile organic matter (Broesder et al. 1992), and causing the non-enzymatic browning effect, consisting of the polymerization of sugars with aminoacids resulting in a brown complex similar to lignin. The so-called artifact lignin can block the accessibility of the substrate reducing its digestibility (Parissi et al. 2001). On the other hand, altering the particle size of the substrates can influence both the rate and extent of degradation of plant material as it releases cell compounds and creates new surfaces for biodegradation to take place (Palmowski and Muller 2000). Finally, the combined influence of storage conditions and particle size reduction in the BMP assessment of plant material is insufficiently reported and was included as part of this study.

Underestimation of the methane potential can also take place as the result of inhibition when operating anaerobic reactors with a pH outside the optimum range (Angelidaki and Sanders 2004). Maintenance of a stable pH is a major problem when digesting ligno-cellulosic material, due to its poor buffering capacity and the risk of VFA accumulation (Banks and Humpreys 1998). The inoculum type, substrate to inoculum ratio (S/I) in conjunction with the buffering system are crucial for ensuring a stable environment for microbial conversions to take place (Angelidaki and Sanders 2004; Hashimoto 1989; Moreno et al. 1999; Neves et al. 2004). Neves et al (2004) reported lower conversion of kitchen waste at lower alkalinity conditions, the impact of the S/I ratio being different for different inoculum types. No specific study has been found providing comparison among buffering systems in the BMP evaluation of plant material but evidence using other substrates and different set-ups suggest that an impact can be expected. Muller et al. (2004) found a lag phase and lower biodegradation in the absence of carbonate buffer in the assessment of the anaerobic degradation of polyhydroxybutyrate (PHB) powder when carbonate was not added. Paulo et al (2005) and Conrad et al (2000) noticed that phosphate buffer can exert a toxic effect on acetoclastic methanogens.

2 MATERIALS AND METHODS

2.1 Departing set-up and preliminary calculations

The departing set up for measuring the extent of anaerobic biodegradability was a modified version of the method described by Owen et al (1979). All the experiments were carried out in 500 ml serum bottles (approx. 600 ml working volume) under the addition of nutrients for optimal anaerobic conversion as follows: Macronutrient solution (Dose 0.4 ml): NH_4Cl, 170 g l^{-1}; $CaCl_2.2H_2O$, 8 g l^{-1}; $MgSO_4.4H_2O$, 9 g l^{-1}; Micronutrient solution (Dose 0.2 ml): $FeCl_3.4H_2O$, 2 g l^{-1}; $CoCl_2.6H_2O$, 2 g l^{-1}; $MnCl_2.4H_2O$, 0.5 g l^{-1}; $CuCl_2.2H_2O$, 0.03 g l^{-1}; $ZnCl_2$, 0.05 g l^{-1}; H_3BO_3, 0.05 g l^{-1}; $(NH_4)_6Mo_7O_{24}.4H_2O$, 0.09 g l^{-1}; $Na_2SeO_3.5H_2O$, 0.1 g l^{-1};$NiCl_2.6H_2O$, 0.05 g l^{-1}; EDTA, 1 g l^{-1}; HCl 36%, 0.001 g l^{-1}; Resazurin, 0.5 g l^{-1}. A phosphate buffer solution was used for all tests using a 20 mM concentration, except in experiment 3, where the phosphate buffer was compared to a carbonate buffer solution and the impact of various molarities of both buffers was assessed.

Substrate and inoculum amounts were added considering the OxiTop® pressure limitation, a minimum substrate concentration of 1 gCOD l^{-1} to avoid mass transfer limitations, and following the recommendations by Angelidaki and Sanders(2004) of keeping a maximum S/I ratio proportional to the hydrolysis constant and the Specific Methanogenic Activity (SMA) of the inoculum. The calculation on the amount of substrate to add was performed as shown in Equation 3.1. The maximum pressure increase allowed by the OxiTop® measuring head is 0.3 atm. Hence, following the ideal Gas law, assuming a 50:50 CH_4:CO_2 gas composition and a liquid volume of 150 ml, the maximum allowed gas production at 35ºC is *0.0054 mol*. If the CO_2 is not removed from the headspace that means **0**.*0027 moles CH_4 or 0.043 g CH_4*. As stochiometrically 4 g COD are reduced per gCH_4, the maximum amount of substrate to add is *0.17 gCOD*. Under the previous conditions that means a substrate concentration of *1.14 g COD l^{-1}*.

$$S[\mathrm{gCOD}] = 32\left[\frac{\mathrm{gCOD}}{\mathrm{mol}_{\ \mathrm{CH_4}}}\right] \times 50\% \times \frac{0.3[\mathrm{atm}] \times 4.5 \cdot 10^{-1}[\mathrm{l}]}{8.3144\left[\frac{\mathrm{l\ atm}}{\mathrm{mol}\ ^{o}\mathrm{K}}\right] \times 308.16[^{o}\mathrm{K}]} \qquad (3.1)$$

Considering an SMA of a suspended inoculum of 0.1 gCOD gVS^{-1} and assuming a first-order hydrolysis constant for 1 cm particle size plant material of 0.2 d^{-1}, a maximum S/I ratio of 0.5 gCOD gVS^{-1} (0.1/0.2) should be employed. The amount of inoculum to add follows from the substrate concentration and the calculated S/I ratio expressed in [gVS gVS^{-1}]. From the analysis of 35 plant samples as part of the CROPGEN Project, an average COD content of plant biomass of 1.35 gCOD gVS^{-1} was assessed. Hence for this set-up *2.9 g l^{-1}* (1.14/0.4) suspended inoculum is needed.

The bottles were filled starting with the medium solution and demineralized water, followed by the addition of the inoculum and finalizing with the addition of the substrate. When using NaOH pellets, they were dosed inside a plastic pellet holder with aeration holes just underneath the screw-cap for closing the vial at the top. After filling the bottles, they were flushed with N_2 gas for 1 minute, tightly sealed and incubated at 35 ^{o}C. In the experiment being performed with carbonate buffer, a gas mixture 70:30, N_2:CO_2 was used instead. The bottles were shaken at 120 rpm during the first 8 days of the assay, afterwards they were shaken occasionally. A schematic representation of the employed set-up is presented in Figure 3.2.

Biogas production was measured as pressure increase at a constant volume, using the Oxitop® system. Biogas composition as well as VFA and soluble COD concentrations were followed during the test. The tests were performed in triplicates or duplicates. Blank bottles, containing all additions except substrate were used to correct for inoculum methane production.

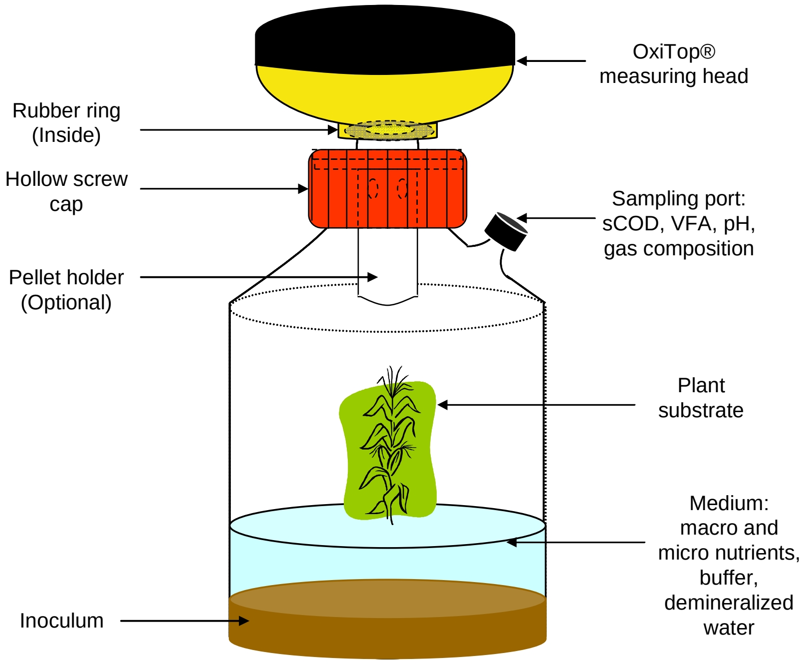


Figure 3.2 Schematic representation of the batch set-up employed

2.2 Experimental design

Different experiments were conducted to verify the influence of the NaOH pellets, substrate pretreatments, the inoculum type and S/I ratio, and the type and molarity of buffer in the BMP test. The departing set-up was equal for all tests, whereas specific conditions changed according to the variable being manipulated. Table 3.1 provides an overview of the tests performed.

Table 3.1 Outline of the experiments performed for optimization of an OxiTop ® protocol for BMP determination

Treatment	Variable	Type of inoculum, S/I ratio	Type of substrate
1 NaOH pellets	Amount of NaOH absorbent, i.e. 0, 0.25, 0.5, 1, 2 and 5 g	Digested primary sludge, S/I = 0.4	Endive – *blended and frozen*
2 Sample treatment	Sample storage and comminution	Digested primary sludge, S/I = 0.4	Mustard – *Brassica juncea* Carrot – *Daucus carota* Endive – *Cichorium endivia* Green beans – *Phaseolus vulgaris*
	Drying samples at 65°C	Digested primary sludge, S/I = 0.4	Mustard – *Brassica juncea* Green beans – *Phaseolus vulgaris*
3 Inoculum	Inoculum type	4 types of inoculum, S/I=0.4	Green beans – *blended and frozen*
	Substrate to Inoculum ratio	Granular sludge and inoculum mixture, S/I =0.4, 1.5, 3	
4 Buffer	Buffer type and molarities	Digested primary sludge S/I=0.4	Green beans –*blended and frozen*

The influence of NaOH as CO_2 absorbent was studied using different amounts of pellets, i.e. 0, 0.25, 0.5, 1, 2 and 5 g. The influence of different substrate pretreatments was studied using four substrates, two more homogeneous, i.e. green beans and endive, and two non-homogeneous: mustard and carrots. Combined sample storage and particle size reduction was studied in four treatments: fresh 1 cm pieces, freshly blended, frozen blended and dry grinded samples to pass a 1 mm mesh. The effect of inoculum type was assessed by comparing a highly methanogenic sludge with a more hydrolytic one plus their combination in the conversion of a plant substrate. As well, different S/I ratios were assessed for the methanogenic sludge and the sludge mixture. Finally, carbonate and phosphate buffering systems were compared as well as their molarities to check for their toxicity and their influence in BMP.

2.3 Inocula

Digested primary sludge (DPS) originating from a sewage treatment plant (Ede, The Netherlands) was used as main source of inoculum. In experiment 2, in which different sludges and S/I ratios were assessed, granular sludge (GS) originating from a mesophilic upflow anaerobic sludge blanket (UASB) reactor treating alcohol distillery effluents, was used as additional inoculum source. DPS and GS were stored in gas tight plastic containers at 4^{o}C and left at ambient temperature for half a day before conducting the experiments. Fresh DPS was brought two weeks before experiment 2 took place and kept at 35^{o}C, this sludge was also used in the same experiment in conjunction with the GS for the sludge mixture (MS). Methanogenic activity measurements were performed in duplicate applying two consecutive feedings for all the sludges using the above described set-up. Sodium acetate and glucose were used as substrate, at concentration of 1 g l^{-1} and under initial substrate to inoculum ratio of 0.5 g COD gVS^{-1}. Test follow-up and calculations were performed according to guidelines provided by Cho et al (2005), results presented in Table 3.2.

Table 3.2 Characteristics of the sludges used in the experiments

Inoculum	VS [gVS g^{-1}]	COD [gO_2 gVS^{-1}]	SMA acetate [mgO_2 gVS^{-1} d^{-1}]	SMA glucose
Fresh Digested Primary Sludge (Fresh DPS)	0.02	1.64	34.03± 8.0	86.98±3.7
Stored Digested primary sludge (DPS)	0.02	1.37	1.83 ±1.2	18.51±1.0
Granular sludge (GS)	0.11	1.20	96.83± 1.0	113.66±21.6
Sludge Mixture (MS)	0.07	1.24	74.40± 0.1	95.11±3.2

2.4 Substrates

Four substrates were used for the different experiments as shown in Table 3.1. The substrate samples were collected fresh, divided in their constituent parts and weighted separately. The total amount of sample was divided in four fractions following the proportions of their constituents, one portion used fresh cut in 1 cm pieces, a second was blended using a 40% dilution with demineralized water and being further divided in two fractions, one to be used fresh and the other to be frozen at -18^{o}C. A fourth fraction was dried at 65^{o}C during one day and grinded to pass a 1mm mesh. Characteristics of the substrates are shown in Table 3.3.

Table 3.3 Substrate characteristics

Substrate	TS [gDM g^{-1}]	VS [%DM]	COD [gO_2 gVS^{-1}]	Total Fibre [g gVS^{-1}]	Lignin [g gVS^{-1}]	Hemi-cellulose [g gVS^{-1}]	Cellulose [g gVS^{-1}]	N [%VS]
Mustard	0.098	92	1.21	0.52±0.00	0.06±0.00	0.13±0.00	0.33±0.01	5.18
Carrot	0.132	92	1.36	0.17±0.01	0.06±0.01	0.03±0.00	0.07±0.00	2.24
Endive	0.069	81	1.42	0.22±0.01	0.05±0.02	0.04±0.00	0.13±0.02	4.01
Green beans	0.079	93	1.41	0.19±0.00	0.03±0.00	0.05±0.00	0.11±0.00	5.82

2.5 Analytical methods

For the characterization of the substrates and sludges, TS, VS and Total COD were performed according to standard methods (APHA 1998). For drying plant samples a WTC Binder Labortechnik (Tuttlingen, Germany) oven was used. Freeze drying was performed in liquid nitrogen in a GRI 20-85 MP freeze drier (Wijk bij Duurstede, The Netherlands) equipped with two condensers. Comminution was performed in a Retsch BV grinder (Haan, Germany) equipped with 1 mm sieving device, and blending was performed in a Turrax commercial laboratory blender. Fibre analysis was performed according to van Soest Method (1991) using the dry grinded samples. Nitrogen analysis was performed according to modified Kjeldahl method, in which the sample is digested using H_2SO_4 and H_2O_2 and $CuSO_4$ as catalyst. All nitrogen is converted to $(NH_4)_2SO_4$, which is later determined by adding an excess of NaOH and by distilling the liberated NH_3. This free NH_3 is collected in H_3BO_3 solution and titrated with HCl solution. All analyses were performed in duplicate.

When following the experiments, liquid samples were analyzed for soluble COD and VFA. The samples were taken from the side port of the bottle using a syringe, and then centrifuged for ten minutes at 10.000 rpm in a Microlite Therme IEC Boomlab centrifuge (Meppel, The Netherlands), the supernatant being used for the assessment. Dr. Lange kits (Düsseldorf, Germany) were used for assessing soluble COD, the samples being measured in a Dr. Lange Xion 500 model LPG-385 photo-spectrometer (Düsseldorf, Germany). VFA was analyzed in a Hewlett Packard 5890A gas chromatograph equipped with a glass column packed with Supelcoport and coated with 10% Fluorad FC 431 combined with a Hewlett Packard 6890 series injector (Palo Alto, U.S.A.). The temperatures of the flame ionization detector, injection port and columns were 280°C, 200°C and 130°C, respectively. Gas composition was followed with a Hewlett Packard 5890A gas chromatograph, the oven, injection port and detector temperature were 45°C, 110°C and 99°C, respectively. The column measuring O_2, N_2 and CH_4 was a molseive 0.53mm x 15µm, while the column measuring CO_2 was a paraplot 0.53mm x 20µm.

2.6 Calculations

The BMP, expressed as liters methane at standard temperature and pressure of 273°K and 10^5 Pa per amount of substrate volatile solids added [lCH_4-STP gVS^{-1}], is calculated from the maximum methane production of the sample bottle corrected by the maximum methane production of the blank bottle. The maximum moles of methane produced are calculated by applying the ideal gas equation to the total pressure increase and multiplying the biogas moles by the percentage of methane in the headspace. The amount is subsequently transformed to liters methane by multiplying by 22.4 l(STP) mol^{-1} (Equation 3. 2).

$$\mathrm{BMP} = \frac{\left[\left(\frac{(\mathrm{P_s} + P_{atm}) \times \mathrm{V_s}}{\mathrm{R} * \mathrm{T}}\right) \times \frac{\%CH_{4s}}{100}\right] - \left[\left(\frac{(\mathrm{P_{bl}} + \mathrm{P_{atm}}) \times \mathrm{V_{bl}}}{\mathrm{R} \times \mathrm{T}}\right) \times \frac{\%CH_{4bl}}{100}\right]}{\mathrm{S_o}} \times 22.4 \quad (3.2)$$

Where P_s is the pressure in sample bottle [Pa], P_{atm} is the atmospheric pressure [Pa], P_{bl} is the pressure in blank bottle [Pa], V_s is the headspace volume of the test bottle [m^3], V_{bl} the headspace volume of the blank bottle [m^3], T is the temperature 308.16 [°K], R is the universal gas constant 8.3114 [Pa m^3 mol^{-1} °K^{-1}], %CH_{4s} is the percentage methane in the test bottle, %CH_{4bl} is the percentage methane in the blank bottle and S_o is the amount of substrate added [gVS].

Biodegradability (B_o) as the maximum percentage COD added converted to methane is calculated as the ratio between the net maximum accumulated methane as COD divided by the total COD amount added in the bottle. Equation 3.3 expresses the B_o in its COD equivalents.

$$B_o = \frac{CH_{4,max}}{S_o} \times \frac{2.86}{COD_s} \times 100 \qquad (3.3)$$

Where 2.86 correspond to the COD equivalence of 1liter methane at standard temperature and pressure and COD_s is the COD of the sample in [gCOD gVS^{-1}].

2.7 Digestion time

The maximum digester gas production is defined as the digester gas production reached by each treatment replicate at the end of their digestion time, i.e. when their brut gas production was not incrementing more than 1% for at least 3 days. According to the previous, the time length of the tests varied among treatments between 33-54 days, depending on the time required to meet the previous criteria.

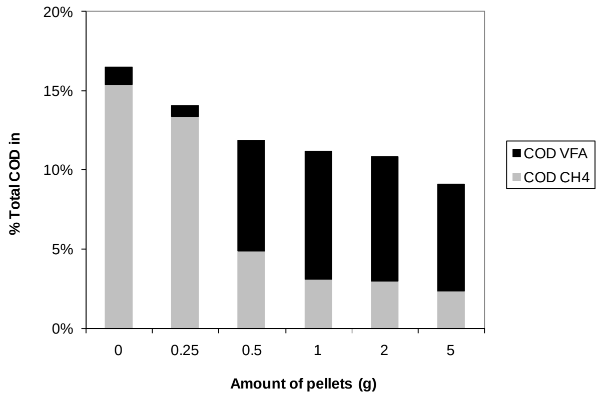
3 RESULTS

3.1 Effect of NaOH pellets

In the presence of the NaOH pellets, a concomitant accumulation of VFA and increase in pH occurred resulting in a lower CH_4 recovery. After one day incubation all treatments with pellets addition showed a sudden increment of the pH, which rose from 7.2 to 8.2 - 8.8 and remained high until the end of the treatments, except in the case of the bottles with 0.25 g pellets which showed a gradual diminishment of the pH towards the neutral range.

After 32 days, 91%, 36%, 22%, 18% and 18% of the biogas production relative to the bottle without pellet addition was recovered in the bottles with 0.25 g, 0.5 g. 1, 2 and 5g pellets, respectively. Further, it was found that the low methane production in the bottles with pellets was accompanied by VFA accumulation, as can be observed in Figure 3.3 where the brut COD conversion in the treatment can be observed. When correcting the brut CH_4 production for that in the blank bottles, results lead to biodegradability misinterpretation since when subtracting the inhibited blank bottles, overestimation of the net CH_4 production resulted. That was strikingly evident in the 0.25 and 0.5g pellet treatments, in which the calculated BMP was 220% and 126% of that assessed in the treatment with no pellet addition. Overestimation of the BMP was also the result of incomplete absorption of CO_2 in the treatments containing 0.25 g pellets, in which incremental amounts of CO_2 in the headspace were assessed after day 8. In all other treatments complete absorption was observed.

Results of the assessment of the various plant materials showed similar results, i.e., the majority of the treatments performed using NaOH pellets showing 70-90% lower BMP than that assessed under non-inhibiting conditions (Figure 3.4).



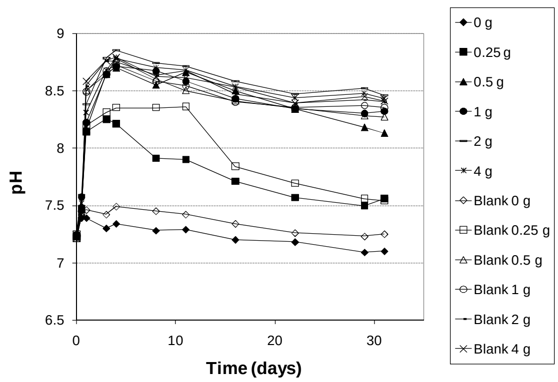


Figure 3.3 Effect of NaOH pellets in brut COD conversion (left) and pH (right) during BMP assessment of frozen blended endive

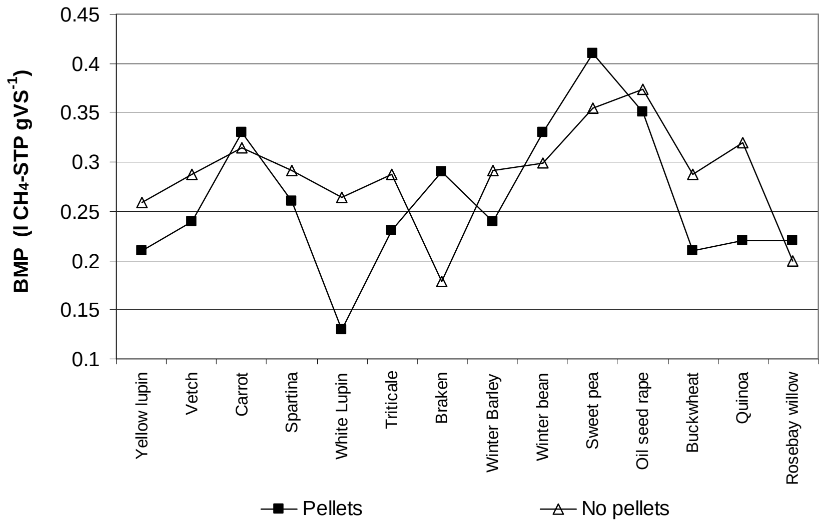


Figure 3.4 Comparison of BMP values of different plant species assessed with and without NaOH pellets for CO_2 absorption

3.2 Effect of sample treatment in the BMP of plant material

Figure 3.5 presents the condensed results of the laboratory digestion experiments of the plant material using different pretreatments. From the results it can be observed that blending did not exert an important impact in the BMP value but particularly influenced the experimental replicability of the carrot and endive samples. As well, freezing and blending did not particularly influence the BMP of the materials. Drying and grinding plant material influenced the BMP assessment of all the species except for carrot, resulting in an BMP increase of 44, 25 and 43% for mustard, endive and green beans, respectively, with regard to the fresh 1 cm samples.

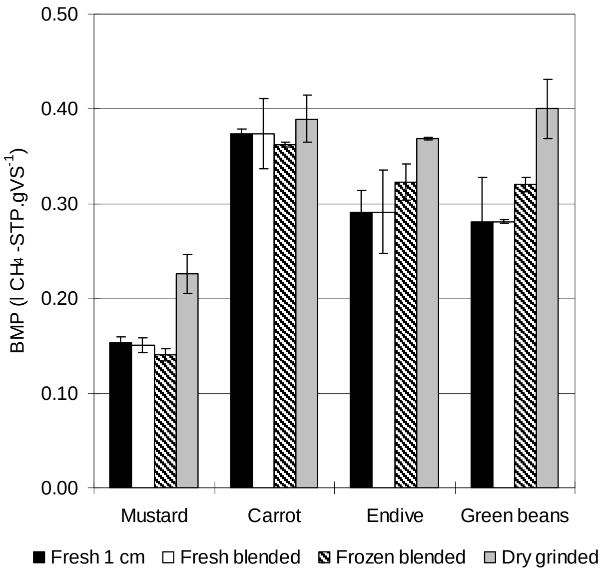


Figure 3.5 Effect of sample treatment in the assessed BMP of mustard, carrot, endive and green bean samples

The increase in assessed BMP was plotted as a function of the available total fiber. The availability of total fiber was defined as a surface based relation relative to lignin content, in line with earlier research by Conrad et al (1984) on the nutritional recovery of cell wall components by ruminants. A good correlation, i.e. R^2=99%, was found between the increase in BMP with comminution and the proportion of lignin surface in relation to the total fiber surface, which includes lignin, hemi-cellulose and cellulose. Due to the low amount of data points we compared these results using other data coming from the experiments of Sharma el et al (1988). In this case only cellulose and lignin content were considered for the surface based relation, since hemicellulose was not reported in the mentioned study. The increasing trend in biodegradability was evident as the surface proportion of lignin in relation to the sum lignin plus cellulose diminished. Data from our study again showed again a good correlation R^2=98% while considering all data points, the surface based relation showed a correlation of R^2=68% (Figure 3.6).

The biogas production rate did not show important variation among the different treatments for the evaluated substrates, the average maximum rate of biogas production, being 47, 49, 57 and 61 ml biogas (STP) $gVS^{-1}d^{-1}$ for mustard, endive, green beans and carrot, respectively.

The effect of drying the samples at 65°C was assessed in a separate experiment using 1 cm particle size samples of green beans and mustard. Both substrates were selected due to their higher nitrogen content in order to assess the influence of the possible afore mentioned enzymatic browning effect in the BMP. While the biogas evolution in time was similar in shape, a lower BMP value of dried samples in comparison to frozen samples was found in both cases, giving a difference of 9 and 13% relative to the value found with the frozen samples (data not shown).

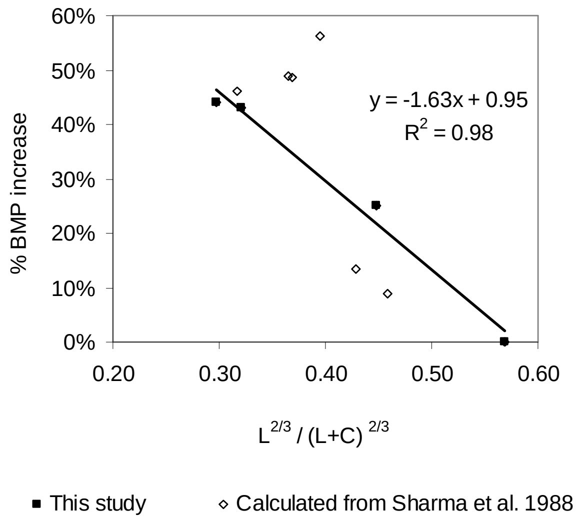


Figure 3.6 Percentual increase in BMP value of plant samples resulting from particle size reduction as a function of relative surface lignin content (L: lignin, C: cellulose)

3.3 Effect of sludge type and S/I in the BMP assessment of plant material

GS and DPS were used in the experiment conducted to assess the influence of sludge type in the BMP of blended-frozen green beans samples. BMP assessed with the fresh and stored DPS and GS were similar, whereas MS gave a distinctly higher BMP value. Maximum rates of biogas production did not vary substantially among the fresh DPS, GS and MS, being 176, 135 and 177 ml biogas $gVS^{-1}d^{-1}$, respectively. However, after an initial comparable production, the production rate of the stored DPS was much lower than the others, i.e. 38 ml biogas $gVS^{-1}d^{-1}$. The lag phase in the biogas production curve using DPS coincided with the accumulation of acetic acid in the test bottles (See Figures 3.7, 3.8 and 3.9).

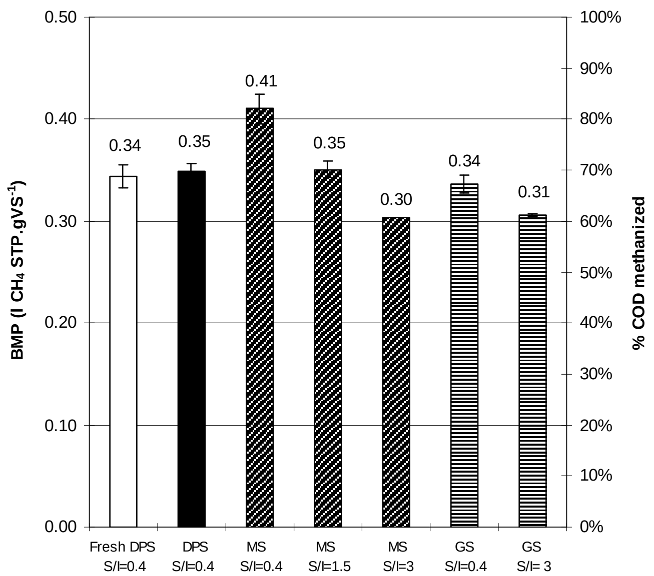


Figure 3.7 Influence of sludge type and S/I ratio in BMP assessment of frozen blended green beans using two types of anaerobic inocula (DPS: Digested primary sludge, GS: Granular sludge, MS: Mixture sludge)

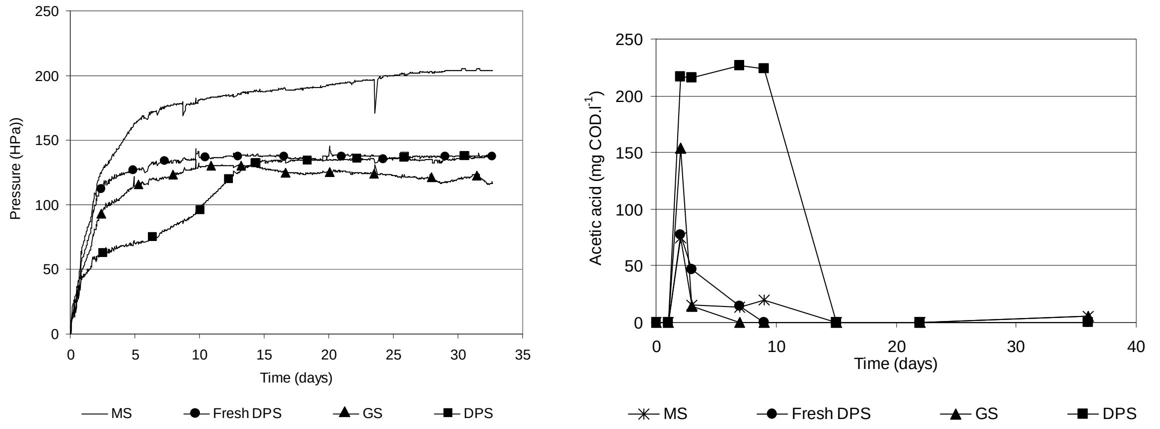


Figure 3.8 Biogas production (left) and acetate accumulation (right) during BMP assessment of frozen blended green beans samples using different anaerobic inocula (Abbreviations as in Figure 3.7)

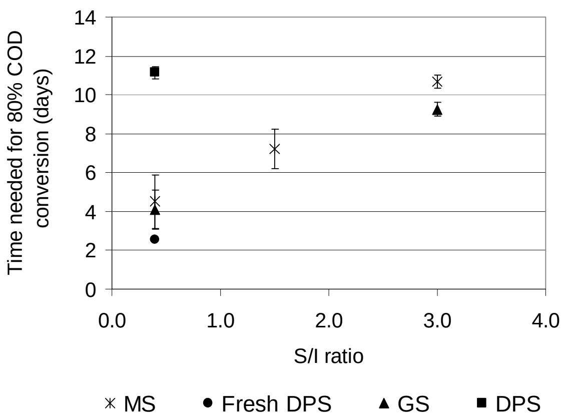


Figure 3.9 Digestion time required to achieve 80% COD methanization during the anaerobic digestion of frozen blended green beans using two types of anaerobic inocula (Abbreviations as in Figure 3.7)

The results of the SMA test (Table 3.2) indeed showed different activities of the sludges particularly with regard to the acetate conversion capacity. The highest SMA on acetate and glucose were found using the granular sludge as inoculum. Glucose conversion rates were similar for all the sludges except for the stored DPS which showed a poor performance. In addition, in the case of the fresh and stored DPS, acetate conversion rates to methane were significantly lower than the SMA assessed on glucose.

The influence of S/I was assessed for the sludge mixture and the granular sludge. In both cases a decrease in the BMP was observed with increasing S/I ratio. The extent of the effect was, however, different for the two sludges, the influence of the S/I ratio being more evident in the MS than in the GS treatments (Figure 3.7).

Test duration as given by the digestion time needed to achieve 80% COD conversion strongly depended on sludge quality and S/I ratio (Figure 3.9). The digestion time of the stored DPS was almost 3 times longer as the fresh DPS, GS and MS. In addition, the digestion time was linearly correlated with the S/I ratio in the case of MS. The latter can be attributed to the limitedly available conversion capacity for VFAs.

3.4 Effect of buffer type and molarity in the BMP of plant material

Experiments were performed to determine the influence of buffer type in the BMP assessment. The treatments having carbonate buffer and phosphate buffer at 20 mM concentration differed in their biogas production rate. The bicarbonate buffered bottles showed a distinctly faster biogas production curve as well as shorter digestion time. The final BMP value was, however, similar.

Further, the influence of both buffers was assessed at different molarities. Carbonate buffer did not show an influence in the BMP test when used at 20, 35 and 50 mM. However, a clear inhibitory effect is observed in the biogas production curves of phosphate buffered bottles with molarities of 30 and 50 mM. The inhibition observed was accompanied by a concomitant accumulation of VFA, with acetic acid accounting for the majority of it, i.e. 80%-90% (Figures 3.10 and 3.11).

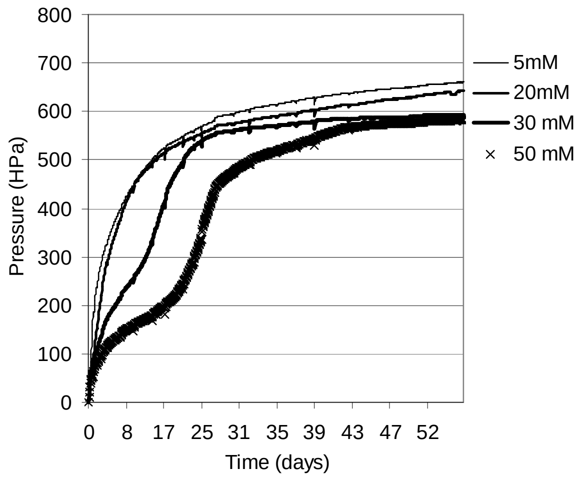


Figure 3.10 Pressure increase during the anaerobic digestion of frozen blended green beans samples at different phosphate buffer molarities

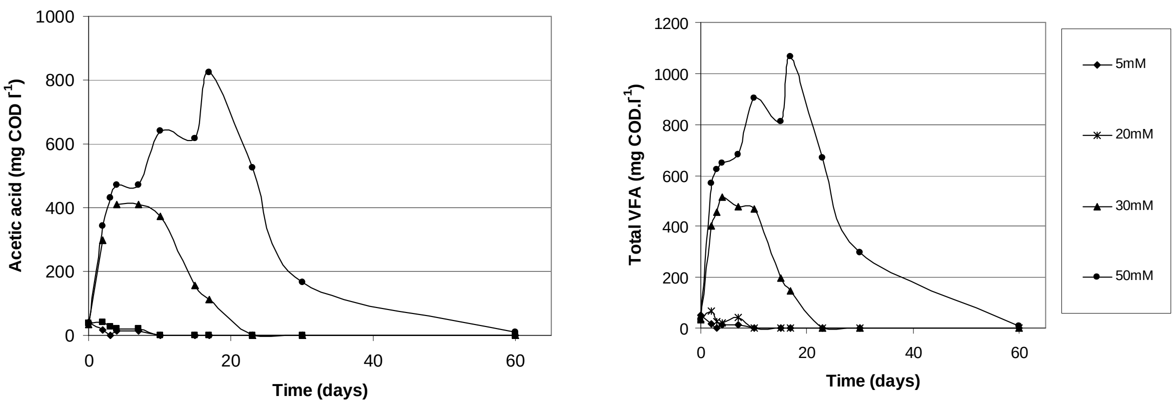


Figure 3.11 Acetate (left) and total VFA (right) evolution during batch digestion of blended frozen samples of green beans using phosphate buffer at different molarities

pH was stable in all treatments. Assessed BMP values showed similar results in the 5 mM and 20 mM treatments, whereas the treatments at higher molarities showed in average 12% and 21% lower BMP values. Notably, the influence of the phosphate buffer in the blank bottles was also severe which explains the higher BMP value assessed for the 50 mM treatment due to the lower methane production of its associated blank bottles.

4 Discussion

Our results clearly indicate the importance of the test conditions during the assessment of anaerobic biodegradability of plant material. Differences in BMP as high as 44%, 25% and 21% were found when varying pretreatments, inocula type, and buffer molarity and composition. Further, the use of NaOH pellets under our test conditions impacted detrimentally the BMP assessment.

Following, our results are examined in detail and their implications are highlighted in the form of recommendations for the BMP assessment of plant material using the OxiTop® set-up.

4.1 Impact of NaOH pellets

The presence of the NaOH pellets severely influenced the stability of the BMP test as shown by the pH increase and VFA accumulation. The severe increase in pH despite the presence of 20mM phosphate buffer provided evidence that the CO_2 absorption capacity of the pellets at all the tested concentrations negatively impacted the carbonate system in the liquid phase. Indeed when calculating the concentration of bicarbonate based on the pH and CO_2 concentration in the gas phase, a 4 fold lower concentration of bicarbonate results in the bottles with pellet addition. By carrying out additional experiments it was also found that acetate and propionate were the main VFAs present and that the H_2 concentration severely incremented in the bottles with pellets addition (data not shown).

VFA conversion to acetate and hydrogen is thermodynamically only favourable when acetate and particularly hydrogen are efficiently removed by the methanogenic bacteria (Archer et al. 1986; Thauer et al. 1977). A possible high hydrogen partial pressure immediately results in an accumulation of propionate and butyrate, which may subsequently inhibite hydrogenotrophic methanogenesis (Harper and Pohland 1986; Kaspar and Wuhrmann 1978). Likely, in our research, the NaOH pellets captured the CO_2 present in the gas phase forcing the bicarbonate and the carbonic acid in the liquid phase to dissociate and disappear from the liquid phase. Under low concentrations of CO_2 in the liquid phase, hydrogenotrophic methanogenesis cannot proceed resulting in an increase in the H_2 partial pressure, which in turn will negatively impact both acidogenesis and acetogenesis reactions. Acidogenesis under high pH_2 will lead to the formation of more reduced intermediates such as propionate, butyrate, and lactate. Finally, the resulting alkaline conditions will also inhibit acetoclastic methanogenesis.

4.2 Impact of substrate pretreatment

Among the different pretreatments tested, drying and grinding of the substrates showed the most pronounced effects. The observed increase in biodegradability is in line with the findings of Palmowski and Muller (2000) who found total biogas production of hay and sunflower seeds to increase up to 20% by comminution. Similarly, Chynoweth and Jerger (1985) showed an approximate 18% increase in the final methane yield of hybrid poplar when reducing particle size from ≤ 8 mm to ≤ 0.8 mm. Sharma et al (1988) found an increase of 56% in the maximum methane yield of grass samples when diminishing particle size from 30 mm to 1 mm.

The observed effect was examined in more detail in relation to the physical-chemical composition of the examined materials as presented in Figure 3.6. The lower content of lignin with respect to total fiber in samples of mustard and green beans was found to be related to a higher increase in biodegradability as compared to endive samples. The fact that the biodegradability of carrot is not affected can be easily explained by its low content of cellulose in relation to lignin, and its high proportion of soluble matter as compared to the other plant samples.

It has been reported that cellulose and hemicellulose are fully anaerobically biodegradable in their pure form (Chynoweth and Jerger 1985; Noike et al. 1985). However, their availability for bacterial attack depending on the structure in which they are embedded, especially in relation lignin content (Jimenez et al. 1990; Reid 1989; Tong et al. 1990; Turick et al. 1991). Furthermore, it is known that the rate and extent of hydrolysis correlates with the available surface sites for bacterial attack (Hills and Nakano 1984; Sanders et al. 2000). Therefore, an increase in comminution, which leads to the increase in the suitable sites for enzymatic attack, is expected to exert a higher influence in samples containing more biodegradable particulate material than in those with higher amounts of non-biodegradable material, i.e. lignin, and/or insignificant amounts of particulate in relation to soluble matter. More research is desirable to further confirm this hypothesis, such research should be oriented towards the development of models correlating both biomass composition and particle size with biodegradability using a higher range of variation in sample composition and applying the same test conditions.

4.3 Effect of sludge type and S/I in BMP assessment of plant material

Differences in hydrolysis capacity, intermediate conversion capacity and/or tolerance to toxicity are expected when microbial populations are different as is the case in the inocula used in this study. In general GS is characterized by a high conversion rate of VFA to acetate and subsequently to methane (Gonzalez-Gil et al. 2001). DPS has a much lower SMA and, owing to its flocculent structure, is more susceptible to biodegradable toxic compounds such as non-dissociated VFAs (Neves et al. 2004; Rozzi and Remigi 2004b).

In this study, GS and DPS differed in SMA, and, whereas different methane production rates were evident, a similar BMP value was assessed when used independently during the digestion of frozen blended samples of green beans at low S/I ratio. Strikingly, an increase in biodegradability was found when using a sludge mixture. Very likely, the DPS in our study has a higher hydrolytic activity compared to GS, whereas the GS removes more efficiently the intermediates than the DPS. A mixture, logically, will then result in the higher conversion rates.

With respect to the influence of S/I ratio in the BMP assessment, our results showed an increase in biodegradability at decreasing S/I ratio, results that are in line with previous findings of Hashimoto(1989) and Neves et al (2004). The first author previously reported a reduction in biodegradability at increasing S/I ratios when digesting ball-milled straw using a cattle manure inoculum. Neves et al (2004) performed experiments for kitchen waste using two different types of inoculum, at four different S/I ratios and two alkalinity levels. At an alkalinity level of 37 mg $NaHCO_3$ $gCOD^{-1}$ using suspended sludge, they found that the biodegradability and rate of degradation diminished dramatically when increasing the S/I ratio from 0.5 to 1 and 1.35 (VS basis), whereas in the case of the granular inoculum, the performance was only slightly affected. Both results are in agreement with our current findings.

The drop in BMP with increasing S/I ratio, might be ascribed to luxury uptake or substrate storage under conditions of high substrate (Chudoba et al. 1992). This, however, cannot directly affect the ultimate BMP measured over prolonged periods of time since the stored substrate eventually will be methanized as a result of bacterial decay. In our experiments both our test bottles and blank bottles have ceased biogas production when they were finalized.

A more logic explanation for the drop in BMP with increasing S/I ratio is the occurrence of pH related VFA inhibition at specific trophic levels. In our study, we observed that at S/I = 0.4, average pH values were similar and total VFA concentrations non inhibitory, whereas in the case of higher S/I ratios, overall pH value fluctuated in the range 6.5-7.7 and VFA concentrations were much higher as compared to reference values at S/I = 0.4, i.e. 248 and 263 mg COD l^{-1} for MS and GS, respectively (Figure 3.12). Results show a clear relation between the average pH value and the assessed BMP value. DPS and MS were much more affected by pH and/or VFA content than GS. It is also interesting to note that the BMP value assessed for the MS and the GS at the highest S/I ratio were similar. In both cases a very similar average pH value was found although VFA values are different.

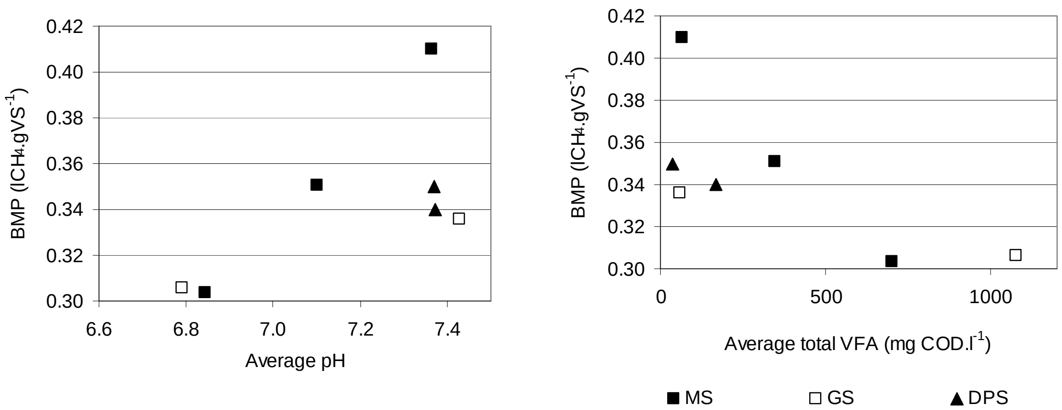


Figure 3.12 BMP values in tests performed using different inocula and S/I ratio as a function of pH (left) and VFA concentrations (right) (Abbreviations as in Figure 3.7)

On one hand, a decrease in pH inhibits the specific substrate conversion rate while on the other hand the fermentation pathways may be altered. Also hydrolysis is likely impacted by a pH decrease directly affecting the BMP of the substrate. A drop in pH may affect the charge and/or solubility of the substrate as well as the enzymatic activity, as the tertiary structure of hydrolytic enzymes is sensitive to pH changes. In a mixed anaerobic environment, hydrolytic enzymes with different pH optima are likely to be present (Sanders 2001).

4.4 Effect of buffer type and molarity on the BMP of plant material

Results show a clear inhibitory effect of the applied phosphate buffer on conversion rates and BMPs, accompanied by acetic acid accumulation. Our results are in agreement with previous findings of Conrad et al (2000) and Paulo et al (2005), who studied the inhibition of (acetoclastic) methanogenesis by phosphate buffer in anaerobic environments using non-plant samples. Our present work evidences that phosphate buffers exceeding 20mM may negatively affect the BMP assessment of plant material. Even at 20mM sometimes an effect was found in the control bottle leading to a possible misinterpretation of the assessed BMP value.

In the applied set-up using DPS a 5 mM phosphate buffer apparently sufficed since only 0.15 mM VFA accumulated, and pH was stabilized at 7.15 ±0.11.

Logically, the required buffer molarity depends on the amount of substrate added and the methanogenic activity of the inoculum used, both impacting the expected H^+ accumulation. In addition, the tolerance to toxicity from phosphate is expected to change according to the type of microbial culture. Hence, it is recommended to always run a “test-test” in order to check for the influence of these factors, especially when working close to the 20mM concentration.

4.5 Recommendations for an OxiTop® set-up for the BMP assessment of plant material

The optimization of a BMP set-up requires the definition of the essential criteria and the main goal to attain. Criteria essential from a BMP test are simplicity and reliability of the results. Simplicity can be indicated by the time required for the preparation and performance of the assessment plus the complexity of the equipment required. Reliability is the result of test stability and reproducibility of the assessment.

Regarding the goal of the assessment, two objectives can be the case, either comparability of the results with reality in a way that results can be used for reactor design, or the screening of substrates for maximum conversion. Certainly, test conditions are very different when willing to achieve a test close to reality or to maximize substrate conversion, especially in what refers to sample pre-treatments, concentrations, reactor type, feeding mode and microbial environment, i.e. use of buffers, nutrients.

In this study the use of the OxiTop® system was meant to provide a simpler and reliable test for screening purposes. Regarding the simplicity of the test, the OxiTop® test has been shown to provide the possibility of following biogas production in time with minimum human interference. However, as the use of the NaOH pellets is not advisable due to its interference with test stability, analysis of the CH_4 content in the produced biogas is still needed.

With respect to the reliability of the OxiTop® protocol, reproducibility of the test is in direct relation with the limited sample representativeness imposed by the pressure limit of the

OxiTop® head. Under the conditions of the set-up employed a maximum 0.2 g COD biodegradable substrate can be added. A higher amount of sample could be added provided that the biogas is released in time when approaching the pressure limit. However, such procedure requires more complicated calculations as the composition of the headspace changes after new biogas has been accumulated. Reproducibility of the test as given by the standard deviation showed to be in the range 2-10% and no clear relationship could be observed from the type of pretreatment or type of sample and this particular matter. Regarding quantitative results, blending and freezing samples showed to be comparable to 1 cm particle size, however, the blending procedure is complicated and difficult to standardize. Drying and grinding should be favoured if maximum conversion, reproducibility and comparability among literature values is desired. Such a procedure allows for higher homogeneity enhancing reproducibility and replicability of the test plus it can be easily incorporated in a protocol. Not to underestimate are also the additional practical advantages like the fact that dried grinded samples can be stored for a longer period of time in a reduced space and can be used as well for COD, calorimetry and fiber analysis determination. To avoid the non-enzymatic browning effect, freeze drying should be favoured. Further research is needed relating particle size and lignocellulosic composition of plant samples in order to better relate results to full scale applications.

Test stability in a BMP test has been shown to be directly related to pH conditions in the assessment. Different inocula show different capacities for the conversion of intermediates to methane and tolerance to toxicity. The previous mainly influencing the conversion rates and test duration but likely also the BMP assessment in relation to pH/VFA toxicity as found in this study. A balanced culture that includes a very active methanogenic population, combined with a low S/I ratio of about 0.4 provides maximum BMP results and minimizes test duration, i.e. 3-6 days for 80% COD conversion. Storage time of inoculum sludges, especially in the case of suspended inoculum, should be minimized since it seriously affects its intermediate conversion capacity.

In this study, the toxicity effect of increased molarity of the phosphate buffer was shown during plant substrate anaerobic conversion. The maximum allowable phosphate buffer concentration might be set at 20mM as higher concentrations may negatively affect the BMP assessment of plant material considering its observed effect in the control bottle. Carbonate buffer offers as advantage the possibility of increasing the molarities without noticeable toxicity effects, therefore allowing higher substrate concentrations. In this case it is advised to use N_2/CO_2 mixture gas for flushing bottles to avoid the increase of the pH. When deciding on the buffer molarity to employ, a small range of pH fluctuation is to be allowed in the test, again considering possible toxicity interference.

An important aspect of the BMP test which deserves further study is the influence of the blank bottle in the assessment. So far, the calculations developed suppose an equal methane generation per gVS inoculum in both the blank bottles and the bottles containing the test substrate. In fact, per definition, the absence of substrate make the blank bottle already different in kinetic (Chudoba et al. 1992) and toxicity behaviour. Such difference may already impact the corrected biogas production curves.

An optimized OxiTop® protocol following previous recommendations was developed and used in the BMP assessment of 15 plant samples as part of the CROPGEN Project. The results shown in Figure 4.1 (see Chapter 4), show the possibility of using the OxiTop® set-up for screening for plant samples suitable for anaerobic digestion even based on biogas production only, as final methane production varied in a narrow range i.e. 61-71%. Reproducibility of the test was excellent, average difference in biogas production among duplicates being 3% and fluctuating between 1 and 5%.

5 ACKNOWLEDGMENTS

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Chapter 4

Identifying valuable plant material for sustainable energy production by determination of its anaerobic biodegradability

Abstract

The Biochemical Methane Potential (BMP) of fifteen European species potentially valuable for building sustainable crop rotations was assessed by means of an optimized OxiTop® protocol. The study elucidated correlations between maximum anaerobic biodegradability (B_o) and chemical composition of plant material striving for simpler ways of screening for suitable biomass for anaerobic digestion. Results indicate a reciprocal correlation (R^2=86%, t<0.0001) between B_o and the sum lignin plus cellulose as given by the acid detergent fiber method (ADF). Model equations including more variables like hemicellulose, crude protein or starch show a similar predictive value (R^2=87-88%) but lower significance (t>0.1). Results indicate that the lignin content, as measured by the acid detergent lignin method (ADL), does not accurately predict B_o (R^2=61%). Conceptual models are developed and compared with the empirical ADF model. The predictive value of these models is found to be similar but their complexity increases. When enlarging our database with data from previous studies, the type of chemical analyses employed for substrate characterization showed to be crucial. Our empirical model was consistently confirming ADF as a good parameter for prediction of B_o. The developed model was used to predict B_o of 114 European plant samples, further identifying interesting crops and crop residues for sustainable crop rotations.

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1 INTRODUCTION

Producing energy by AD from crop material and residues is a renewable and carbon neutral, technologically viable option that allows the recirculation of nutrients and organic matter back to land, minimizing the need for external inputs and enhancing soil fertility (Ahring and Westermann 2004; Chynoweth 2004; Lehtomaki et al. 2008). AD of crops and agroresidues provide possibilities for storage and energy use on demand, contribute to sustainable energy self-sufficiency and bring opportunities to farmers by means of rural income diversification(Chynoweth et al. 2001).

In Europe incentives are given for the use of crop material as (co) substrates for anaerobic reactors (Banks et al. 2007; Weiland 2003). They are interesting co-digestion materials for waste material of inferior energy quality such as animal manure, that allow to increase the energy output per unit reactor volume (Lehtomaki et al. 2007; Weiland 2003). Currently, a limited assortment of crop material including maize, triticale, sunflower and grasses are preferred crop substrates (Weiland 2003). There is, however, potential for using other species to build crop rotations adapted to specific environmental conditions, degraded soils, and multipurpose situations (Amon et al. 2007a). The latter is of particular importance considering the ongoing discussions on competitive land use for food or energy purposes and environmental impacts of intensive agricultural systems. In a sustainable agroecosystem, needs for food, energy and conservation are addressed in an integrated way, whereas diversity is the key issue for enhancement of soil fertility minimizing external inputs.

The more than 250 thousand higher plants species in the world and the variations imposed by cultivation methods, plant growth stage and plant parts, contribute to the diversity of materials potentially available for anaerobic digestion (Deren et al. 1991; Gunaseelan 1997; Lehtomaki 2006; Saint-Joly et al. 2000). Knowledge on the anaerobic biodegradability of such potential substrates is needed in order to screen for the most suitable ones adapting to specific context conditions.

Anaerobic biodegradability is defined as the susceptibility of a test substance to undergo a biologically mediated degradation without an external electron acceptor (Angelidaki and Sanders 2004). The biochemical methane potential (BMP) test is used to assess the maximum anaerobic biodegradability (B_o) from an organic substrate under defined conditions. The BMP test is however time consuming and not standardized (Angelidaki and Sanders 2004; Colleran and Pender 2002; Rozzi and Remigi 2004b), which limits the possibilities for accurately screening materials and compare results among different research works.

Studies have been performed to relate anaerobic biodegradability of lignocellulosic biomass to their chemical composition. The characteristics reported to influence the degree of anaerobic degradation of lignocellulosic material are the content of lignin, hemicellulose, mannose (amongst hemicelluloses), cellulose as well as the cellulose crystallinity, the degree of association between lignin and carbohydrates, the wood-to-bark ratio and the presence of toxic components (Chandler et al. 1980; Chynoweth et al. 1993; Gunaseelan 1997; Jimenez et al. 1990; Lehtomaki et al. 2003; Tong et al. 1990). Previous research has attempted to define mathematical equations for estimating anaerobic biodegradability based on lignocellulosic substrate composition. However, as only substrates other than crop material have been studied (Chandler et al. 1980; Eleazer et al. 1997; Tong et al. 1990) established relationships cannot be directly applied for crop materials. In other research, the focus was in developing crop specific models (2007a; 2007b), which might not be applicable for a wider crop spectrum. Furthermore, the different studies vary in their methods for assessing BMP and characterizing plant material, which might very well explain their different outcome.

In the present study, the maximum anaerobic biodegradability of 15 selected European plant species, showing potential as part of sustainable agro-ecosystems, is assessed by means of an optimized anaerobic protocol (Pabon-Pereira et al. 2009). Lignocellulosic composition is assessed using the van Soest method (van Soest et al. 1991). The method is standardized and widely used in the field of animal sciences for predicting the energy of lactation based on lignocellulosic composition. Potentially a great amount of data on composition of crop/feed material could be available for the estimation of the anaerobic digestion potential. In this study, empirical models are developed to predict anaerobic biodegradability based on van Soest fibre analysis. Further, conceptual models assigning biodegradability values to individual fibre fractions are compared with empirical ones. The predictive strength of the developed equation is contested by comparing our results with previous research. Finally the model showing the highest statistical significance and easiness of application is used to predict the anaerobic biodegradability of 114 European plant samples.

2 MATERIALS AND METHODS

2.1 Plant material

The selected plant species derived from an evaluation conducted as part of the EU Cropgen project, taking into account attractive agronomic features, such as low energy input and nitrogen fixation potential, their availability and multipurpose use. The test substrates consisted of 6 legumes, 2 perennial herbs, 2 pseudocereals, 2 cereals, 1 vegetable, 1 grass and 1 oil crop. Most of the crop material used for this study was grown in glasshouse, i.e. legumes, pseudocereals, whereas few others were collected from the field in UK, i.e. triticale. Samples were freeze dried, grinded and sieved to pass through a 0.2 mm mesh, the previous to avoid interference of particle size in biodegradability assays as has been previously reported (Moller et al. 2004; Pabon-Pereira et al. 2009; Sharma et al. 1988). Samples were fully characterized in terms of TS, VS, COD, elemental composition (CHNO), fiber analysis and starch (Table 4.1). In addition the proportion of soluble COD (sCOD) was assessed as a means to distinguish between the plant material immediately solubilized and that remaining suspended.

Table 4.1 Characteristics of plant samples employed as substrate for the biodegradability experiments

Common name	Scientific name	Crop type	TS [gTS g^{-1}]	VS [%TS]	COD [gO_2 gVS^{-1}]	TF [g gVS^{-1}]	L [g gVS^{-1}]	C [g gVS^{-1}]	H [g gVS^{-1}]	Starch [g gVS^{-1}]	Protein [g gVS^{-1}]
Yellow lupin	*Lupinu luteus*	Legume	0.15	91%	1.54	0.58	0.04	0.41	0.13	0.00	0.15
Vetch	*Vicia sativa*	Legume	0.24	93%	1.47	0.51	0.06	0.32	0.13	0.03	0.18
Carrot	*Daucus carota*	Vegetable	0.11	90%	1.37	0.29	0.01	0.17	0.11	0.00	0.18
Spartina	*Spartina anglica*	Wild grass	0.32	89%	1.42	0.77	0.05	0.26	0.46	0.00	0.12
White lupin	*Lupinus albus*	Legume	0.14	93%	1.46	0.65	0.03	0.32	0.30	0.01	0.21
Triticale	*Triticum secale*	Cereal	0.70	97%	1.43	0.47	0.04	0.22	0.21	0.32	0.08
Braken	*Pteridium aquilinum*	Fern-perennial	0.16	94%	1.51	0.63	0.20	0.32	0.11	0.05	0.20
Sweet clover	*Melilota officinalis*	Legume	0.33	94%	1.58	0.53	0.03	0.32	0.18	0.00	0.17
Winter Barley	*Hordeum vulgare*	Cereal	0.38	95%	1.43	0.65	0.02	0.23	0.40	0.22	0.09
Winter bean	*Vicia faba*	Legume	0.15	92%	1.52	0.42	0.03	0.24	0.15	0.01	0.26
Sweet pea	*Pisum sativum*	Legume	0.15	90%	1.53	0.29	0.02	0.20	0.07	0.11	0.24
Oil seed rape	*Brassica napus*	Oil crop	0.26	93%	1.62	0.54	0.05	0.33	0.15	0.02	0.13
Buckwheat	*Fagopyrum esculentum*	Pseudo cereal	0.17	90%	1.45	0.44	0.05	0.26	0.12	0.04	0.14
Rosebay willow	*Chamaenerion angustifloium*	Herb-perennial	0.38	94%	1.53	0.76	0.09	0.40	0.14	0.02	0.15
Quinoa	*Chenopodium quinoa*	Pseudo cereal	0.22	86%	1.35	0.27	0.01	0.13	0.23	0.19	0.13

TF: Total Fiber; L: Lignin; C: Cellulose; H: Hemicellulose.

2.2 Biochemical Methane Potential test

The experimental set up for measuring the rate and extent of degradation was an optimized Oxitop® (WTW, Giessen, GERMANY) protocol previously developed (Pabon-Pereira et al. 2009) as a modified version of the method described by Owen et al (1979). The test lasted 40 days, it was assured that the gas production has ceased by controlling the change in pressure in the bottles ensuring less than 1% brut gas production in at least 3 days.

2.3 Inocula

A sludge mixture consisting of active suspended digested primary sludge and anaerobic granular sludge was added, keeping a Substrate to Inoculum ratio (S/I ratio) equal to 0.5 (VS basis) to guarantee adequate presence of hydrolytic and methanogenic microbial populations. The digested primary sludge, with 0.023 gVS l^{-1} and 1.70 gCOD l^{-1} originated from a wastewater treatment plant working at mesophilic temperatures. The granular sludge having 0.058 gVS l^{-1} and 0.82 gCOD l^{-1} originated from a mesophilic upflow anaerobic sludge blanket (UASB) treating alcohol distillery effluents.

2.4 Analytical methods

For the characterization of the substrates and sludges, freeze drying was performed in liquid nitrogen in a GRI 20-85 MP freeze drier (Wijk bij Duurstede, The Netherlands) equipped with two condensers. Comminution was performed in a Retsch BV grinder (Haan, Germany). TS and VS were performed according to standard methods (APHA 1998). The elemental analysis (EA) of the freeze dried grinded materials was performed in a Thermoquest CE-instruments 1110 CHNS-O equipped with a prepacked quartz reactor column. From the EA, COD was calculated applying the Bushwell formula (Symons and Buswell 1933). Crude Protein content was calculated by multiplying the nitrogen content assessed by elemental analysis by 6.25 g protein per g N (Undersander et al. 1993). Fibre analysis was performed according to van Soest (1991) using the freeze dried grinded samples, the Neutral Detergent Fibre (NDF); Acid Detergent Fibre (ADF); and Acid Detergent Lignin (ADL) being determined in this way. All analyses were performed in duplicate or triplicate. Description of the methods used to follow up of the experiments is described in Chapter 3 of this thesis.

2.5 Calculations

The BMP, expressed as liters methane at standard temperature and pressure of 273^{o}K and 10^{5} Pa per amount of substrate volatile solids added [lCH_4-STP gVS^{-1}], is calculated from the maximum methane production of the sample bottle, corrected by the maximum methane production of the blank bottle. The maximum number of moles of methane produced is calculated by applying the ideal gas equation to the total pressure increase and multiplying the biogas moles by the percentage of methane in the headspace. Detailed calculations are described in Chapter 3 of this thesis.

The biodegradability (B_o) achieved under our defined test conditions is defined as the maximum percentage COD added converted to methane and is calculated as the ratio between the net maximum accumulated methane as COD divided by the total COD amount added in the bottle(Veeken and Hamelers 1999), as shown in Equation 4.1.

$$B_o = \frac{CH_{4,\max}}{S_o} \times \frac{2.86}{COD_s} \times 100 \qquad (4.1)$$

Where $CH_{4,max}$, is the maximum net amount of methane produced at final digestion time [l], S_o is the amount of substrate added [gVS], 2.86 corresponds to the COD equivalence of 1 liter methane at standard temperature and pressure [gCOD l^{-1}] and COD_s is the COD of the sample [gCOD gVS^{-1}]. Whereas B_o refers to the substrate converted to methane, there is a portion of the substrate that remains in the form of bacterial biomass and is not directly accounted by equation 1. Such amount cannot be directly measured and hence needs to be estimated. In the conceptual models developed in the discussion section of this work this aspect is taken into consideration.

The maximum biodegradability of the particulate material B_p is calculated using Equation 4.2.

$$B_p = \left(\frac{COD_{methane,t=\max} + COD_{s,t=\max} - COD_{s,t=0}}{COD_{in} - COD_{s,t=0}} \right) \qquad (4.2)$$

Where $COD_{methane,\ t=max}$ is the COD equivalent concentration of methane produced at final digestion time [gCOD l^{-1}], $COD_{s,\ t=max}$ is the soluble COD at final digestion time [gCOD l^{-1}], $COD_{s,\ t=0}$ is the concentration soluble COD at time t=0 [gCOD l^{-1}], and COD_{in} is the total initial COD concentration in the bottle [gCOD.l^{-1}].

Similarly, the maximum biodegradability of the soluble material B_s is calculated using Equation 4.3.

$$B_s = \left(\frac{COD_{s,t=0} - COD_{s,t=\max}}{COD_{s,t=0}} \right) \qquad (4.3)$$

3 RESULTS

3.1 Anaerobic biodegradation of the assessed plant material

The maximum biogas amount was reached in most cases after 25 days digestion, whereas less than 1% net gas production was produced in the last 8-10 days of the experiment (see Figure 4.1). Reproducibility of the test was excellent, average difference in biogas production amongst duplicates was 3% and fluctuating between 1 and 5%. Measured maximum net biogas production in all plant species was between 0.22 and 0.56 l gVS^{-1}, 80% of the species being in the range between 0.34 and 0.44 l gVS^{-1}. Biogas composition showed an average 65% of methane in the final gas, varying in the range 61-71%. The methane concentration increased in time (56-65%) during the first 4 days of the study, thereafter remained stable.

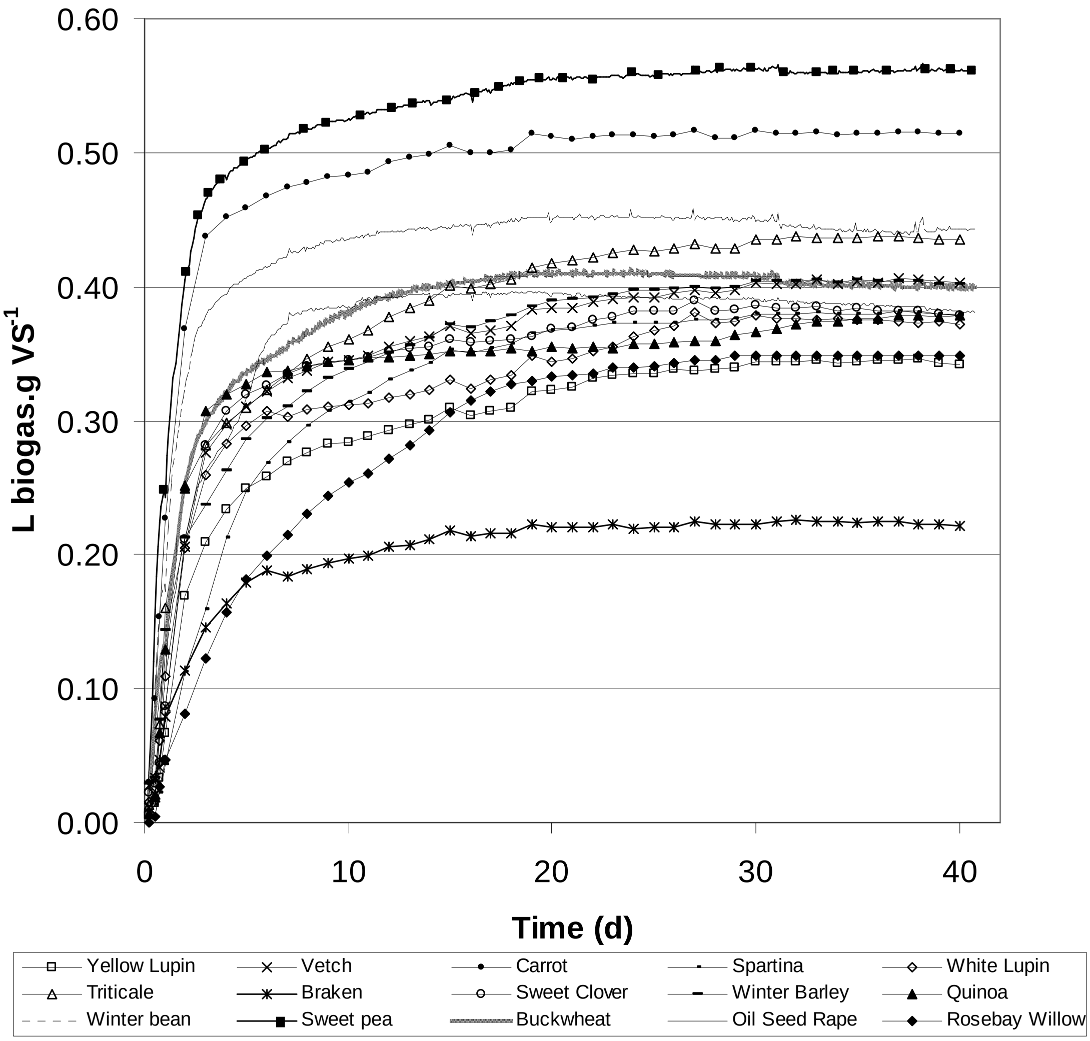

Figure 4.1 Net biogas evolution during the BMP assessment of fifteen plant samples by means of an optimized BMP protocol

Table 4.2, presents the BMP and B_o assessed for the tested materials. BMP ranged from 0.18 to 0.37 being in average 0.29 $lCH_4 \cdot gVS^{-1}$ and in line with data previously reported (Lehtomaki et al. 2008; Sharma et al. 1988). Two leguminous species, sweet pea and winter bean, showed the highest BMP values, i.e. above 0.35 l $CH_4.gVS^{-1}$, followed by carrot and the (pseudo) cereals buckwheat and quinoa. The two samples of perennial wild species, braken and rosebay willow, showed the lowest B_o, i.e. below 37%.

Biodegradability was also analyzed in relation to the form of the COD in the samples, i.e. particulate or soluble. The proportion of particulate COD of the total COD was in average 77%, varying from 50 to 88%. The achieved average maximum degradation of particulate and soluble COD was 46 and 94%, respectively. Whereas anaerobic degradation of particulate COD showed a variation in the range 22-62%, the soluble COD biodegradability varied in a more narrow range (86-100%) (See Table 4.2).

Table 4.2 BMP and biodegradability as assessed from batch digestion of 15 European plant species

Specie	BMP [lCH_4 gVS^{-1}]	BMP [lCH_4 $gCOD^{-1}$]	B_o [%COD]	B_p [%pCOD]	B_s [%sCOD]
Yellow lupin	0.26±0.01	0.16±0.01	47%	36%	92%
Vetch	0.29±0.02	0.20±0.01	56%	43%	99%
Carrot	0.31±0.01	0.23±0.01	66%	31%	100%
Spartina	0.29±0.01	0.21±0.01	59%	52%	97%
White lupin	0.26±0.01	0.18±0.01	52%	35%	100%
Triticale	0.29±0.00	0.20±0.00	57%	52%	86%
Braken	0.18±0.01	0.12±0.01	34%	22%	92%
Sweet clover	0.29±0.01	0.18±0.01	53%	42%	88%
Winter barley	0.30±0.01	0.21±0.01	60%	51%	93%
Winter bean	0.35±0.02	0.23±0.02	66%	55%	89%
Sweet pea	0.37±0.03	0.24±0.02	70%	61%	93%
Oil seed rape	0.29±0.02	0.18±0.01	51%	59%	90%
Buckwheat	0.32±0.02	0.22±0.01	63%	54%	98%
Rosebay willow	0.20±0.01	0.13±0.01	37%	-	-
Quinoa	0.33±0.02	0.24±0.01	70%	-	-

B_o: Proportion of Total COD converted into methane by the end of the digestion time. B_p: Proportion of the particulate COD that was methanized by the end of the digestion time. B_s: Proportion of the soluble COD that was methanized by the end of the digestion time.

3.2 B_o and plant composition

The amounts of specific structural fiber components varied between species (see Table 4.1 and Figure A4.1.1, Appendix 4.1). Samples were mainly composed of hollocellulose, i.e. cellulose and hemicellulose, in the range 0.27-0.72 g gVS^{-1} whereas the assessed fraction of lignin was found to be much smaller viz. in the range 0.01-0.20 g gVS^{-1}. Crude protein fractions were also found to be substantial ranging between 0.08-0.26 g gVS^{-1}, whereas starch fractions were generally low and only important in samples of (pseudo) cereals namely triticale, winter barley and quinoa [g gVS^{-1}]. The previous features in composition can be attributed to the crop selection, as six out of the fifteen species studied were legumes, which are crops known to have significant portions of proteins, low starch content and a great variety of growth forms, i.e. from small herbaceous species to large, woody trees.

The individual fibre fractions and the fractions of crude protein and starch were analyzed for their relation to B_o of the tested plant samples. Single and multiple variable equations were obtained by means of linear regression and tested by F-statistics using the statistical program Genstat 9th edition (Table 4.3). The best fit was obtained by correlating the ADF content of the plant samples with the assessed BMP value, yielding a correlation coefficient (R^2=86%) and a high level of significance <.0001. The linear model based on the individual components lignin and cellulose had a similar correlation coefficient with both cellulose and lignin, showing a good level of significance, i.e. ≤0.005. The total fiber content was the poorest predictor of B_o (R^2=37%). As well, lignin content alone showed to be a poor indicator for overall maximum anaerobic biodegradation (R^2=61%) although its importance is ratified by the fact that the statistical relations tested show better correlation when this fraction is included in the equations. The cellulose content showed to be significantly related to biodegradability in most of the models studied. Increasing the number of variables involved in the model, including starch and/or crude protein content, only slightly affected the correlation coefficient, whereas the level of significance of these other predictor variables remained low.

Table 4.3 Number of parameters (p), Coefficient of determination (R^2) and significance (t values) for the estimation of biodegradability from different plant components

Model variables	p	R^2	Predictor variables (t values)						
			NDF	ADF	C	H	L	CP	St
ADF	2	86	-	0.000	-	-	-	-	-
C, L	3	87	-	-	0.000	-	0.001	-	-
ADL=L	2	61	-	-	-	-	0.000	-	-
NDF	2	37	0.010	-	-	-	-	-	-
C	2	65	-	-	0.000	-	-	-	-
C,H	3	63	-	-	0.000	0.953	-	-	-
C,L,St	4	88	-	-	0.000	-	0.000	-	0.138
C,L,CP	4	88	-	-	0.000		0.000	0.132	-
C,H,L	4	87	-	-	0.000	0.385	0.001	-	-

NDF: Neutral Detergent Fiber (representing C+H+L); ADF: Acid Detergent Fiber (representing L+C); ADL: Acid Detergent Lignin; C: Cellulose; H: Hemicellulose; L: Lignin; CP: Crude Protein; St: Starch

Figure 4.2 presents an illustration of the test for linearity between fiber components and substrate biodegradability. Although it can be observed that braken, the sample with the highest lignin content, exerts an important leverage effect in the equation relating lignin with biodegradability, when omitting this sample the strength of the correlation does not change (R^2=60%).

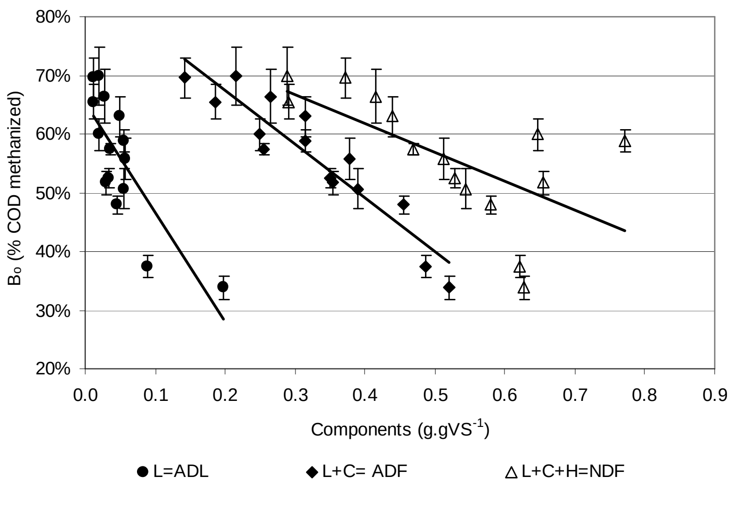

Figure 4.2 Percentage maximum methanized COD (B_o) in dependence of fiber components

4 DISCUSSION

Our results have shown a strong correlation between fibre components and biodegradability of plant material of different origin. Hereafter, the meaning of the developed model and of the BMP values is examined in more detail and set in a broader context.

4.1 Interactions among plant cell wall components and B_o.

Models obtained by linear regression of single or multiple parameters are empirical, hence assessed correlations not necessarily imply a direct causal relation. The value of a specific model has to be judged against available knowledge, in our case on the anaerobic degradation properties of lignocellulosic materials.

Plant material is composed of cell soluble material and different types of structural tissues namely, lignin, cellulose and hemicellulose. Cell contents contained within the boundaries of the cell wall include sugars and storage or reserve carbohydrates, such as starch, fructosans and galactans, as well as crude protein and lipids. They vary a lot in proportion amongst different species and are highly biodegradable. Structural tissues in turn, can make up to 90% or more of the composition of wood (Chynoweth and Jerger 1985), whereas less and more variable proportions are present in herbaceous materials. Cellulose is the main constituent of the primary, most external, cell wall of green plants, whereas variable amounts of lignin and hemicellulose along with cellulose are present in the secondary wall. Lignin is a complex compound non-uniform in chemical and physical composition (Lewis and Yamamoto 1990). The compound is mainly refractory under anaerobic conditions although there is evidence that shows its (partial) degradation in anaerobic environments (Benner et al. 1984; 1982; Op den Camp et al. 1988).

In the past, lignin has been proposed as the single indicator for estimating the anaerobic biodegradability of lignocellulosic material (Chandler et al. 1980). However, our findings are in agreement with previous findings of Tong (1990) and Chynoweth (1993), reporting the poor value of lignin as a sole predictor.

Apart from its recalcitrance, the impact of lignin on anaerobic biodegradation is mainly associated to its role in lignocellulose complexes. The occurrence of lignin within the lignocellulosic matrix has been reported to hamper the extent and rate of degradation of the more degradable hollocellulose components (Barton and Akin 1977; Selinger et al. 1996). The mechanism through which lignin affects hollocellulose decomposition could either be through blocking the access of microorganisms to the more degradable areas (Benner et al. 1984), or through inhibitory effects coming from lignin compounds or its hydrolysates. A study carried out with excavated refuse samples suggests that bioavailability of degradable carbohydrates rather than toxicity limited methane production (Wang et al. 1994).

Our results clearly show that the sum lignin plus cellulose as assessed by the van Soest method, correlates better with the anaerobic biodegradability compared to a single component correlation. Recently, Buffiere et al (2006) indicated a link between the sum lignin and cellulose and biodegradability of organic wastes, however no statistical analysis was reported.

According to our results, under reported test conditions the relation can be described by Equation 4.4 where L is Lignin [gVS g^{-1}] and C is Cellulose [gVS g^{-1}].

$$B_o = 0.86 - 0.92(L + C) \qquad \text{with } L \neq 0 \text{ and } C \neq 0 \qquad (4.4)$$

Statistically, such interaction between lignin and cellulose can be tested by including an extra term in the equation accounting for the product terms of the two variables. Equation 4.5 shows the tested equation, which has a similar coefficient of determination (R^2=88%) and good significance (F_{test}<0.001). The interaction amongst the variables is proven by the fact that the extra parameter is different than 0 (=1.87) implying that the effect of the individual variables is dependant on the value of the other. Given that the individual significance of the extra term remains low, i.e. t=0.137 > 0.005, and Equation 4.5 involves more variables, Equation 4.4 is preferred.

$$B_o = 0.81 - 0.69(L + C) - 1.87(L * C) \qquad (4.5)$$

Equation 4.4 proposes a logic approach to biodegradability as follows. It establishes an absolute maximum biodegradability of 0.86 for our population, which is in close relation to the calculated conversion efficiencies reported by Tong (1990) accounting for bacterial growth and decay. It also proposes a decreased biodegradability in relation to the sum lignin plus cellulose. Since the ADF value is expressed in [g gVS^{-1}] a conversion factor of 1.2 gCOD gVS^{-1} corresponding to average COD content of lignin and cellulose (Angelidaki and Sanders 2004; Moller et al. 2004; Wang et al. 1994) is implicit in the term 0.92. Hence, it is suggested that about 77%, viz.0.92/1.2, of the sum lignin plus cellulose is not degraded.

4.2 Estimation of B_o based on individual fiber components.

Equation 4.4 was further compared with conceptual models where the individual fractions of plant components are given different biodegradability values considering their properties. The equations depart from an overall equation assigning different biodegradability properties to cellulose (C_i), hemicellulose (H_i) and the cell solubles (CS_i) as shown in Equation 4.6.

$$B_{oi} = (B_{oC} \times C_i \times C_{av}) + (B_{oH} \times H_i \times H_{av}) + (B_{oCS} \times CS_i) - X_b \qquad (4.6)$$

In Equation 4.6 the subscript i in the equation refer to each of the plant material tested. The method of minimization of sum of squares was used to estimate the individual biodegradabilities of cellulose (B_{oC}), hemicellulose (B_{oH}) and cell solubles (B_{oCS}) and to estimate the average amount of substrate converted to microbial biomass (X_b). Note that B_{oi}+X_b accounts for the total degraded COD.

Different mathematical relations for the definition of the fractions of bio-available cellulose (C_{av}) and hemicellulose (H_{av}) were tested. Model I and II are a first approximation into an individual quantitative relation between the biodegradability of the fractions of cellulose and lignin, and hemicellulose and lignin, respectively. Model III is similar but considers both cellulose and hemicellulose to act as one entity. In Model IV the relation between lignin and hollocellulose availability (CH_{av}) is considered to be surface related as previously proposed by Conrad et al. (Conrad et al. 1984) when estimating maximum rumen digestibility of animal feeds. Such surface relation considers that lignin and the rest of cell walls are located close surface to surface and that the surface of any geometric object can be calculated as the square of the mean linear dimension of its two third power of its mass. Table 4.4 presents the models I, II and IV developed and their statistical performance.

Table 4.4 Equations, number of parameters (p), Coefficient of determination (R^2) and significance (t values) for the estimation of anaerobic biodegradability based on a deterministic approach.

Model		Assumption tested	R^2	RSS	F_{pr}
I	$\hat{B}_o = (0.22\times C_i \times C_{av}) + (1.01\times(NDS_i + H_i)) - 0.17$	$C_{av} = \frac{C-L}{C}$	86	0.006	<0.001
II	$\hat{B}_o = (0.58\times C_i \times C_{av}) + (0.85\times(H_i)\times H_{av})(1.14\times NDS_i) - 0.25$	$C_{av} = \frac{C-L}{C}$ $H_{av} = \frac{H-L}{H}$	81	0.016	<0.001
III	$\hat{B}_o = (0.74\times(C_i + H_i)\times CH_{av}) + (1.04\times NDS_i) - 0.25$	$CH_{av} = \frac{C+H-L}{C+H}$	73	0.011	<0.001
IV	$\hat{B}_o = (0.86\times(C_i + H_i)\times CH_{av}) + (1.07\times NDS_i) - 0.28$	$CH_{av} = \left(1 - \frac{L^{2/3}}{NDF^{2/3}}\right)$	75	0.011	<0.001

C: Cellulose; H: Hemicellulose; L: Lignin; $_{av}$: available; NDS: Neutral Detergent Solubles

The four conceptual models tested were found to be statistically sound if judging from the R^2 and F_{test} value. In addition, all models give reasonable values of biodegradability of non cell wall components (B_{oCS}) and microbial biomass (X_b). B_{oCS} is in the range 1.01-1.14, which means a 72-81% biodegradability considering an average COD content of cell solubles of 1.3-1.5 gCOD gVS^{-1}. On the other hand, 11-19% of the added substrate is expected to end as bacterial cell yield (X_b) if assuming an average anaerobic bacterial composition of $C_5H_7O_2$ N giving a COD content of 1.42 gCOD gVS^{-1}. Nonetheless it is important to note that in the value assessed for X_b also an average error of the equations is embedded. With regard to the biodegradability figures estimated for cellulose and hemicellulose, model IV is closer to the theoretically expected full anaerobic biodegradability of cellulose and hemicellulose in their pure form (Chynoweth and Jerger 1985; Noike et al. 1985).

All models developed, including the empirical one (Equation 4.4), were used to predict anaerobic biodegradability based on the chemical composition of the various assessed crops (Figure 4.3). It can be observed that the predictions of the empirical equation (Equation 4.4) and model I relating the fraction lignin to cellulose are in close agreement. In addition, all models would allow screening for suitable plant material for anaerobic digestion in a similar way as the experiment performed. However, equations including hemicellulose, Models II, III and IV, particularly fail to predict B_o of one of the samples, i.e. spartina. Spartina is the specie with the highest hemicellulose content and the only grass specie included in this study. Grasses seem to have significant amounts of acid soluble lignin, whereas the hemicellulose content in the primary cell wall is higher (Hatfield and Fukushima 2005). When looking closer into the relationship between total fiber and biodegradability (Figure 4.2, Tables 4.1 and 4.2), it is clear that the three data points showing the highest content of hemicellulose, i.e. spartina, white lupin and winter barley, showed higher B_o than other samples having similar total fiber content but higher relative cellulose content, such as braken and rosebay willow. When the model is tested omitting the three species showing higher hemicellulose content, its predictive value greatly increases (R^2=90-94%) suggesting that this fiber component is better biodegradable than cellulose and lignin.

Our observations are in agreement with previous research in which hemicellulose was found to be more biodegradable than cellulose in experiments carried out with water hyacinth and Bermuda grass (Ghosh et al. 1985). It has also been reported that hemicellulose needs to be degraded firstly, followed by cellulose according to its location within the lignocellulose matrix (Leschine 1995). From the previous, it appears logic that an individual term for hemicellulose content is not required within a mathematical equation linking B_o with substrate composition.

The use of the empirical model (Equation 4.4) requires a third of the effort of the conceptual model as only the ADF fraction, representing lignin plus cellulose, needs to be assessed avoiding the need of separately assessing the lignin and NDF amount. Therefore it is preferred as compared to the conceptual models for simplification of the prediction of anaerobic biodegradability.

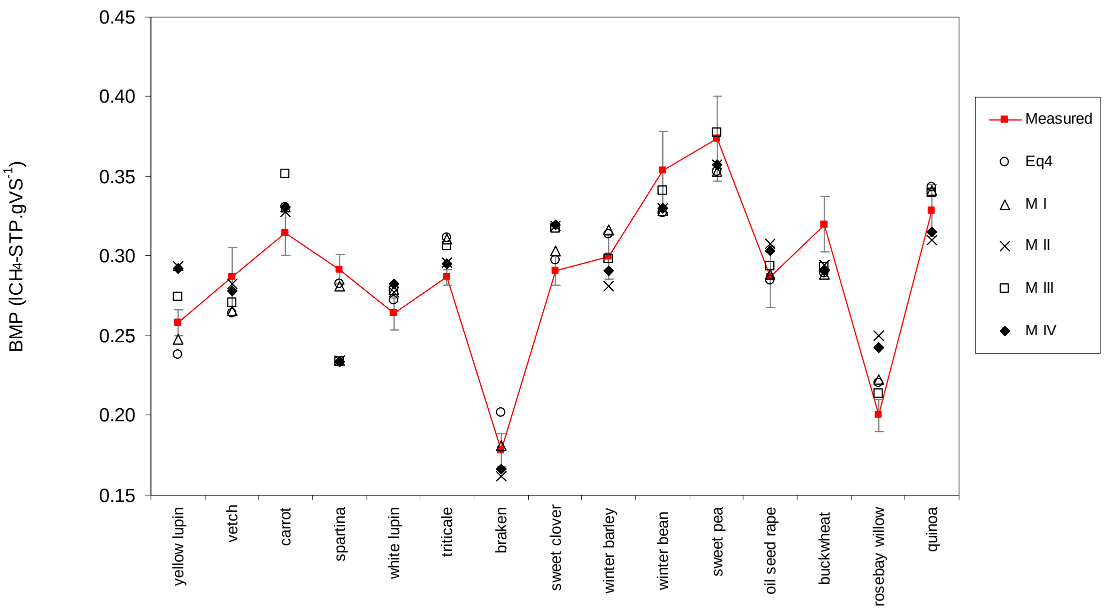

Figure 4.3 BMP estimation using different model equations
Equations are described in Table 4.4

4.3 Comparison with previous research

Thus far it has been shown that B_o of diverse crop species can be approximated by use of simple linear models. We subsequently compared our results with data from previous biodegradability studies (Amon et al. 2007b; Buffiere et al. 2006; Chandler et al. 1980; Eleazer et al. 1997; Ghosh et al. 1985; Moller et al. 2004; Pareek et al. 1998; Tong et al. 1990). When plotting the data from all studies (See Figure A4.1.2 in Appendix 4.1) a great dispersion of data points is found not being possible to establish a singular preferred correlation among the components tested and B_o, although the link amongst B_o and substrate composition can be observed from the dispersion of the data points. Three different reasons could be explanatory. Firstly, differences in composition due to the variability in substrate origin, i.e. presence of toxic compounds, proportion of structural and non-structural components, are expected and could potentially influence the computed outcome. Secondly, the accuracy of the BMP test is to be considered, as mentioned before biodegradability assays are influenced by different test conditions as reported elsewhere (Angelidaki and Sanders 2004; Muller et al. 2004; Pabon-Pereira et al. 2009; Rozzi and Remigi 2004b). Thirdly, variation is expected with regard to the chemical analyses procedures. Apart from van Soest, other methods for the evaluation of structural components of lignocelluloses material are available, i.e. Klasson lignin, TAPPI, Near Infrared Resonance (NIR) and Nuclear Magnetic Resonance (NMR), and although related they are expected to deliver different results (Fernandes and Lier van 2007; Fukushima and Hatfield 2004; Hatfield and Fukushima 2005; Hatfield et al. 2006; Jung et al. 1997). Especially with regard to lignin analysis, the mentioned methods deliver different quantitative estimates, their accuracy depending largely in the type of crop, their crude protein content and potential soluble lignin (Fukushima and Hatfield 2004; Hatfield and Fukushima 2005; Jung et al. 1997). Studies conducted in the past for predicting biodegradability have used different methods hence limitations are evident in their comparability. Whereas Pareek (1998), Ghosh et al (1985) and Buffiere et al (2006) have used the ADL method as in this study, Chandler et al (1980), Moller et al (2004), Tong et al (1990) and Eleazer et al (1997) used the Klason or 72% sulphuric acid method for lignin determination. When plotting only the data of studies using the van Soest method, the correlation is stronger in this case, whereas when plotting results from studies using other methods, correlations are not found (Figure A4.1.2 in Appendix 4.1). Although residues other than plant material are plotted in both cases and differences in methods for BMP determination are expected, these factors seem to be less crucial than the type of chemical analysis procedure used for sample characterization.

4.4 Using the ADF Model for B_o estimation

The equations presented in this study strive to give an indication on the maximum achievable anaerobic biodegradability of plant material under applied optimal conditions. They are useful for screening for the material best suitable for anaerobic digestion from the perspective of their maximum intrinsic energy potential.

The ADF model (Equation 4.4) was further used to predict the anaerobic biodegradability of other material suitable for building sustainable crop rotations. The database employed in the study by Stenberg et al (2004) containing 114 lignocellulosic samples characterized using the van Soest method for fibre analyses. The database contains Northern European agricultural plants and anatomical components, including cereals, pasture grasses, legumes, vegetables, fiber crops, energy crops and catch crops. The variation of sample composition was similar to that of our research NDF, ADF and ADL varying in the ranges 0.15-0.83, 0.07-0.65 and 0.01-0.17 g gTS^{-1} with average values of 0.51, 0.33, 0.04, g gTS^{-1}, respectively. Average predicted anaerobic biodegradability was 53%, whereas a fourfold difference was found between minimum and maximum values, i.e. 21% and 79%. Clear differences were also found amongst different plant parts. The average biodegradability of green leaves, mature straw, pods, stems and whole plants was 63%, 39%, 71%, 44% and 53%, respectively. The previous show how crop residues like straws and stems have in general low anaerobic potential per unit solids. Nonetheless, interestingly, the pods of barley and maize along with the green leaves of oilseed-rape, sugar beet, carrot and hemp were found to be the most promising substrates showing between 70% and 79% anaerobic biodegradability. Hence, a choice for residues instead of plants competing with food is still possible without compromising methane yield per unit solids. Among whole plant samples, legumes and grasses showed the highest anaerobic biodegradability, yet it is possible to find other agricultural crops like oil seed rape similarly suited from the perspective of their anaerobic biodegradability. The database and predicted biodegradability is available in Table A4.1.1 in Appendix 4.1.

Apart from intrinsic anaerobic biodegradability, the overall energy yield for real application will depend among other aspects like the agricultural yield and volatile solids content of the substrates. Further, building sustainable crop rotations suitable for multiproduct manufacture entails the study of other variables including: the suitability of the agricultural crops for applications different than anaerobic digestion, their intrinsic and complementary agricultural and environmental features as well as economic and social aspects. For example, seed legumes such as beans and peas are valuable protein sources for humans and that their straws and also other legume crops like clover, alfalfa, and lupin are valuable as feed sources for livestock. Also grass can be eaten by cattle and transformed in meat and milk which are high value products. Integrated studies covering the different variables are needed in order to build multipurpose sustainable crop rotations adapted to different conditions.

4.5 Final conclusion

Anaerobic biodegradability of lignocellulosic material was empirically found to be related to the amount of cellulose plus lignin as analytically assessed by the van Soest method, i.e. the ADF value. Among the models developed, those omitting hemicellulose showed a higher predictive value. The latter can be attributed to the higher hemicellulose anaerobic conversion and the fact that it needs to be degraded previously to cellulose.

Apart from being theoretically meaningful, the ADF-based empirical model requires the least effort compared to the conceptual models as individual fractions of cellulose, hemicellulose and lignin do not need to be assessed, which enhances the accuracy of the model's estimation. The model also showed to be consistent when biodegradability data from previous studies performing the van Soest sample characterization was employed. The model was further used to predict the anaerobic biodegradability of other material suitable for building sustainable crop rotations. In our study legumes show to have a very good potential as part of sustainable crop rotations due to their intrinsic anaerobic biodegrability plus additional agronomic advantages. In addition, grasses and residual green leaves of different crops are promisable from the perspective of their anaerobic biodegradability. Still, considering the overall objective of developing sustainable crop rotations to deliver food, feed, energy and other material outputs, the contribution of AD to add value to biomass system remains a challenge to be undertaken as part of integrated studies. The empirical model developed provides a simple estimation procedure to screen for useful biomass materials for AD considering local/regional availability.

Acknowledgment

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Appendix 4.1

Additional information is supplied in this appendix including: Figure A4.1.1. Comparative analysis on the chemical composition of the 15 European plant samples studied. Figure A4.1.2. Relation between anaerobic biodegrability and substrate composition using data from previous studies Table A4.1.1 Classification, van Soest analysis and predicted anaerobic biodegradability (B_o) of 114 Northern European Plant samples.

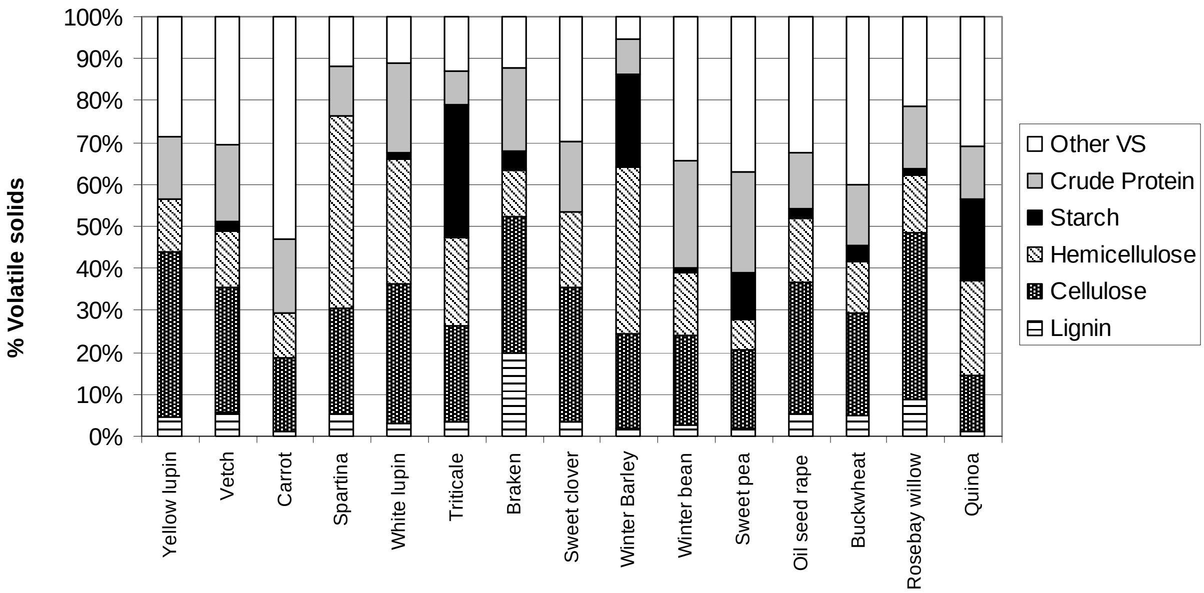
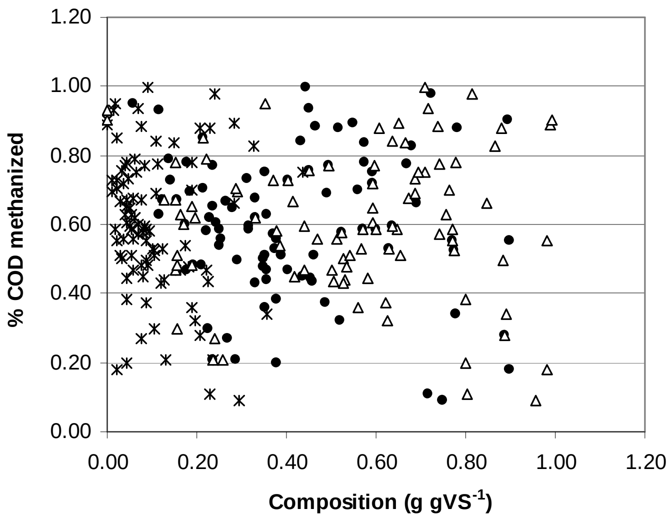
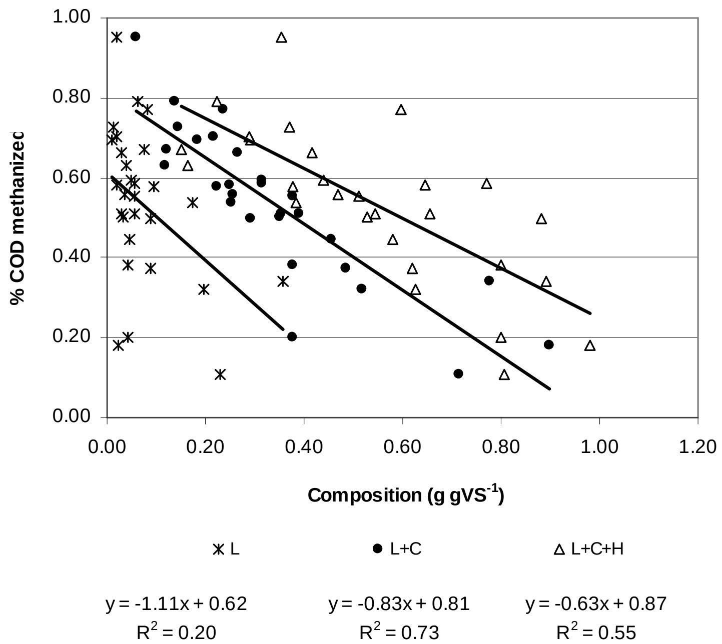


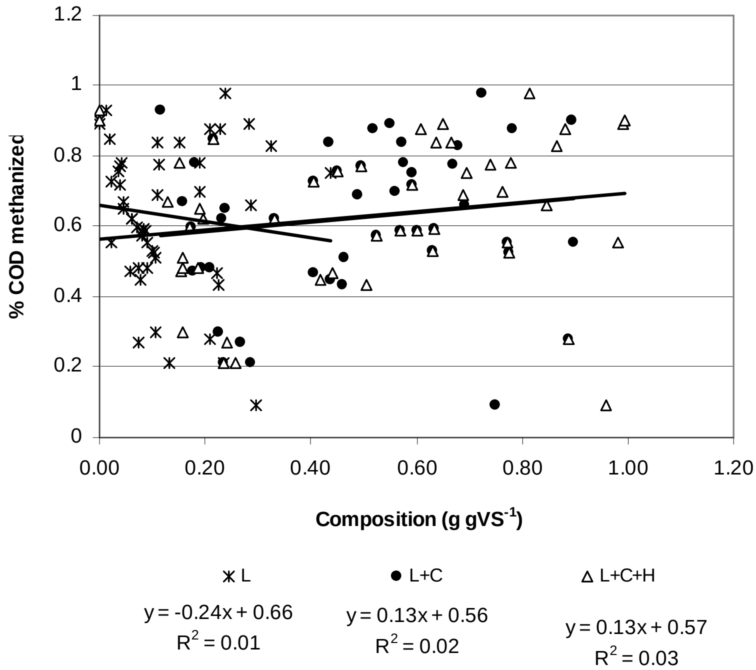
Figure A4.1.1 Volatile Solids composition of the 15 European plant samples evaluated.



a.



b.



c.

Figure A4.1.2 Biodegrability estimation using data from previous studies: a. Data from studies using different fiber analysis methods (Amon et al. 2007b; Buffiere et al. 2006; Chandler et al. 1980; Eleazer et al. 1997; Ghosh et al. 1985; Moller et al. 2004; Pareek et al. 1998; Tong et al. 1990); b. Data from 3 studies using van Soest method for substrate characterization (Buffiere et al. 2006; Ghosh et al. 1985; Pareek et al. 1998) and this research; c. Data from studies using methods different than van Soest (Amon et al. 2007b; Chandler et al. 1980; Eleazer et al. 1997; Moller et al. 2004; Tong et al. 1990)).

Table A4.1.1 Classification, van Soest analysis and predicted biodegradability (Bo) of 114 Northern European Plant samples (Data from (Stenberg et al. 2004)). (Bo was predicted assuming an average VS value of 92%TS as assessed in this study).

English name	Latin name	Plant Class	Plant part	NDF [mg gDM^{-1}]	ADF [mg gDM^{-1}]	ADL [mg gDM^{-1}]	Predicted B_o [%COD]
Barley	*Hordeum vulgare distichon*	Cereals	Green leaves	772.9	431.1	25.6	43%
Wheat	*Triticum aestivum*	Cereals	Green leaves	748.4	423.9	51.9	44%
Wheat	*Triticum aestivum*	Cereals	Green leaves	689.3	402.2	32.6	46%
Barley	*Hordeum vulgare distichon*	Cereals	Green leaves	645.9	367.7	26.7	49%
Elefant Grass	*Miscanthus gigantus*	Alternative crops	Green leaves	704.1	356.5	20.5	50%
Barley	*Hordeum vulgare distichon*	Cereals	Green leaves	691.0	355.9	22.9	50%
Wheat	*Triticum aestivum*	Cereals	Green leaves	671.8	350.9	55.1	51%
Bent grass	*Agrostis capillaris*	Grasses	Green leaves	443.1	333.2	60.7	53%
Meadow Fescue	*Festuca pratensis*	Grasses	Green leaves	482.9	279.2	15.2	58%
Maize	*Zea mays*	Other agric. crops	Green leaves	588.6	277.3	5.8	58%
Cock's-foot	*Dactylis glomerata*	Grasses	Green leaves	535.9	276.9	14.4	58%
Onion	*Allium cepa*	Horticultural crops	Green leaves	352.3	276.1	72.9	58%
Oats	*Avena sativa*	Cereals	Green leaves	482.6	274.2	25.5	59%
Winter-rye	*Secale cereale*	Cereals	Green leaves	447.7	255.9	34.5	60%
Oil Radish	*Raphanus sativus*	Catch crops	Green leaves	247.5	250.8	30.8	61%
Cock's-foot	*Dactylis glomerata*	Grasses	Green leaves	474.3	245.4	14.9	61%
Yellow Lupin	*Lupinus luteus*	Legumes	Green leaves	301.9	224.6	28.4	64%
Chicory	*Cichorium intybus*	Catch crops	Green leaves	214.2	218.9	16.6	64%
English ryegrass	*Lolium perenne*	Grasses	Green leaves	410.9	213.7	10.5	65%
Barley	*Hordeum vulgare distichon*	Cereals	Green leaves	362.8	210.2	15.1	65%
Flax	*Linum usitatissimum*	Alternative crops	Green leaves	303.3	198.8	65.9	66%
Oats	*Avena sativa*	Cereals	Green leaves	352.8	188.0	4.4	67%
Hemp	*Cannabis sativa*	Alternative crops	Green leaves	224.3	172.5	35.8	69%

English name	Latin name	Plant Class	Plant part	NDF [mg gDM^{-1}]	ADF [mg gDM^{-1}]	ADL [mg gDM^{-1}]	Predicted B_o [%COD]
Leek	*Allium porri*	Horticultural crops	Green leaves	211.8	170.7	16.5	69%
Carrot	*Daucus carota*	Horticultural crops	Green leaves	216.6	156.2	31.0	70%
Chicory	*Cichorium intybus*	Catch crops	Green leaves	198.7	152.6	11.4	71%
Cabbage	*Brassica oleraceae*	Horticultural crops	Green leaves	196.8	147.4	2.0	71%
Phacelia	*Phacelia tenacetifolia*	Catch crops	Green leaves	242.6	144.0	18.7	72%
Alfalfa/Lucerne	*Medicago sativa*	Legumes	Green leaves	194.6	141.1	15.7	72%
Crimson Clover	*Trifolim incarnatum*	Legumes	Green leaves	224.6	134.4	11.3	73%
Oilseed-rape	*Brassica napus oleifera*	Other agric. crops	Green leaves	245.4	126.2	19.9	73%
Oilseed-rape	*Brassica napus oleifera*	Other agric. crops	Green leaves	169.9	124.9	0.6	74%
Sugarbeet	*Beta vulgaris spp.*	Other agric. crops	Green leaves	231.3	123.6	6.1	74%
White Clover	*Trifolium repens*	Legumes	Green leaves	153.6	105.0	9.1	76%
Cabbage	*Brassica oleraceae*	Horticultural crops	Green leaves	150.3	102.7	0.9	76%
Turnip-rape	*Brassica rapa oleifera*	Catch crops	Green leaves	181.7	95.3	7.7	76%
Sunflower	*Helianthus…*	Other agric. crops	Mature straw	742.1	627.5	115.0	23%
Hemp	*Cannabis sativa*	Alternative crops	Mature straw	700.0	589.1	88.1	27%
Turnip-rape	*Brassica rapa oleifera*	Catch crops	Mature straw	763.4	584.5	126.5	28%
Pea	*Pisum sativum*	Legumes	Mature straw	766.5	563.9	107.1	30%
Pea	*Pisum sativum*	Legumes	Mature straw	749.5	548.9	111.8	31%
Yellow Mustard	*Sinapis alba*	Catch crops	Mature straw	727.3	509.5	113.7	35%
Barley	*Hordeum vulgare distichon*	Cereals	Mature straw	817.3	473.4	44.8	39%
Wheat	*Triticum aestivum*	Cereals	Mature straw	791.9	457.0	36.6	40%
Wheat	*Triticum aestivum*	Cereals	Mature straw	754.3	448.5	47.3	41%
Barley	*Hordeum vulgare distichon*	Cereals	Mature straw	673.7	406.6	40.2	45%
Red Fescue	*Festuca rubra*	Grasses	Mature straw	717.6	403.9	42.6	46%
Meadow Foxtail	*Alopecurus*	Grasses	Mature	675.9	358.5	25.4	50%

English name	Latin name	Plant Class	Plant part	NDF [mg gDM^{-1}]	ADF [mg gDM^{-1}]	ADL [mg gDM^{-1}]	Predicted B_o [%COD]
	pratensis		straw				
Bluegrass	*Poa pratensis*	Grasses	Mature straw	650.7	341.3	23.6	52%
Oats	*Avena sativa*	Cereals	Mature straw	543.2	306.2	20.5	55%
Oilseed-rape	*Brassica napus oleifera*	Other agric. crops	Pod walls	567.0	428.6	90.0	43%
Oilseed-rape	*Brassica napus oleifera*	Other agric. crops	Pod walls	529.1	390.9	72.4	47%
Maize	*Zea mays*	Other agric. crops	Pods	509.2	230.5	3.4	63%
Wheat	*Triticum aestivum*	Cereals	Pods	394.3	193.7	20.9	67%
Barley	*Hordeum vulgare distichon*	Cereals	Pods	480.6	175.5	11.3	68%
Wheat	*Triticum aestivum*	Cereals	Pods	287.6	126.7	11.4	73%
Barley	*Hordeum vulgare distichon*	Cereals	Pods	251.9	76.2	3.2	78%
Maize	*Zea mays*	Other agric. crops	Pods	197.1	68.9	0.7	79%
Hemp	*Cannabis sativa*	Alternative crops	Stem	794.9	649.3	100.4	21%
Flax	*Linum usitatissimum*	Alternative crops	Stem	765.2	629.1	168.0	23%
Flax	*Linum usitatissimum*	Alternative crops	Stem	677.1	576.7	138.7	28%
Flax	*Linum usitatissimum*	Alternative crops	Stem	730.8	563.8	166.3	30%
Oilseed-rape	*Brassica napus oleifera*	Other agric. crops	Stem	731.3	554.8	113.5	31%
Oilseed-rape	*Brassica napus oleifera*	Other agric. crops	Stem	719.9	544.8	106.7	32%
Elefant Grass	*Miscanthus gigantus*	Alternative crops	Stem	785.8	518.2	60.0	34%
Barley	*Hordeum vulgare distichon*	Cereals	Stem	828.2	515.5	69.3	34%
Wheat	*Triticum aestivum*	Cereals	Stem	816.6	510.3	50.7	35%
Wheat	*Triticum aestivum*	Cereals	Stem	819.0	506.6	76.7	35%
Wheat	*Triticum aestivum*	Cereals	Stem	797.8	469.2	94.7	39%
Barley	*Hordeum vulgare distichon*	Cereals	Stem	767.6	464.3	41.6	40%

English name	Latin name	Plant Class	Plant part	NDF [mg gDM^{-1}]	ADF [mg gDM^{-1}]	ADL [mg gDM^{-1}]	Predicted B_o [%COD]
Yellow Lupin	*Lupinus luteus*	Legumes	Stem	537.6	454.6	74.2	41%
Alfalfa/Lucerne	*Medicago sativa*	Legumes	Stem	559.2	444.6	111.0	42%
Red Clover	*Trifolium pratense*	Legumes	Stem	514.8	406.3	65.4	45%
Cock's-foot	*Dactylis glomerata*	Grasses	Stem	659.4	364.3	25.8	50%
Cock's-foot	*Dactylis glomerata*	Grasses	Stem	638.3	355.0	22.0	51%
Wheat	*Triticum aestivum*	Cereals	Stem	617.2	355.0	60.4	51%
Maize	*Zea mays*	Other agric. crops	Stem	596.3	344.3	14.9	52%
Persian Clover	*Trifolium resupinatum*	Legumes	Stem	440.0	339.4	85.4	52%
Wheat	*Triticum aestivum*	Cereals	Stem	572.6	337.9	36.2	52%
Barley	*Hordeum vulgare distichon*	Cereals	Stem	629.7	332.4	23.1	53%
Maize	*Zea mays*	Other agric. crops	Stem	566.4	329.1	14.7	53%
Maize	*Zea mays*	Other agric. crops	Stem	581.2	329.1	16.6	53%
Bent grass	*Agrostis capillaris*	Grasses	Stem	393.5	313.0	49.7	55%
Wheat	*Triticum aestivum*	Cereals	Stem	498.4	290.6	23.4	57%
English ryegrass	*Lolium perenne*	Grasses	Stem	494.0	256.0	6.7	60%
White Clover	*Trifolium repens*	Legumes	Stem	239.4	181.2	17.3	68%
Red Clover	*Trifolium pratense*	Legumes	Stem	277.3	176.2	24.3	68%
Flax	*Linum usitatissimum*	Alternative crops	Whole plant	708.0	585.1	125.0	28%
Broad Bean	*Vicia faba*	Legumes	Whole plant	636.4	527.1	97.9	33%
Barley	*Hordeum vulgare distichon*	Cereals	Whole plant	816.4	512.2	54.8	35%
Black Mustard		Other agric. crops	Whole plant	629.7	481.7	87.8	38%
Flax	*Linum usitatissimum*	Alternative crops	Whole plant	613.9	466.8	111.0	39%
Flax	*Linum usitatissimum*	Alternative crops	Whole plant	525.0	383.8	96.9	48%
Oil Radish	*Raphanus sativus*	Catch crops	Whole plant	450.5	383.1	64.5	48%
Ribbed Melilot	*Melilotus officinalis*	Legumes	Whole plant	435.4	379.0	64.9	48%
Bluegrass	*Poa pratensis*	Grasses	Whole	661.3	375.0	25.2	49%

English name	Latin name	Plant Class	Plant part	NDF [mg gDM^{-1}]	ADF [mg gDM^{-1}]	ADL [mg gDM^{-1}]	Predicted B_o [%COD]
			plant				
Common Bird's-foot-trefoil	*Lotus corniculatus*	Legumes	Whole plant	461.1	359.1	87.6	50%
Tall fescue	*?? Pratense*	Grasses	Whole plant	585.2	346.3	32.0	51%
Timothy	*Phleum pratense*	Grasses	Whole plant	612.6	333.2	18.8	53%
Maize	*Zea mays*	Other agric. crops	Whole plant	688.3	332.2	7.7	53%
Cock's-foot	*Dactylis glomerata*	Grasses	Whole plant	571.1	324.1	16.0	54%
Maize	*Zea mays*	Other agric. crops	Whole plant	676.5	317.6	1.1	54%
Tall fescue	*?? Pratense*	Grasses	Whole plant	507.5	294.0	20.1	57%
English ryegrass	*Lolium perenne*	Grasses	Whole plant	514.5	273.8	21.9	59%
Crimson Clover	*Trifolim incarnatum*	Legumes	Whole plant	435.5	273.1	57.7	59%
Timothy	*Phleum pratense*	Grasses	Whole plant	511.7	271.8	14.1	59%
Winter Vetch	*Vicia villosa*	Legumes	Whole plant	344.0	262.3	50.5	60%
Alfalfa/Lucerne	*Medicago sativa*	Legumes	Whole plant	336.1	255.5	44.7	60%
Egyptian Clover	*Trifolium alexandrinum*	Legumes	Whole plant	342.8	244.8	35.0	62%
White Clover	*Trifolium repens*	Legumes	Whole plant	314.3	226.7	63.9	63%
Crimson Clover	*Trifolim incarnatum*	Legumes	Whole plant	310.4	220.9	24.4	64%
White Clover	*Trifolium repens*	Legumes	Whole plant	247.2	198.9	48.1	66%
Red Clover	*Trifolium pratense*	Legumes	Whole plant	267.4	195.1	19.8	67%
Oilseed-rape	*Brassica napus oleifera*	Other agric. crops	Whole plant	247.1	184.0	13.6	68%

APPENDIX 4.2

Additional information relating plant chemical composition to hydrolysis rates

During the anaerobic degradation of complex organic matter, hydrolysis is generally regarded as the rate-limiting step (Batstone et al. 2002; Hobson 1983; Noike et al. 1985; Pavlostathis and Giraldo-Gomez 1991). In the hydrolysis step, complex suspended compounds and colloidal matter are converted into their monomeric or dimeric components, such as aminoacids, single sugars and long chain fatty acids (LCFA) (Sanders et al. 2000). The many intervening factors and the complex nature of the substrates make the hydrolysis process a complex one (Mata-Alvarez et al. 2000). Because of the previous, understanding the hydrolysis process and assessing properly the implied parameters is of crucial importance for crop selection and proper reactor design.
The hydrolysis rate of degradable particulate organic matter in anaerobic systems can be described by a first-order reaction equation. The calculation of the hydrolysis rate in batch reactors is done using Equation A4.2.1 which relates the first order hydrolysis constant, the digestion time and effluent concentration (Angelidaki and Sanders 2004).

$$COD_{p,t=t} = COD_{p,t=0} \times (1 - B_p) + B_p \times COD_{p,t=0} \cdot e^{-k_h \cdot t} \quad \text{(A4.2.1)}$$

After linearization this yields:

$$\ln \frac{COD_{p,t=t} - COD_{p,t=0} \times (1 - B_p)}{COD_{p,t=0} \times B_p} = -k_h \times t \qquad \text{(A4.2.2)}$$

Where $COD_{p,t=t}$ is the concentration of particulate substrate in the bottle at time t (biodegradable + non biodegradable) [gCOD l^{-1}], $COD_{p,t=0}$ is the concentration of particulate substrate at time t=0 (biodegradable + non biodegradable) [gCOD l^{-1}], B_p is the biodegradable fraction of particulate substrate, $0<B_p<1$; k_h is the first order hydrolysis constant [d^{-1}] and t is the batch digestion time (d). In all cases, calculation of X_{ss} is done by subtracting the total COD solubilised (soluble COD plus COD methanized at time t) from the total plant COD added at the start up. The ultimate biodegradability of the particulate material B_p was calculated using Equation 4.2.

Results
Evaluation of intermediates in time showed a small accumulation of VFA during the first days of digestion for some plant species, ranging from 3 to 15% in relation to the final COD solubilized, i.e. the sum of methane and acidification products. Therefore, hydrolysis rates were assessed considering not only methane production but also intermediates evolution in time. The hydrolysis of the plant samples could be excellently described by first-order kinetics (See Figure A4.2.1).

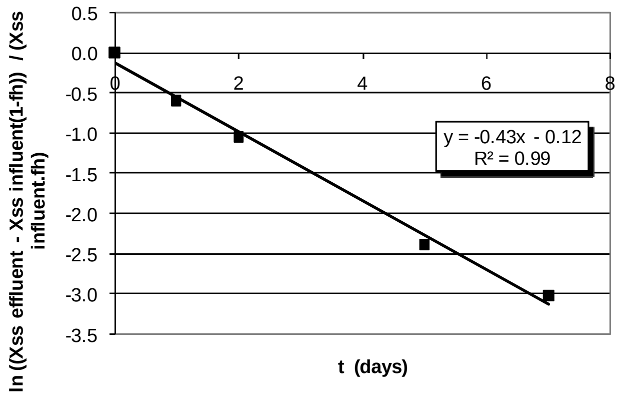


Figure A4.2.1 Assessment of the first-order hydrolysis constant during anaerobic digestion of vetch as a representative plant sample

The first-order hydrolysis constants (k_h) assessed ranged from 0.22-0.72 d^{-1} being in average 0.46 d^{-1}, in accordance with data previously reported for materials of similar characteristics (Tong et al. 1990; Veeken and Hamelers 1999). Results are presented in Table A4.2.1

Table A4.2.1 First order hydrolysis constants as assessed from batch digestion of 13 European plant species

Specie	k_h [d^{-1}]
Yellow lupin	0.49
Vetch	0.43
Carrot	0.61
Spartina	0.22
White lupin	0.43
Triticale	0.43
Braken	0.24
Sweet clover	0.54
Winter barley	0.32
Winter bean	0.66
Sweet pea	0.72
Oil seed rape	0.48
Buckwheat	0.48

The calculated first-order hydrolysis constants related to the fiber components of the plant material being digested (Figure A4.2.2).

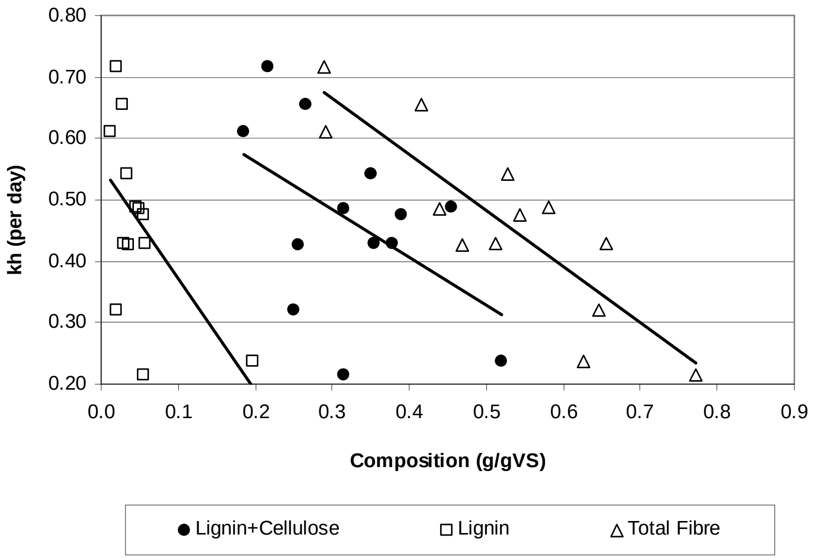


Figure A4.2.2. First-order hydrolysis constants in dependence of fibre components

The assessed first-order hydrolysis constants were found to be linearly correlated to the total fiber content of the plant material (R^2=73%), whereas both ADF and ADL were found to be poor predictors. However, accounting for hemicellulose and lignin content provides a better estimation (R^2=86%). Increasing the number of variables of the equation by including cellulose or starch did not improve the predictive value, whereas including crude protein showed a better estimation (R^2=94%) although the level of significance of crude protein remained relatively low (.004). Relation with any of the individual components alone was not found to be enough for predicting first-order hydrolysis constants (Table A4.2.2).

Table A4.2.2 Number of parameters (p), Coefficient of determination (R^2) and significance (t values) for the estimation of first-order hydrolysis constants from different plant components

Model variables	p	R^2	Predictor variables *t values*						
			NDF	**ADF**	**C**	**H**	**L**	**CP**	**St**
NDF	2	73	.000	-	-	-	-	-	-
ADF	2	26	-	0.042	-	-	-	-	-
L,H	2	86	-	-	-	.000	.000	-	-
L,H,C	3	86	-	-	0.373	.000	.000	-	-
L,H,CP	3	94	-	-	-	.000	.000	.004	-
L,H,St	3	85	-	-	-	.000	.000	-	.515
C	2	1.5	-	-	.300	-	-	-	-
H	2	34	-	-	-	.017	-	-	-
L	2	26	-	-	-	-	.042	-	-

NDF: Neutral Detergent Fiber; ADF: Acid Detergent Fiber; C: Cellulose; H:Hemicellulose; L=ADL: Lignin; CP:Crude Protein; St:Starch

Results shown in Table A4.2.2 suggest that the overall matrix of components in the plant cell wall determines the plant biomass rate of degradation. Therefore, the models can be simplified as suggested by equations A4.2.3 and A4.2.4 giving the highest statistic significance.

$$K_h = 0.94 - 0.91NDF \qquad \text{(A4.2.3)}$$

$$K_h = 0.76 - 2.25L - 0.96H \qquad \text{(A4.2.4)}$$

If considering that the hydrolysis process is surface related and the plant cell wall is a complex matrix in which cellulose fibrils are embedded with other polymers, including hemicelluloses, pectin, proteins and lignin, it is indeed expected that the total fiber fraction, and particularly the fractions of lignin and hemicellulose, influences the hydrolysis rate. The fact that hemicellulose was found to be of importance in contrast to our findings for the biodegradability case, could be related to the location of hemicellulose in the cell wall surrounding the cellulose microfibrils and occupying spaces between them, and the fact that hemicellulose must be degraded, at least in part, before cellulose in plant cell walls can be effectively degraded (Leschine 1995).

Chapter 5

Impact of crop-manure ratios and digestion time on the fertilizing characteristics of liquid and solid digestate during codigestion

Abstract

The influence of maize silage-manure ratios on the digestate characteristics was studied in dependence of the applied digestion time. The change in nutrients availability, heavy metals content and the methane production potential of the digestate was followed in multiflask experiments at digestion times 7, 14, 20, 30 and 60 days. In addition, the distinction between the availability of nutrients in the liquid and solid part of the digestate was evaluated. Anaerobic digestion favored the availability of nutrients. After 61 days 20-26% increase in NH_4^+ and 20-36% increase in PO_4^{3-} was found. Manure showed a positive effect in the methane production rate and the total amount of nutrients in the digestate. Longer digestion time and higher maize ratio in the feedstock positively influenced the availability of PO_4^{3-}. No relation was found between the crops: manure ratio and the NH_4^+ behavior in relation to initial concentrations. Inorganic nutrients were found to be mainly available in the liquid portion of the digestate, i.e. 80-92% NH_4^+ and 65-74% PO_4^{3-}. The introduction of manure into a maize digestion system was found to increase by 18% its energy balance as compared to the artificial fertilizer option. The recirculation of maize silage or of manure digestate did not allow significant energy savings. In terms of energy efficiency manure digestion is the most attractive option.

Pabon-Pereira CP, de Vries JW, Zeeman G, van Lier JB

A modified version of this chapter was presented orally in the 9th Latinamerican Workshop and Symposium in anaerobic digestion.in Eastern Island, Chile. October 19-23, 2008. Available in Proceedings.

1 INTRODUCTION

Maize silage is widely used as substrate for digesters in Europe as single substrate or codigested with other crops and/or manure. Codigestion of manure with energy crops is widely implemented not only due to availability of both substrates but also because of the positive effect of manure on digestion stability (Weiland 2005).

In addition to the energy-rich biogas, the residual semi-solid and/or liquid by-product, i.e. digestate is another interesting feature of the AD process. The stabilized product, rich in nutrients, has attractive characteristics for reuse in agriculture. The characteristics of the digestate are affected by several parameters, such as the composition of the input material, the applied hydraulic retention time (HRT) and the reactor configuration.

It has been recognized that nutrients become more mineralized during codigestion of different manure-crop mixtures containing less than 40% crop content in CSTRs at 20 days HRT (Lehtomaki et al. 2007). It is also reported that at ratios higher than 30-40% crop to manure and HRTs < 20 days, digestion becomes instable (Hashimoto 1986; Lehtomaki et al. 2007).

In the present research the impact of maize silage-manure ratios on the digestate characteristics was studied in dependence of the applied digestion time. The emphasis of the study was the change in nutrients availability, heavy metals content and the methane production potential of the digestate at digestion times exceeding 20 days, and codigestion ratios higher than 30% maize silage. In addition, the distinction between the availability of nutrients in the liquid and solid part of the digestate was evaluated to get insight in possibilities for optimizing the reuse of digestate in practice.

2 MATERIALS AND METHODS

2.1 Experimental design

Multiflask batch experiments were performed in order to provide a well homogenized sample for liquid/solid characterization. The experiments were performed in 500 ml bottles applying four different input ratios of maize silage and manure, i.e., 100, 70, 50 and 30% maize , volatile solids (VS) basis, and six different digestion periods, i.e., 0, 7, 14, 20, 30 and 61 days.

A 5% total solids (TS) content was applied in both experiments to minimize diffusion limitation. The bottles were incubated at 35°C providing continuous mixing at 120 rpm. Reactors were inoculated with inoculum adapted to maize in the case of 100% maize feedstock and with inoculum adapted to maize-manure mixture in case of mixed feedstock and buffered using sodium hydroxide according to requirements for optimal pH conditions (0-8 $gNaHCO_3/l$). Gas was collected using gasbags attached to the batch bottles. Gas composition, intermediates and digestate characteristics, i.e. pH, nutrient and heavy metals were followed in time. Distinction was made on digestate characteristics between the solid and liquid portion of the digestate by centrifuging for three minutes at 3000 rpm (IEC, international equipment company, Centra CL3). This centrifugation speed was chosen in order to compare the data with relevant literature (Lehtomaki and Bjornsson 2006) and practical applications where centrifugation of manure takes place at speeds up to 4000 rpm (VCM). In addition, distinction between inorganic and organic fractions of N and P was made in both fractions by analyzing for the inorganic portion of the respective nutrient. Figure 5.1 shows the approach used for the nutrient analyses and calculations. The shaded blocks correspond to fractions analytically assessed while the white blocks were assessed by subtraction.

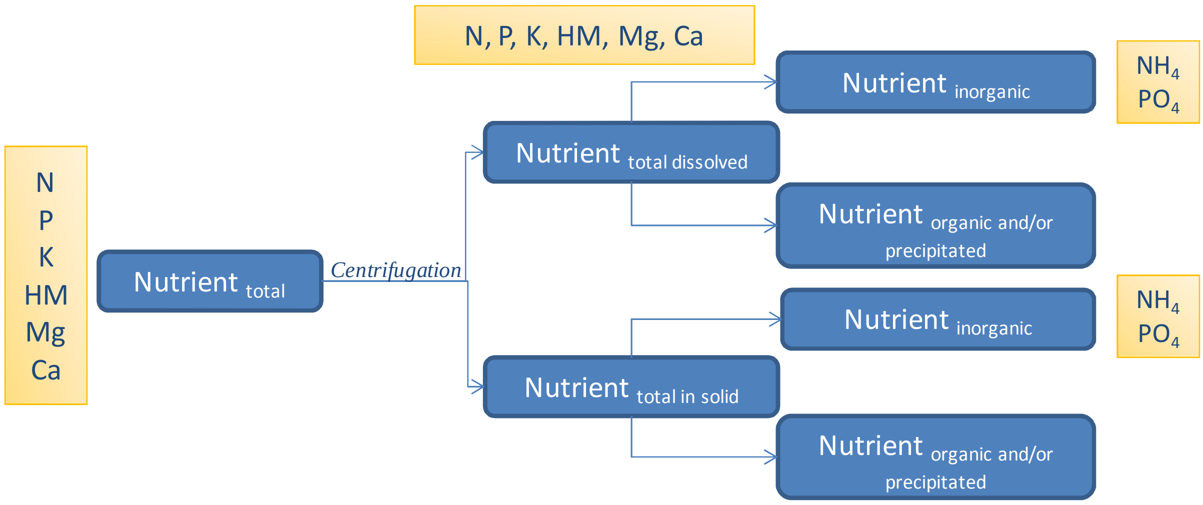


Figure 5.1 Scheme showing the approach used for nutrient analyses and calculations

In addition to the multiflask experiments, the ultimate biodegradability of the input materials and mixture ratios was assessed in duplicate using an optimized test protocol previously developed (Pabon-Pereira et al. 2009). The remaining methane potential in the digestate was then calculated as the difference between the ultimate biodegradability and that obtained at the 61 day digestion time using the multiflask experiment.

2.2 Origin and characteristics of substrates and inocula

Two different inocula were used, an adapted suspended inoculum from a digester processing only maize and an inoculum adapted to co-digesting maize and manure. The suspended inoculum adapted to maize silage digestion originated from the second of two-phase CSTRs reactors operating on maize silage at 60 days HRT each at 40°C (Corntec, Germany). The co-digestion inoculum originated from an anaerobic plug flow digester co-digesting manure, maize and grass silage at 14 days HRT and 41°C. The maize silage originated from a farm in Germany (Leer). It has been harvested and ensiled approximately a year before it was collected. The manure has its origin in the northern part of the Netherlands where it was taken fresh from the manure pit constructed under the cow housing. The cows were fed with a ration of grass silage, maize silage, a waste product from grain fermentation and concentrates. All materials were stored for 1 week prior to be used in the experiments. Full characterization of the input materials is shown in Table 5.1.

Table 5.1 Characteristics of substrates and inocula

Parameter	Unit	Maize	Manure	Maize inoculum	Codigestion inoculum
SMA	[gCOD $gVS^{-1}d^{-1}$]	-	-	0.36/0	0.19/0.04
TS	[$gTSg^{-1}$]	0.31	0.08	0.09	0.09
VS	[$gVSg^{-1}$]	0.30	0.07	0.07	0.08
Density	[g l^{-1}]	395	1004	959	913
COD_{total}	[$gCODgVS^{-1}$]	1.17	1.24	1.09	1.06
$COD_{soluble}$	[$gCODgVS^{-1}$]	0.50	0.05	0.27	0.34
VFA_{total}	[$gCODgVS^{-1}$]	0.06	0.05	0.01	0.05
N_{total}	[mg gTS^{-1}]	12.3	37.2	42.7	42.3
C_{total}	[mg gTS^{-1}]	444	408	401	398
C/N $_{ratio}$	-	34.60	19.98	16.55	15.79
P_{total}	[mg gTS^{-1}]	1.66	8.37	8.95	8.89
K_{total}	[mg gTS^{-1}]	8.79	17.46	44.26	44.50
Ca_{total}	[mg gTS^{-1}]	1.92	17.57	42.24	11.81
Mg_{total}	[mg gTS^{-1}]	1.70	9.07	4.78	6.72
Fe_{total}	[mg gTS^{-1}]	0.05	0.68	1.22	2.38
PO_4 -P	[mg gVS^{-1}]	-	6.08	1.41	1.06
NH_4-N	[mg gVS^{-1}]	3.19	12.05	18.98	21.81
Alkalinity	[$mgCaCO_3$ l^{-1}]	4.62	6.08	1.41	1.06
pH	-	3.72	7.03	7.92	7.91
Cd	[µg gTS^{-1}]	<DL	0.08	0.20	0.29
Cr	[µg gTS^{-1}]	<DL	1.03	0.39	6.28
Cu	[µg gTS^{-1}]	4.52	69.27	16.14	30.56
Ni	[µg gTS^{-1}]	<DL	4.43	4.45	3.05
Pb	[µg gTS^{-1}]	0.94	1.77	2.76	2.80
Zn	[µg gTS^{-1}]	31	170	104	158

<DL Below detection limit

2.3 Analytical methods

In order to keep ammonium nitrogen in the digestate samples, the total nitrogen was analyzed by adding a 0.44 M tartaric acid ($C_4H_6O_6$) solution to the samples in a ratio of 250g of sample with 300g of acid. The samples were left to acclimatize for one hour and dried at 70°C during 1 night (Binder artikel nr: 9010-0080, Tuttlingen, Germany). Samples used for total carbon, calcium, potassium and heavy metal content were also dried under the same conditions without acid. After drying the samples were stored or directly grinded to decrease the particle size to ensure a representative sample. Samples for heavy metal, Ca, Mg and K total were destructed in a microwave (Milestone high performance microwave digestion unit mls 1200 mega, milestone microwave laboratory systems, Sorisole, Italy) by adding approximately 0.5g of sample and 10ml of aqua regia (7.5ml HCL and 2.5ml HNO_3). After destruction the samples were quantitatively washed (with Millipore water) and filtrated with Schleicher & Schuell 589 ash free filter paper circles (Schleicher & Schuell GmbH, Germany) into 50ml flasks. The samples obtained, were diluted four times before measuring.

N_{total} and C_{total} was measured using a CE-instruments 1110 CHNS-O Elemental Analyzer with a CHNS column rapped in teflon, length 2 meters, external diameter of 6 mm and internal diameter of 4 mm. P_{total}, NH_4-N and PO_4-P were measured using an Auto Analyzer Skalar type 1520 (SAN^{plus} System). P_{total} and $P_{total\ dissolved}$ samples were prepared according to standard methods (ETE, 2005). The ICP-OES system used was a Varian Vista-MPX CCD Simultaneous ICP-OES. COD_{total} analysis was performed according to standard methods (ETE, 2005). To obtain the $COD_{soluble}$ and the total nitrogen dissolved the Dr. Lange tests LCK 514 and LCK 238 were used (Dr. Lange, Düsseldorf, Germany). After the procedure the samples were measured in a Dr. Lange Xion 500 model LPG-385 photo-spectrometer (Hack Lange GMBH, Düsseldorf, Germany).

The gas composition was measured with a 'Hewlett Packard 5890A (Palo Alto, U.S.A.)' gas chromatograph (oven temperature: 45°C, injection port: 110°C, detector temperature: 99°C; column length measuring oxygen, nitrogen and methane: 30 meters, model Molselve 0.53mm x 15µm; column to measure carbon dioxide: 25 meters, model Paraplot 0.53mm x 20µm). To measure the VFA component of a sample a Hewlett Packard 5890A gas chromatograph combined with a Hewlett Packard 6890 series injector (Palo Alto, U.S.A.) was used. The temperatures of the flame ionization detector, injection port and columns were: 280°C, 200°C and 130°C respectively. The column used was an Altech 14539 AT™-Aquawax- DA with a length of 30 meters, internal diameter of 0.32 mm and a 0.25 µm thick coating.

3 Results

3.1 Multiflask experiment

In the multiflask experiment, the bottles containing manure produced methane and converted the soluble chemical oxygen demand (COD) and volatile fatty acids (VFA) more rapidly as compared to digesters fed with only maize silage High VFA concentrations (8-12 gCOD l^{-1}) were present during the first fifteen days of the experiment, acetic and propionic acid accumulating in same proportions up to 5 mgCOD l^{-1} each. pH remained mostly in the neutral range during the experiment, although fluctuations (6.5-7.8) occurred during the first fourteen days of digestion (Figure 5.2).

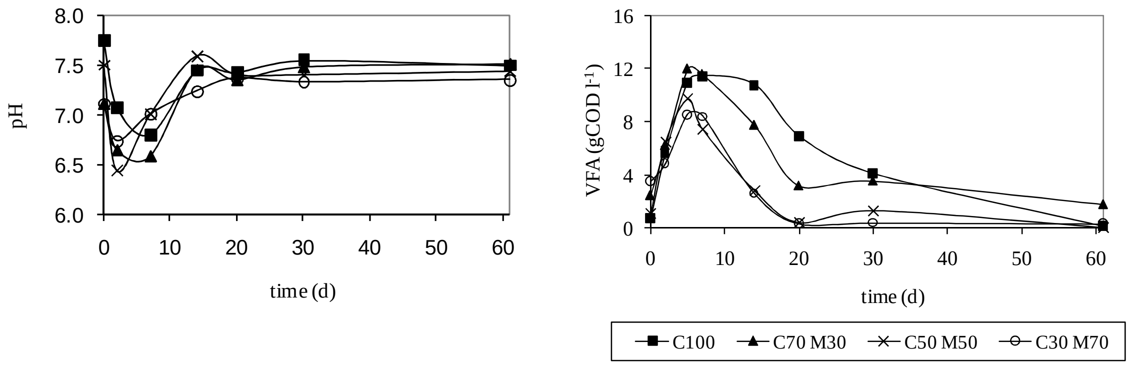


Figure 5.2 pH (left) and VFA evolution (right) during co digestion of maize silage and manure at different ratios in multiflask batch experiment

Around 85% of the methane was produced after 30 days in codigestion bottles as compared to 66% in the 100% crop treatment.

Total N and P content at the start of the experiment were favored in manure treatments. When incubation started, 38-49% of the total nitrogen was present in the liquid portion of the mixture, and of this 40% was NH_4^+. The amount of nitrogen present in the liquid digestate by the end of the experiment increased 21% in the crop treatment compared to the initial amount, while in the manure treatments it remained constant. % NH_4^+ of total N at time 0 was comparable in all treatments (19-23%). By day 7 this amount has increased (25-35%) meaning an extra 24-40% mineralized nitrogen as compared to the start of the experiment. As digestion proceeded, NH_4^+ remained at this higher value up to day 20. Thereafter, two treatments decreased their %NH_4^+, i.e. C100 and C50M50, while the other treatments showed further increase. By day 61, 18-30% of the nitrogen was available as ammonia, only two treatments showing an increase in nitrogen mineralized as compared to the start of the experiment, i.e. 30% (Figure 5.3). The evolution of NH_4^+ in the liquid and solid part of the digestate showed no major fluctuations, in general 80-92% of NH_4^+ being found in the liquid portion of the digestate.

At the start of the incubation, 32-38% of total P was available as PO_4^{3-} in all the treatments. Such fraction mostly present in the liquid part of the digestate (65-74%). Evolution of PO_4^{3-} in time showed no variation in manure treatments, except for day 7 when an increase in PO_4^{3-} was evident. The maize treatment showed a different pattern its proportion of PO_4^{3-} increasing in time. Proportion of PO_4^{3-} to total P by the end of the experiment was higher compared to the start of incubation (20-36% increase) in all cases except in the treatment with higher manure content (Figure 5.3). The evolution of PO_4^{3-} in the liquid and solid part of the digestate showed no variation in time with respect to the start of incubation.

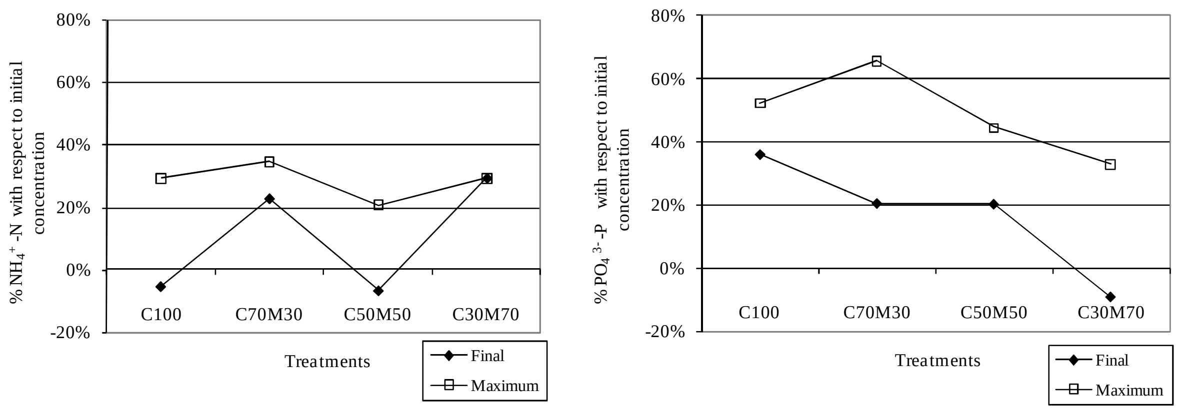


Figure 5.3 Final and maximum change in nutrient mineralization during co-digestion of different ratios of maize silage and manure in multiflask batch experiment: Nitrogen (left), Phosphorus(right).

During the experiments, potassium was mostly present in the liquid portion of the digestate. Dissolved magnesium, calcium and heavy metal concentrations were higher during the first 14 to 20 days of digestion, thereafter becoming mostly stable. Sulphate concentrations on the other hand mainly show an increase from day 30 to day 61. Total amounts of heavy metals assessed in the treatments did not exceed the European regulations (Table 5.2). However Dutch limits, which are stricter, were exceeded in the case of Zn and Cu. The fluctuations and changes in the dissolved metal concentrations showed again a pattern related to pH fluctuations at the start of the experiment, thereafter remaining constant.

Table 5.2 Heavy metal recommendations and amounts assessed in the multiflask experiment during this study

Metal	**Cd**	**Pb**	**Hg**	**Ni**	**Zn**	**Cu**	**Cr**
Country / Unit	**µg/gTS**	**µg/gTS**	**µg/gTS**	**µg/gTS**	**µg/gTS**	**µg/gTS**	**µg/gTS**
EU recommendation	20	750	16	300	2500	1000	1000
EU maximum	40	1200	25	400	4000	1750	1500
The Netherlands	1.25	100	0.75	30	300	75	75
This study	0.3-0.7	2.6-5.1		6.2-8.0	164-425	39-113	6.0-11.4

Source: Several authors in (Al Seadi 2006).

3.2 Ultimate biodegradability and multiflask biodegradation

The ultimate biodegradability of the substrates and inocula used in the experiments was assessed by means of an optimized biological methane potential (BMP) test. As shown in Figure 5.4, the ultimate biodegradability assessed at optimal conditions, i.e. nutrient addition, mixture inocula incl. granular sludge, until methane production (38-40 days) was directly proportional to the relative proportion of the individual components. Further it can be observed that the obtained net amounts of methane in the multiflask batch experiments after 61 days digestion exceeded the assessed BMP values in most of the cases.

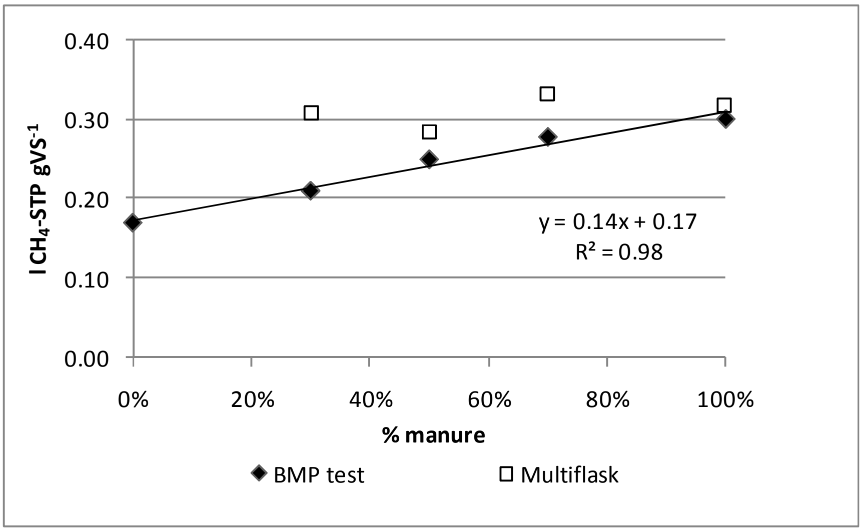


Figure 5.4 Biological Methane Potential and multiflask biodegradation after 61 days incubation of different mixtures of maize silage and manure

4 DISCUSSION

4.1 On the availability of nutrients during codigestion of maize and manure

Our results have clearly shown the linear increase in the Biochemical Methane Potential of crop manure mixtures as the proportion of maize increased in the mixture. Similar findings were reported by Hashimoto (1986) during digestion of straw-manure mixtures in fed-batch reactors suggesting this linear relationship is maintained as long as optimal conditions are ensured. Still our results were increased under multiflask conditions. It was noticed that the inocula produced a higher amount of methane in the BMP test as compared to the multiflask experiment, i.e. 0.10 vs. 0.06 lCH_4 gVS^{-1} for maize inoculum and 0.20 vs. 0.12 lCH_4 gVS^{-1} for codigestion inoculum. Since the main difference among the two tests was the nutrient addition, it is hypothesized that due to lower nutrient availability in multiflask test bottles as compared to the multiflask blank bottles, lower endogenous methane production from inoculum material was present in the test bottles leading to an overestimation of the methane production in the multiflask experiment when blank results were subtracted.

In our study up to 20-26% increase in N availability was found using a batch set-up. Previously Lehtomaki et al (2007) reported increases in NH_4^+ in relation to N total of 26%, 25% and 14% during the continuous codigestion at 20 days HRT of manure with sugar beet tops, grass and straw, respectively. Similarly, other authors have reported the increase in ammonium availability in digestate as compared to initial conditions in pilot and full scale digestion (Timmerman et al. 2005; Vincent et al. 1988). The previous suggests that this pattern is independent of digester type when using well adapted inocula. Further, it is important to recognize that digestion time exerted an effect in N availability in our experiments. Whereas the increase in NH_4^+ concentrations during the first week of the experiments can be attributed to the hydrolysis of proteins present in the individual components, after the first 20 days of the experiment, two treatments showed a diminishment in the concentration of mineral nitrogen.

In the case of phosphorus an increase in availability was also found but in this case an important effect of pH is noticed. PO_4^{3-} concentrations showed a concomitant behaviour with pH especially evident in all treatments having manure addition. Phosphate is known to form many precipitates, such as: $Fe_3(PO_4)_2$, $Ca_3(PO_4)_2$, $MgNH_4PO_4 \cdot 6H_2O$ (struvite), $AlPO_4$ (Martí Ortega 2006). These precipitates dissolve when the digestate becomes more acid which is the case during the first period of digestion in this study. Further evidence of the occurrence of this phenomenon is the magnesium and calcium which were found to follow a similar pattern as phosphorus concentrations in the digestate. Furthermore the absence of such behaviour on the maize treatment can be attributed to the much lower content of Ca, Mg and Fe in maize silage as compared to manure. Despite the possible precipitation observed for magnesium and calcium, the main part of these nutrients was found to be dissolved. After 20 days of digestion, magnesium, calcium and heavy metal concentrations become more or less stable corresponding with a stable pH. A clear positive effect of anaerobic digestion in the availability of phosphorus is seen by the end of the experiments, when pH is neutral. A linear positive effect of crop addition in PO_4^{3-} availability is observed in all treatments up to 50% maize silage content.

4.2 Codigestion of maize and manure in context

Maize is the most dominating crop for methane production in Europe(Amon et al. 2007b), its high energy yield per unit land as compared to other crops making it especially attractive. It is also very appealing as in a situation with a surplus of animal manure, as maize is one of the few crops for which high manure applications per ha are allowed. Nonetheless energy in the form of fuels, fertilizer and other agricultural inputs is required for growing maize.

In the Netherlands manure production per ha is larger than the nutrient need per hectare due to the intensive livestock production systems. Hence it can be acquired for free from livestock producers against transport costs only.

In addition, when bringing manure into a biogas farming system also nutrients are imported “for free” this means that provided digestate is recirculated, incoming indirect energy in artificial fertilizers is diminished. As reported in this study, the digestate from anaerobic digestion has interesting positive advantages for fertilization. Proportion of N available for plant growth as compared to N in undigested manure is increased. Such properties have been shown to increase maize growth and total N in maize plants in their early vegetative stages of growth in acid soils as compared to artificial fertilizers and undigested manure (Morris and Lathwell 2004).

The impact of the previously mentioned features was quantified by roughly comparing the energy balance and the Net Energy Value (NEV) of alternative AD systems using maize silage and/or manure for biogas production. The objective was to analyze the added value of manure as a source of energy and nutrients to AD systems using energy crops. Six systems were defined, four of them (A, B, C and D) produce biogas entirely from maize silage while they differ in its fertilization, i.e. using artificial fertilizer, digested maize silage, manure and digested manure, respectively. System E co digests maize and manure (50:50 TS basis), the digestate being returned to the maize fields. Finally System F is built for comparison purposes and considers only the digestion of manure. Although we are aware that manure is the output of an entire animal production system that requires energy and nutrient inputs we choose the system boundary as such that manure is a readily available resource that can be obtained against transportation costs. Figure 5.5 shows the flows considered and their relevance for the different systems studied.

The amount of maize silage produced was fixed to13.5 ton TS $ha^{-1}yr^{-1}$ for an application of 130 kg available N $ha^{-1}yr^{-1}$ assuming 80 KgN $ha^{-1}yr^{-1}$ to be available from the previous year (Gerin et al. 2008). In system A the entire amount was supplied from artificial fertilizer, whereas in systems B-E priority was given to other flows and artificial fertilizers were supplied only as they were required to fit the yield. Amounts of manure and digestate applied were assumed to be the maximum allowed by the EU Directive, i.e. 170 Kg N $ha^{-1}yr^{-1}$. Available N in manure and maize silage were assumed to be 40% and 15% of total N, respectively, by comparing our results with other studies (Baserga 2000; Gerin et al. 2008; Stockdale and Beavis 1994). A

23% increase in N availability was assumed for digested residues following the conclusions of this research.

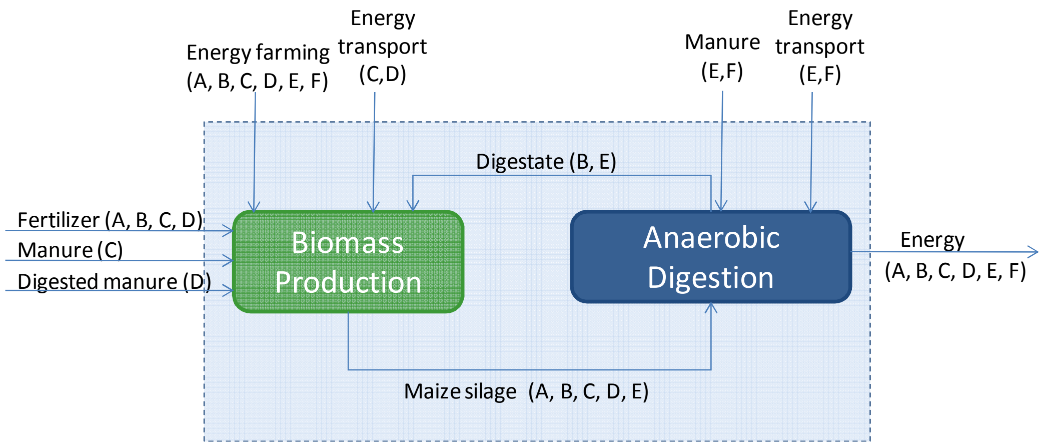


Figure 5.5 Overview of the studied biogas systems. The arrows represent material or energy flows as relevant for the different systems, i.e. letters in each flow.

The comparison of the systems was performed quantifying energy inputs and outputs in MJ ton^{-1}maize yr^{-1}, Energy inputs for maize silage production included farm activities and fertilizer use as reported by Gerin et al (2008). Additional energy input was the transport of manure or manure digestate when brought into the system assuming a 10 km distance and an energy use of 1.6 MJ ton^{-1}km^{-1} representing 30 ton truck transport with empty return (Berglund and Borjesson 2006; Gerin et al. 2008). Table 5.3 summarizes the outcome of the analysis.

Table 5.3 Analysis of alternative AD systems having different substrate inputs and fertilization[a]

AD system	OUTPUT	INPUT			$E_{balance}$	NER
	Energy yield	**Farming**	**Transport**	**Artificial fertilizer**		
	[MJ ton^{-1}]	**[MJ ton^{-1}]**	**[MJ ton^{-1}]**	**[MJ ton^{-1}]**	**[MJ ton^{-1}]**	**[MJ $_{out-in}$ MJ_{in}^{-1}]**
A. Maize artificially fertilized	3907	149	0	217	3540	0.10
B. Maize fertilized w/maize digestate	3907	149	0	174	3584	0.11
C. Maize fertilized w/manure	3907	149	12	104	3642	0.14
D. Maize fertilized w/ manure digestate	3907	149	12	78	3668	0.15
E. Maize manure codigestion (50:50 TS basis) and digestate fertilization	4421	149	25	44	4202	0.19
F. Manure	629	0	16	0	613	0.38

NER: Net Energy Ratio, representing the ratio: (Energy output-energy input) / energy input

[a] ton in the table refers to ton maize silage except in system F where is refers to ton manure. [b]Note that per ton maize 1.6 ton manure are added, i.e.energy yield of the mixture is 1718 MJ ton^{-1}.

As can be observed the manure system (F) produced the lowest net energy output per ton whereas it was the most energy efficient system as no energy is allocated for substrate production, i.e.38 MJ net output MJ^{-1} input. By comparing this net energy output with that of the different systems, it is calculated that 247±4 ton manure can replace a hectare of energy maize.

The trade-off among higher nutrient content and no energy demand for manure production versus the need for transportation and the lower energy value of manure showed to neutralize leading to no net energy benefits in systems A to D, i.e. only 1% and 3% increase in the net energy balance of systems B and C as compared to system A. In the case of system D, when digested manure is introduced to fertilize maize, the artificial N fertilizer requirements of the crop are almost met and a 4% increase in the net energy outcome with respect to system A. Only system E codigesting maize and manure showed a 19% higher net energy output as compared to system A which is the result of the combined effect of the nutrient and energy import of manure and the higher energy value of maize.

As can be seen transport did not exert and important influence in the energy balances. Systems C, D and E required the introduction of manure or manure digestate from outside the system, per ton maize 0.7, 0.7 and 1.6 ton manure or digestate were calculated considering a total manure N content of 40 gN Kg TS^{-1} and the maximum N allowance per ha maize. From this basis the additional energy input for transport was calculated. Checking the sensitivity of the systems it was found that the energy balance of the manure system (F) becomes negative after 400 km distance, while 1700 km distance is the limit for system E. These values are just indicative as in reality they are expected to be lower once the full direct and indirect energy inputs to the systems as well as efficiencies in recovery of digestate and methane energy are considered. As an example, for Swedish conditions it has been estimated that the energy balance of and AD facility treating manure becomes negative when 200 km distance exist and return transport is added (Berglund and Borjesson 2006).

5 CONCLUSIONS

Anaerobic digestion favored the availability of nutrients. After 61 days 20-26% increase in NH_4^+, and 20-36% increase in PO_4^{3-} was found in most treatments. A positive effect of manure addition was observed in the conversion of intermediates during the experiment and on the total nutrient content of the digestates. On the other hand, maize silage favored the ultimate amount of methane produced as well as the phosphorus mineralization.

Digestion time showed an impact in N availability. After 7 days maximum NH_4^+ amounts were reached and maintained up to 20 days digestion. Inorganic nutrients were found to be mainly available in the liquid portion of the digestate, 80-92% NH_4^+ and 65-74% PO_4^{3-}, the proportion of total mineralized nutrients in the liquid and solid part of the digestates not fluctuating in time. The fluctuations in the dissolved metal concentrations, Mg, Ca and PO_4^{3-} correlated with pH evolution.

In terms of net energy outcome the introduction of digested manure into a farming system was found to increase by 3.1% the energy balance of a maize digestion system. When codigesting maize and manure at 50:50 TS ratio the net energy delivered by the system per ton substrate decreases to 59% of that of pure maize silage digestion artificially fertilized.

In the Netherlands where there is a surplus of manure the calculations show that it is more energy efficient to use manure than crops for biogas production, 250 ton manure being able to provide the same net energy than one hectare maize. However in terms of net energy outcomes the most energy profitable option is the codigestion of maize silage with manure.

Chapter 6

Sensitivity analysis on the net energy contribution of anaerobic digestion to biomass cascades

Abstract

Anaerobic digestion (AD) is a technological simple process that allows adding value to biomass of different origin by allowing recovery of energy, water and nutrients. The net energy gains obtainable from an AD unit are determined by its specific configuration which is turn is shaped by context conditions. Context conditions include boundary conditions and the conditions imposed by other processes or activities delivering inputs or receiving the outputs of the facility, which can be grouped into input material characteristics, energy demand and digestate demand.

In this chapter the influence of those conditions in the energy balance of an AD facility is theoretically presented and later on exemplified by performing a sensitivity analysis on the AD of different materials under three scenarios. Results allow identifying the critical factors influencing the net energy gain that AD can provide to a biomass cascade.

Pabon-Pereira CP, van Lier JB

1 INTRODUCTION

Anaerobic digestion (AD) is a technological process offering many possibilities to add value to biomass via its conversion to energy in the form of methane and an organic amendment rich in nutrients, water and organic matter, i.e. digestate.

Despite the simplicity of the anaerobic digestion process itself, the configuration of a full scale installation usually requires several units, such as storage, pretreatment, gas and digestate post-treament. The energy balance of the anaerobic digestion facility, $E_{balanceAD}$, is determined by its specific configuration. Technological decisions related to the design process are shaped by the context conditions in which the technology is embedded. Context conditions include boundary conditions and the conditions imposed by the biomass chain itself which can be grouped in input material characteristics, energy demand and digestate demand (Figure 6.1).

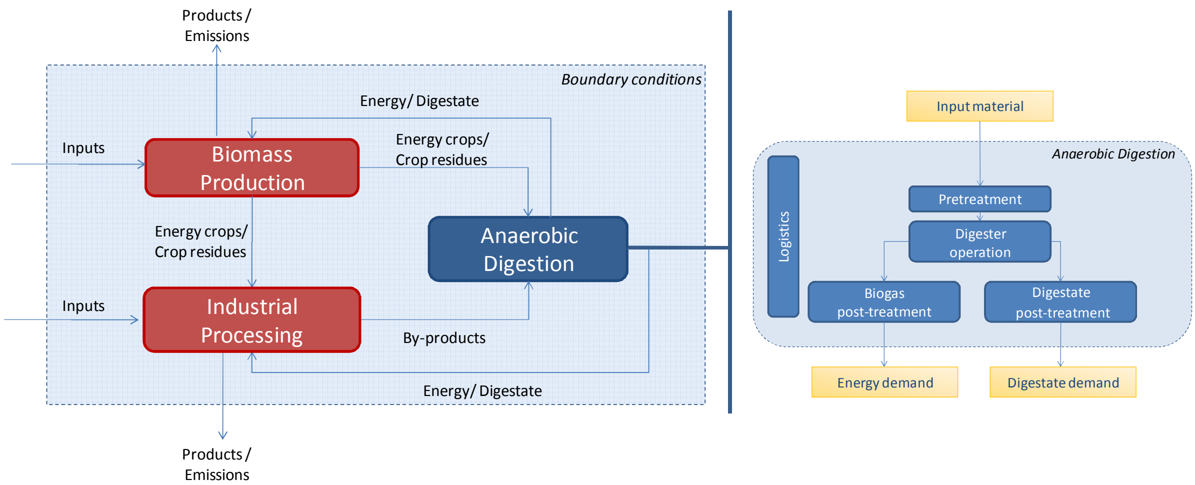


Figure 6.1 Anaerobic Digestion within a biomass cascade

The overall contribution of AD within a cascade is then the result of fine tuning the technological configuration of the AD process to the specific demands coming from the context (Figure 6.2). Boundary conditions of relevance are climate, transport distances of source biomass, environmental regulations and socio-economic restrictions. Main input material characteristics of relevance are the Total Solids (TS) and its organic component as defined by the Volatile Solids (VS) and/or Chemical Oxygen Demand (COD), its biodegradability properties in extent and rate as given by the Biochemical Methane Potential (BMP) and hydrolysis rate (k_h), pH, nutrient content, and toxicity. Obviously, the available amount or flow Q largely determining the specific design. On the other hand the products of the AD process need to be adapted to the receptive environment according to the demands of energy and digestate. Energy can be demanded in the form of raw biogas, i.e. for cooking purposes or in the form of upgraded methane gas for vehicle use or gas grid injection. Further, energy in methane can also be delivered in the form of heat and/or electricity. Finally, decisions regarding digestate post-treatment need to be adapted to the possibilities in the surrounding context for closing material cycles in terms of carbon, nutrients and water.

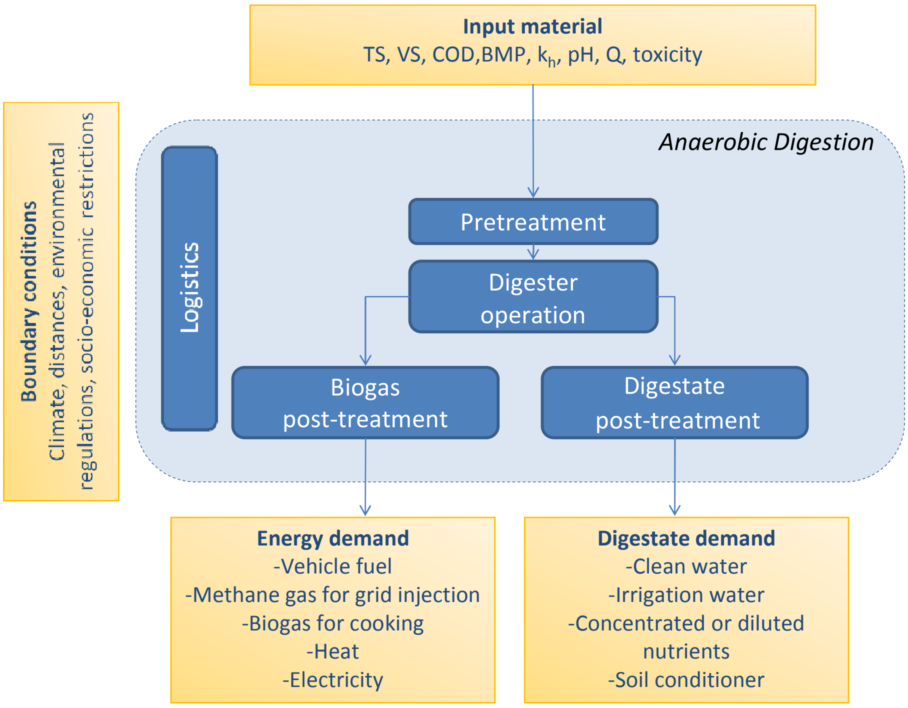


Figure 6.2 External conditions influencing the design of an AD facility
TS: Total Solids; VS: Volatile Solids; COD: Chemical Oxygen Demand;
BMP: Biochemical Methane Potential; k_h: hydrolysis rate; Q: flow.

2 Energy balance of an AD facility

The energy balance of an AD facility is defined as the difference between the energy outputs and the energy inputs of the system, both direct and indirect. The direct energy output of an AD facility corresponds to the brut energy produced, $E_{methane}$, whereas the indirect energy outputs correspond mainly to the energy embedded in the nutrients, E_{nutr}, and water, E_{water}, as accounted by their energy replacement value. Direct energy is used in logistics, E_{log}, pretreatments, E_{pret}, digester operation, $E_{dig.op}$, biogas post-treatment, $E_{biog.post}$, and digestate post-treatment, $E_{dig.post}$, whereas indirect energy inputs are mainly found in the energy used for inputs different than energy needed in the process, like the energy embedded in chemical additives, E_{add} and that used for the building and maintenance the different operational units E_{inf} (Equation 6.1).

$$E_{balanceAD}\left[\frac{MJ}{yr}\right]=\left(E_{methane}+E_{nutr}+E_{water}\right)-\left(E_{\log}+E_{pret}+E_{dig.op}+E_{biog.post}+E_{dig.post}+E_{add}+E_{\inf}\right) \quad (6.1)$$

In the next section the individual terms of equation 1 are described focusing in their intrinsic variability in relation to the context conditions as previously exposed.

2.1 Energy outputs

2.1.1 Methane energy yield ($E_{methane}$)

The maximum possible energy output from a specific substrate is given as a function of its availability, *Av*, and the quality of the substrate as determined by its volatile solids content, *VS*, and its Biochemical Methane Potential, *BMP*. However the real attainable energy output is usually just a fraction of the maximum methane potential and is determined by the efficiency of the treatment process, *Eff*, which in turn is defined by the substrate kinetics and operational conditions of the digester. The overall behavior of the reactor is then the result of the complex interactions between physic-chemical factors and the microbial culture inside of it, can be mathematically described by kinetic models such as ADM1 (Batstone et al. 2002).
The net methane output of an AD facility can be defined as in Equation 6.2, where 35 correspond to the lower heating value of methane (Lehtomaki 2006).

$$E_{methane}\left[\frac{MJ}{yr}\right] = Av\left[\frac{Kg}{yr}\right]\times VS\left[\frac{KgVS}{Kg}\right]\times BMP\left[\frac{m^3CH_4}{KgVS}\right]\times Eff\,[\%BMP]\times 35\left[\frac{MJ}{m^3CH_4}\right] \quad (6.2)$$

Table 6.1 exemplifies how the maximum energy output of different biomass material varies in relation to both BMP and TS content. Values are just indicative as the nature of the biomass material can change considerably according to the circumstances of its production.

Table 6.1 Energy potential of different substrates

Substrate	**TS content [%FM]**	**BMP [m^3 CH_4 $kgVS^{-1}$]**	**Methane yield**	
			[m^3 CH_4 ton^{-1} FM]	**[MJ ton^{-1} FM]**
Energy crops	7-84% [a]	0.17-0.55	30-150 500-12400 [b]	1000-5000 16000-400000 [b]
Crop residues				
-Straw	82%	0.23-0.25	139-145	5000-5300
-Tops and leaves sugar beet	19%	0.36-0.38	36-38	1300-1400
Animal residues				
-Manure				
Pig manure	8%	0.29-0.37	17-22	620-800
Cow manure	8%	0.11-0.24	7-14	260-510
-Slaughterhouse waste	17%	0.57	150	5500
OFMSW	30%	0.5-0.6	100-150	3600-5500
Food residues				
- Vegetable waste	81.4-98.1% [a]	0.19-0.4	150-390	5050-12810
- Fruit waste	86.8-97.2% [a]	0.18-0.73	160-710	5100-23170
Industrial effluents [c]				
- Alcohol refining			3.9	140
- Beer&Malt			1.0	37
- Coffee			3.2	114
- Dairy products			0.9	34
- Fish processing			0.9	32

Substrate	TS content [%FM]	BMP [m^3 CH_4 $kgVS^{-1}$]	Methane yield	
			[m^3 CH_4 ton^{-1} FM]	[MJ ton^{-1} FM]
- Meat& Poultry			1.4	52
- Organic chemicals			1.1	38
- Petroleum refineries			0.4	13
- Plastics & Resins			1.3	47
- Pulp & Paper (combined)			3.2	114
- Starch production			3.5	127
- Sugar refining			11.2	406
- Vegetables, Fruits & Juices			1.8	63
- Wine & Vinegar			0.5	19

Sources: (Berglund and Borjesson 2006; Gunaseelan 2004; IPCC 1996; Lehtomaki 2006)
*FM: Fresh Matter
[a] VS as %TS as in (Gunaseelan 2004), ranges for different tropical vegetable and fruit residues.
[b] Values expressed in m^3CH_4 ha^{-1} yr^{-1} and MJ ha^{-1} yr^{-1}
[c] Industrial output expressed per ton wastewater and calculated following Table 6.9. IPCC guidelines 2006. Volume 5. Chapter 6.

2.1.2 Energy in nutrients (E_{nutr})

AD treatment mineralizes nutrients from complex polymers increasing their availability (See Chapter 5 of this thesis). If nutrients are recirculated into agriculture, energy can be saved in the amount of fertilizer required to grow crops. Nutrients in the form of fertilizers constitute by far the largest portion of primary energy inputs into agricultural systems (Brehmer 2008a), hence recirculation of nutrients back to the field imply indirect energy savings. Savings in energy consumption due to fertilizer replacement within AD facilities based on energy crops have been found to correspond to 2-8% of the energy content of the biogas produced (Berglund and Borjesson 2006). Indications of the energy needed for the digestion of other raw materials such as municipal organic waste, food industry waste, manure is provided in Berglund (2006). Nutrients can also be recovered from industrial effluents. N and P content of industrial effluents can be up to 10 g N l^{-1} and 1 gP l^{-1}, whereas other effluents such as manure and slaughterhouse waste can have a much higher N content, i.e. 18 and 25 g N l^{-1}, respectively (Lehtomaki 2005). The energy gained from reusing nutrients will depend on the type of fertilizer being replaced and the technology used to produce it. For the production of urea, triple superphosphate (TSP) and potassium chloride (KCl) in Europe, Kongsaug (1998) reported 51±9 GJ ton^{-1} N, 1.3±7.5 GJ ton^{-1} P_2O_5, and 2.7±1.3 GJ ton^{-1} KCl, respectively. Gerin et al (2008) reported higher values and broader ranges also for the European case, i.e. 70±34 GJ ton^{-1} N, 12±4 GJ ton^{-1} P_2O_5 and 7.5±2.5 GJ ton^{-1} K_2O, respectively.

2.1.3 Energy in water (E_{water})

This category refers to the water that leaves an AD system and that can be reused either in the form of digestate or as a post treated effluent in the industry as process water, or in the form of a clean effluent for disposal in the environment. Obviously, each of the choices requires different treatment technologies according to the water quality demanded. In many cases aerobic or physical-chemical treatments are required to complement the AD process. Still, as long as the water is not toxically contaminated and complies with the requisites of the receiving industrial or agricultural unit, this water will be replacing fresh water, usually coming from drinking water facilities. For this exercise, the energy replacement value of water is assigned assuming it is replacing water originally treated in a drinking water facility. Average value suggested is 0.5 kWh m^{-3} (Zeeman et al. 2008). A higher value can be expected for sohphisticated technologies such as ultrafiltration, consuming 0.8 kWh m^{-3} of which 0.12 correspond to intake pumping, 0.3 to chemicals production, 0.15 to the water treatment process and 0.25 to potable water distribution (Vince et al. 2008).

2.2 Energy inputs

2.2.1 Energy use in logistics (E_{log})

Energy is needed for transporting and storing materials in the AD facility. Depending on the distances between the industry or field and the AD plant, input and output transport can become more or less relevant. Fluck (1992) presented the average energy consumption for different transport systems as shown in Table 6.2. Truck transport energy consumption will change according to truck capacity, the density of the material being transported and if the capacity of the truck is also used on the return trip. Berglund and Borjesson (2006) presented transport values between 0.7 and 3.5 MJ ton^{-1} km^{-1} depending on the mentioned variables.

Table 6.2 Energy consumption in biomass transport

Biomass transport	Average	Min	Max
	[MJ ton^{-1} km^{-1}]		
Truck	2.5	0.5	4.5
Rail	0.6	0.2	1
Water	0.1	0.05	1.4
Pipeline	1.6	0.2	3

Energy is also needed for storage of substrates. Especially in the case of energy crops, due to seasonality of production, storage is of importance. Ensiling is preferred over drying substrates for conservation because AD is more suited for treating wet material. During silaging, the formation of low molecular weight organic compounds like alcohols and volatile fatty acids is enhanced which in turn diminishes pH, improving the storability of the materials. In addition to the better storability, the increase in methane yield has been reported for sugar beet tops and whole crop maize (Lehtomaki et al. 2005; Neureiter et al. 2005). Amon et al (2007b) reported a 25% increase in methane yield of maize after silaging, i.e. 289 m^3CH_4 $kgVS^{-1}$ vs. 225 m^3CH_4 $kgVS^{-1}$. However, also losses have been found i.e. 17-39% losses of methane potential during grass silaging were reported by Lehtomaki (2005). Silaging is usually performed using a bailer or silo compaction, the first requires about 80 MJ h^{-1} working at a field capacity of 7.45 ha h^{-1} (Brehmer 2008b) while the second option requires 5.6 l diesel ha^{-1} yr^{-1} (Gerin et al. 2008).

2.2.2 Energy use in substrate preparation and pretreatments (E_{pret})

Energy might also be needed to adjust the properties of the raw materials to the AD process. Minimum requirements are substrate homogenization, water addition and/or pH adjustments. Substrate homogenization requires energy for mixing and possibly comminution. Energy required for particle size reduction is in average 0.075 GJ ton^{-1} varying in between 0.032-0.46 GJ ton^{-1} according to the type of feedstock (Brehmer 2008b). AD is not a water demanding process and various technological applications exist for handling materials with different solids content. Nonetheless, for substrates being in between the ranges suitable for certain technologies, water addition might be needed to allow for sufficient substrate homogenization. An example case is water addition when digesting energy crops in Completely Stirred Tank Reactors (CSTRs) to reach a workable 10% TS content. Water addition is an important consideration from an energy balance perspective as it will influence the energy requirements for digester operation and for the handling of the digestate (Berglund and Borjesson 2006).

Pretreatments are aimed specifically at increasing the methane yield of biomass; examples are mechanical or physical pretreatment, steam pretreatment/ explosion, liquid water incubation, acid, alkaline or oxidative pretreatment, and their combination. Most of the pretreatments will increase the available surface area and alter the lignin structure (Hendriks and Zeeman 2009). The choice among them depends not only in their effectiveness but also in their energy requirements and the readiness of the technology for full scale application. Due to the very high energy consumption, particle size reduction seems prohibitive (Brehmer 2008b); other pretreatments will vary in energy requirements depending on the amount of active chemicals needed, both for the treatment and its subsequent neutralization. Energy embedded in the active chemicals as required for their production can vary in between 1.44 and 28.4 GJ ton^{-1} substrate and are applied viz. 0.055 and 0.8 ton ton^{-1} feedstock. In some cases, like in the ammonia and maleic acid pretreatments, the recovery of the chemical is possible. Depending on the structure of the input material, different technologies will be appropriate. Energetically, the most economic pretreatment for complex carbohydrates coming from agricultural waste processing is steam treatment at 3.17 GJ ton^{-1} sugar product whereas for industrial processing residues such as bagasse and press cake is Ammonia Fast Explosion (AFEX) at 3.4 GJ ton^{-1} sugar product and for recalcitrant material such woods and grasses dilute sulphuric acid is the most suitable at 3.53 GJ ton^{-1} sugar product (Brehmer 2008b).

Among pre-treatments, alkali treatment has been reported to offer an important potential for increasing CH_4 yields, whereas it is also cost-efficient and easy to implement (Lehtomaki et al. 2004; Perez Lopez et al. 2005). A dose of 6% NaOH on DM basis and a loading rate of 65 gNaOH l^{-1} were recommended for pretreatment and subsequent anaerobic digestion of corn stover, leading to 48.5% more biogas production (Pang et al. 2008).

2.2.3 Energy use in digester operation ($E_{dig.oper}$)

The main activities involved in the operation of a biogas plant are pumping, mixing and heating. Equation 3 summarizes the calculation of the energy inputs required for each activity (Southampton 2008). The energy for pumping depends on the power of the pumps, P [KW] and the daily working hours of the pumps, t_p [h d^{-1}] . The energy for mixing depends on the type of digester, its volume V [m^3] and the energy consumption of the mixing system, E_m [W m^{-3}], which for a CSTR is in average 5 and can fluctuate between 2.5 and 6.5. The energy required for heating depends on the thickness of the digester wall, insulation material, the flow and temperature of the influent, the difference in temperature between the air and the ground with respect to the digester, and the cross-sectional areas in contact with them.

$$E_{dig.op} = \left(P[kW] \times t_p\left[\frac{h}{d}\right] \times 3.6\left[\frac{MJ}{kWh}\right]\right) + \left(V[m^3] \times 5\left[\frac{W}{m^3}\right] \times 0.864\left[\frac{MJ}{W\ d}\right]\right) + \tag{6.3}$$
$$\left(\left(0.265\left[\frac{J}{m^2\ s\ {}^oC}\right] \times A_{air}[m^2] \times \Delta T_{air}[{}^oC] + 0.235\left[\frac{J}{m^2\ s\ {}^oC}\right] \times A_{ground}[m^2] \times \Delta T_{ground}[{}^oC]\right) x0.0864\left[\frac{MJ\ s}{J\ d}\right] + (C \times Q \times \delta \times \Delta T_{\inf luent})\right)$$

In Equation 6.3, 3.6 MJ kWh^{-1} and 0.0864 MJ $W^{-1}d^{-1}$ are conversion factors, 0.265 and 0.235 are the coefficients of heat transfer in [J m^{-2} s^{-1} $^oC^{-1}$] which include insulation. A refers to area of the digester in contact with air or ground in m^2, ΔT [^{o}C] refers to the change in temperature between the air, ground or influent and the temperature that wants to be maintained in the digester, C is the specific heat of the influent which can be equal to the specific heat of water, 4.187 10^{-3} MJ $kg^{-1o}C^{-1}$, Q [m^3d^{-1}] is the influent flow and δ [kg m^{-3}] is the density of the influent. For European conditions benchmark values for energy consumption as a function of energy yield for the mesophilic digestion of readily degradable crops in a CSTR are 0.03% , 1.1% and 6.6% for pumping, heating and mixing, respectively (Southampton 2008).

2.2.4 Energy use in biogas treatment/conversion ($E_{biog.post}$)

Different uses are possible for the biogas produced. Energy in biogas can be transformed into thermal energy by means of a boiler; it can also be used directly for power generation by means of spark ignition or duel fuel engines, microturbines, combustion gas turbines or fuel cells. Furthermore, biogas can be upgraded and compressed to be used in the biogas grid or as vehicular fuel.

Using biogas for a boiler is a simple application producing 0.21 kW of continuous hot water per m^3 biogas per day. When used for power generation, biogas normally fuels a spark-ignition internal combustion energy which drives a generator. In Germany dual-fuel engines are in use, which are diesel engines that use the compression of the diesel to provide the ignition of the biogas with a typical fuel input of 15% diesel and 85% biogas (Chesshire 2005). Efficiencies in the conversion of biogas to electricity and heat vary between 80-90% according to size of the engine. In general 30-40% of the energy content of the biogas will be recovered as electricity and the rest as heat (Berglund and Borjesson 2006; Chesshire 2005; Salter and Banks 2008). The heat is recovered in two forms: as water from the engine jacket water at 80-90^{o}C and as heat from the engine exhaust gases at 500^{o}C, with proportions of 15-20%, and 35-40% respectively. Relative to the biogas energy input the recovery of the heat in the exhaust gas is suboptimal and in general only 50% of this heat can be used. In systems upgrading biogas for the gas grid between10-14% more energy is recovered as compared to the CHP, i.e. Combined Heat and Power case (Salter and Banks 2008). Scale issues are relevant as small-scale technologies for biogas upgrading and storage are not fully developed (Frederiksson et al. 2006).

Table 6.3 summarizes the information about efficiencies and requirements of each of the options. From the table it can be noted that vehicular fuel and gas upgrading are the most energy efficient options. Engines will follow in efficiencies with an overall 85-90% efficiency but a real usable energy of 70-80% considering losses in heat recovery from the exhaust gases. Fuel cells represent the best option in terms of electricity output but their efficiency is still rather low, i.e. 40-57%.

A crucial consideration regarding the real efficiency delivered by a biogas system is the extent to which the heat demand is coupled, or not, to the quality of the heat delivered by the AD unit. Maximum efficiencies in heat recovery are achieved when temperature differences among the heat donor and the heat acceptor are maximized as dictated by the Carnot cycle, i.e. Carnot efficiency= $1-(T_{cold}/T_{hot})$, although in practice work efficiencies never reach the calculated maximum work potential. In the case of a CHP unit restrictions apply as the heat produced comes at fixed temperature and pressure and its recovery will depend on the temperature at which the heat is demanded in the outer system. In this respect the efficiencies in recovery of the heat can be crucial in determining the realistic net energy output of a digestion system when electricity is the primary type of energy demanded.

Table 6.3 Options for biogas treatment and reuse

End use	**Efficiency**	**Power Output Range**	**Clean-up**	**Comments**
THERMAL				
Boilers	80-85%	Average 500 kW	▪ Little to none except waster condensation/ chiller and possibly hydrogen sulfide scrubbing to less than 1,000 ppm	▪ Simple design and low capital ▪ Often preferred at industrial sites, particularly food processors
POWER GENERATION				
Internal combustion – Spark ignition and dual fuel engines	2.6 kW kW_e^{-1} (30-40% electricity efficiency) 40% usable thermal energy	From 45 kW (i.e. 12 kW_e) Usual range: 100-6,000 kW_e	▪ Water vapor and sulfide (500-1,000 ppm) ▪ Siloxanes 15-30 $\mu g\ l^{-1}$	▪ Power and heat utilization ▪ In the case of a dual fuel engine 8-10% of diesel is injected for ignition.
Microturbine	Comparable to SI engines 26-29%	30-250 kWe 25-100 kW	▪ Water vapor and sulfide (<100 ppmv) ▪ Siloxanes essentially ND	▪ Allow the recovery of the heat in the form of low pressure steam
Combustion gas turbine	Same as internal combustion engines	500-30,000 kW_e	▪ Similar to CHP	▪ Allow the recovery of the heat in the form of steam
Fuel Cell	40-57% depending on type	250-2,500 kW_e 200 kW-2MW	▪ Water vapor and sulfide to ND ▪ Siloxanes ND	▪ Clean technology ▪ High conversion efficiencies
DIRECT MECHANICAL	Depending on application			

End use	Efficiency	Power Output Range	Clean-up	Comments
VEHICULAR FUEL	About 89% of the energy content of the biogas		▪ CO_2, H_2S, NH_3, particles and water plus trace components need to be removed ▪ End product CH_4 above 95%	▪ Replacement of natural gas ▪ High cleaning requirements ▪ Motors need to be adapted ▪ Large storage space
GRID INJECTION	About 89% of the energy content of the biogas		▪ No International Standard available ▪ CO_2, H_2S, NH_3, particles and water plus trace components need to be removed ▪ Energy content was indicated by the Wobbe index needs to be adjusted	▪ Replacement of natural gas ▪ High cleaning requirements

Sources: (Berglund and Borjesson 2006; Persson et al. 2006; Wellinger and Lindberg 2005)

SCFM: Standard Cubic Foot per Minute; CHP: Combined Heat and Power; ND: Not Detectable.

2.2.5 Energy use for digestate post-treatment ($E_{dig.post}$)

The handling and disposal of the digestate produced in an AD facility depends on the characteristics of the substrate and its expected end use. Relevant quality characteristics include solids content, organics content, nutrient content, pathogen content and the presence of metals and toxic compounds. End uses might include application in the field, upgrading for reuse in industry and upgrading for appropriate disposal in surface water. When the original material can be considered “clean” the possibility of closing nutrient and water cycles becomes an appealing option as far as the balance of natural cycles is taken into consideration.

When matching the availability and requirement options, different post treatment alternatives result, including dewatering by filter press, air drying, centrifugation or evaporation, possibly followed by composting or incineration of the solids and/or polishing of the liquids using aerobic technology for discharge in the environment. In addition, a wide array of biological and physical-chemical processes for pathogen and nutrient removal or precipitation can be the case. Struvite precipitation shows very interesting features as it allows recovery of phosphate ions and to a lesser extent ammonium. Struvite is an ammonium magnesium phosphate crystal which is formed in anaerobic digesters when magnesium or calcium is present. Its precipitation can be controlled allowing the recovery of the salt and resulting in phosphorus and nitrogen removal from waste water when the P/N ratio is near to 1 (Lier van et al. 2001). It has been calculated that struvite precipitation requires 8.3 MJ kg^{-1} N treated. However this amount does not include the high input of chemicals required for the process when all nitrogen needs to be recovered, i.e.1.74 kg Mg, 1.95 kg P and 22.7 kg NaOH kg^{-1} N in the influent. Other possibility requiring fewer inputs is the recovery of only phosphorus which is more strategic considering the scarcity of this resource in nature. This would require much less chemical inputs (SenterNovem 2008).

Finally, when digestate is to be applied in the field, energy use for storage, loading, transport and field application are ubiquitous. The energy use varies according to the TS content of the substrate (Berglund and Borjesson 2006).

An overview of the energy inputs for the main processes relevant to digestate reuse is presented in Table 6.4.

Table 6.4 Alternative operations related to digestate post-treatment and reuse

Operation	Average energy use		Unit	Comments
	Liquid	Solid		
Loading	2.5	7	[MJ ton^{-1}]	
Transport	5	7	[MJ ton^{-1}]	For 2 km distance between AD facility and field
Spreading	17	14	[MJ ton^{-1}]	
Dewatering	10		[MJ ton^{-1}]	
Centrifugation	380		[MJ ton TS^{-1}]	
Evaporation	2.3		[MJ kg^{-1} water evaporated]	Depending on the solid content of the input and the required output, 0.8-22.4 MJ KgDS^{-1}
Composting		0.6	[MJ kg DS^{-1}]	Between 0.11-1.12 MJ KgDS^{-1} depending on the technology applied
Combustion		1.08 (elect) 2.7 (thermal)	[MJ kg DS^{-1}]	The net energy output depends on the solid content of the input plus the energy content of the material, i.e. -15.7 up to +16.3 MJ KgDS^{-1} for manure of different solids content and different energy content
N recycling	8.3		[MJ kgN^{-1}]	Struvite precipitation
N removal	75		[kJ kgN^{-1}]	Varies between 6-144 kJ KgN^{-1} depending on the type of technology, i.e. Nitrification-denitrification, Sharon, Sharon Anammox, Partial nitrification, Volume reduction, Air stripping
Aerobic treatment reuse/discharge	5.4		[MJ kg BOD^{-1}]	For activated sludge, energy requirement can be higher, i.e. 15 MJ/Kg BOD.
	5		[MJ 10^{-3}m^{-3}]	For an intermediate rate trickling filter with some nitrification. Depending on the type of trickling filter power demand 7.2-72 MJ/10^3m^3

Sources: (BBT-kenniscentrum 2006; Berglund 2006; Berglund and Borjesson 2006; Tchobanoglous et al. 2004; Wilsenach 2006); DS : Dry Solids ; BOD : Biochemical Oxygen Demand;

2.2.6 Energy in chemical additives (E_{add})

Alkaline addition for pH adjustment or for substrate pretreatment is one of the most common practices in AD facilities. The coproduction of chlorine and sodium hydroxide (NaOH) is one of the main chemical industrial activities in the world having a considerable environmental impact. Considering a total energy use of this industry of 36-49 MJ kg Cl_2^{-1} and considering that for each kg of chlorine 1.12 to 1.43 kg of sodium hydroxide is produced, an average energy use of 24 MJ kg^{-1} NaOH results (EERE 2000).

2.2.7 Energy in infrastructure (E_{inf}):

Energy is needed in the construction and maintenance of the AD facilities, and it can greatly vary depending on the type of installation being built. For an Austrian AD plant the total embodied energy including construction was calculated as 33,753 GJ, which, considering the treatment of 13,000 ton yr^{-1} and amortizing over 25 years, corresponds to approximately 100 MJ ton^{-1} (Southampton 2006).

2.3 Summary

Table 6.5 summarizes the information presented in the previous sections, giving an indication of expected ranges of variation in energy output or input and the main variables affecting the outcome. Since the review is not exhaustive values presented are only indicative.

Table 6.5 Summary of energy inputs and energy outputs for an AD facility per ton input material

	Average	Min	Max	Unit	Variables
ENERGY OUTPUT					
Methane energy yield					
-Energy crops	2,500	1,000	5,000	[MJ ton^{-1}]	TS/VS content, BMP, reactor efficiency
-Crop Residues	3,400	1,300	5,300	[MJ ton^{-1}]	
-Animal residues	2,880	260	5,500	[MJ ton^{-1}]	
- OFMSW	4,550	3,600	5,500	[MJ ton^{-1}]	
-Industrial effluents	208	10	406	[MJ ton^{-1}]	
Energy replaced fertilizer[a]	550 15,000	120 2,000	970 25,000	[MJ tonDM^{-1}] [MJ ha^{-1}yr^{-1}]	Nutrient content; Nutrient demand
Energy in water [b]	0.7	0	2.9	[MJ ton $^{-1}$]	TS content, toxicity,
ENERGY INPUT					
Logistics[c]	2.5	0.5	4.5	[MJ ton^{-1}km^{-1}]	Distance, density
Pretreatments					
-Particle size reduction	75	32	460	[MJ ton^{-1}]	B_o, TS
-Others[e]	3.35	3.17	3.53	[MJ kg $^{-1}$ sugar output]	B_o, TS
Digester operation[f]	8%	1%	22%	% brut energy output	ΔT, V, A, Q, S
Biogas post-treatment[g]	10%	0%	20%	% brut energy output	End use of gas
Digestate post-treatment[h]	130	-16,300	22,400	[MJ ton^{1}]	TS content, End use of digestate
Additives[i]	2,400	0	4,800	[MJ ton^{1}]	pH, non-acidified biodegradable COD
Infrastructure	100			[MJ ton^{1}]	Material, Q

OFMSW: Organic Fraction of Municipal Solid Waste. a. Values refer to potential replacement of fertilizers in agricultural fields producing energy crops for feeding AD systems; Values per Kg N in the influent are presented in the text, section 2.1.2; b. Average value corresponds to the sum of flocculation, flotation, aertation, filtration, calcium removal and UV desinfection; maximum value corresponds to the energy used in a drinking water facility using ultrafiltration technology (Vince et al. 2008) c.Valid for truck transport; d. Calculated based on (Pang et al.

2008) for the treatment of corn stover residues; e. Values reported as energetic optimum for different types of feedstocks by Brehmer (2008b). f. As reported by (Southampton 2008) for energy crop digestion; g. Average value corresponds to a CHP, whereas maximum corresponds to the boiler. h. Average value corresponds to centrifugation followed by separate spreading of the liquid and solid flows. Minimum refers to energy savings from manure combustion, whereas the maximum refers to the evaporation option; i. Calculated according to energy needed for the production of NaOH, i.e. 24 MJ kg^{-1} (EERE 2000) and considering NaOH addition is 50% more than allowed VFA concentration in reactor. For the upper value a 2.5 mM VFA concentration for vinasse digestion was considered indicative (Torry-Smith et al. 2003).

Data in Table 6.5 has been summarized in Figure 6.3. It can be observed that the energy input required for an AD facility varies in a greater range than the possible energy output. In addition, among energy outputs the contribution of water and fertilizer recirculation appears of minimum importance as that of the methane itself whereas in terms of energy input, digestate post-treatment shows the higher range of fluctuation.

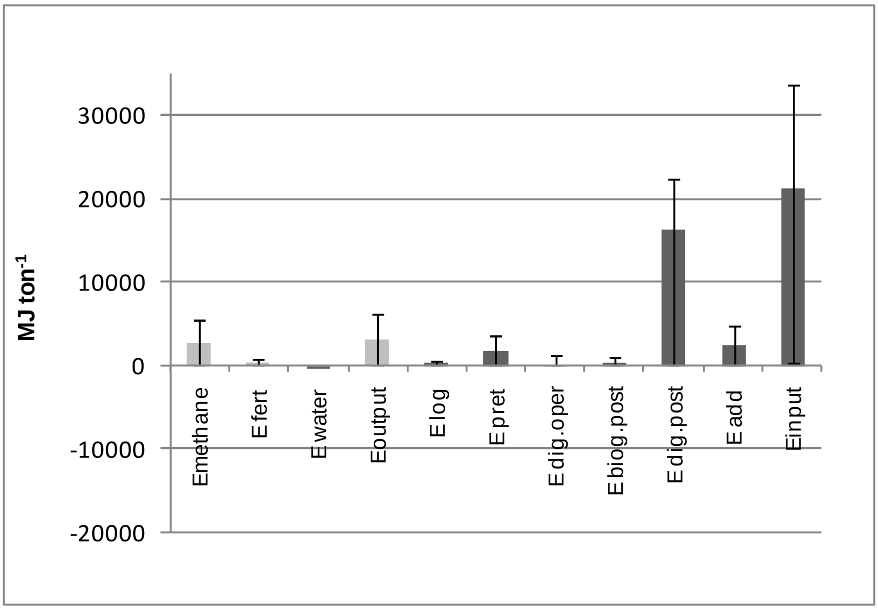


Figure 6.3 Main aspects affecting the energy balance of an AD facility

2.4 Sensitivity analysis based on selected scenarios

Since definite conclusions cannot be made from the general variability presented, a sensitivity analysis is performed for three substrates of different origin, i.e. energy crop (maize silage), animal residues (manure) and industrial effluent (sugarcane vinasse). Table 6.6 shows assumptions made on inputs characteristics.

Systems are analyzed for same substrate availability of 10000 m^3 yr^{-1}, i.e. 28 $m^3 d^{-1}$, using a CSTR system operating at 38^{o}C and 10%TS. Systems are defined as shown in Table 6.7. For each substrate, three cases are defined which portray differences in the boundary conditions and demands. Case 1 shows an optimistic scenario where boundary conditions are positive in terms of transport distance, i.e. 10 km, and temperature. Energy and digestate are possible to be reused, biogas in the form of upgraded methane, and digestate as liquid fertilizer and stabilized solid conditioner. In Case 2, a negative scenario is portrayed. Boundary conditions are suboptimal, temperature being low and transport 10 times higher. Energy is only demanded in the form of electricity whereas digestate is not demanded and needs to be treated. The solids are combusted and the liquid evaporated. Case 3 presents an intermediate case in which boundary conditions are again optimal in temperature and transport demands. Energy is demanded in the form of electricity and heat, and digestate can be partially reused. Hence the solids are composted and the liquid treated for discharge. Pretreatments are not included in the analysis.

Table 6.6 Input characteristics

Variables	Unit	Manure	Maize	Sugarcane vinasse
Availability (Q)	[m^3 d^{-1}]	28	28	28
Density	[kg m^{-3}]	1000	395	1000
TS	[g gFM^{-1}]	0.08	0.31	0.065
VS	[g gFM^{-1}]	0.07	0.3	0.0585
COD	[gCOD gVS^{-1}]	1.17	1.24	1.667
VFA	[gCOD gVS^{-1}]	0.05	0.06	0.4
BMP	[m^3CH_4 $kgVS^{-1}$]	0.17	0.31	0.28
Reactor efficiency	[%BMP]	40%	75%	90%
OLR	[kg VS $m^{-3}d^{-1}$]	2	2	7
N content	[gN $kgTS^{-1}$]	37.2	12.3	4.6
NH_4	[gNH_4-N gN^{-1}]	0.28	0.25	0.6
P content	[gP $kgTS^{-1}$]	8.37	1.66	3
PO_4	[gPO_4-P gP^{-1}]	0.64	0.03	0.3

Sources: Chapters 5 of this thesis and Wilkie et al (2000), Satyawali and Balakrishnan (2007), Pant and Adholeya(2007) and (van Haandel 2005)

Energy consumption for transport of liquids, i.e. manure and vinasse was assumed to be 1.6 MJ ton^{-1} $km^{-1}$when empty return transport is the case as in cases 2 and 3, and 1.0 MJ ton^{-1} km^{-1} when the effluent was transported back as in case1. In the case of maize silage the figures were 1.1 and 0.7 MJ ton^{-1} km^{-1}, respectively (Berglund and Borjesson 2006). Digestate was assumed to be centrifuged in all cases before its application. In all cases the same composition of the output material was assumed, i.e. 20% of the total mass in the solid digestate, which has a 60% TS content. N content in solid digestate was assumed to be 33% of total N (BBT-kenniscentrum 2006).

Table 6.7 System definition used for the sensitivity analysis

System	Substrate	Boundary conditions	Input material			Energy demand	Digestate demand	System description
			Energy	Nutrient	Water			
Mn1	Manure	High T Low dist [a]	Low	High	Medium	Methane gas	Yes	Biogas upgrading; centrifugation; liquid, solid application
Mn2	Manure	Low T High dist [b]	Low	High	Medium	Elec	No	Transport (x10); CHP; centrifugation; evaporation (50%); combustion;
Mn3	Manure	High T Low dist [a]	Low	High	Medium	Elec/Heat	Only solid	CHP; centrifugation; composting; solid application; water treatment; $N_{removal}$
Mz1	Maize silage	High T Low dist [a]	High	Low	Low	Methane gas	Yes	Biogas upgrading; centrifugation; liquid, solid application
Mz2	Maize silage	Low T High dist [b]	High	Low	Low	Elec	No	Transport (x10); CHP; centrifugation; evaporation (50%); combustion
Mz3	Maize silage	High T Low dist [a]	High	Low	Low	Elec/Heat	Only solid	CHP; centrifugation; composting; solid application; water treatment; $N_{removal}$
Vn1	Vinasse[c]	High T Low dist [a]	Low	Low	High	Methane gas	Yes	Biogas upgrading; centrifugation; liquid, solid application
Vn2	Vinasse[c]	Low T High dist [b]	Low	Low	High	Elec	No	Transport (x10); CHP; centrifugation; evaporation (50%); combustion
Vn3	Vinasse[c]	High T Low dist [a]	Low	Low	High	Elec/Heat	Only solid	CHP; centrifugation; composting; solid application; water treatment; $N_{removal}$

a. $T_{substrate}$: 25 °C; T_{air}: 20 °C; T_{ground}: 10°C; Transport: 10km. b. $T_{substrate}$: 15 °C; T_{air}: 10 °C; T_{ground}: 0°C; Transport: 100km. c. $T_{substrate}$: 30°C; other temperature and transport conditions as in a and b, accordingly.

In Case 2, evaporation is assumed to take place up to 60% TS. Thereafter combustion of the solid takes place, the net energy output taken from the tables presented in (BBT-kenniscentrum 2006) considering the same heat value for all digestate, i.e. 17 MJ kg TS^{-1}.

In Case 3, after centrifugation composting of the solid digestate takes place. Assumptions in this case are the same as made in Chapter 7 of this thesis. Nitrogen losses are assumed to be 35% of the influent N content (Borjesson and Berglund 2007).The liquid fraction is assumed to be treated aerobically, considering an energy expenditure of 5.4 MJ kg BOD^{-1} and an average 20% BOD/COD content in digestate. Additional post treatment for nitrogen removal is also included in the calculations.

Calculations of water replacement value are made considering energy expenditure for ultrafiltration, i.e. 2.9 MJ ton^{-1} water recovered. In the case of the maize silage, water addition is considered to reach the 10% digester content, considering an initial 30% TS in the feed material. Hence the water replacement is adjusted by subtracting this amount. Fertilizer replacement calculations are performed considering an energy content of 60 MJ ton^{-1} N and 19 MJ ton^{-1} P.

Calculations on the indirect energy coming from the addition of NaOH are performed considering a safety factor of 1.5 mM with respect to the allowed VFA mM concentration in the reactor. For the assumed retention time and type of material the VFA concentration allowed for the assumed retention times were 0.05, 0.28 and 5 mM for manure, maize and vinasse reactors, respectively (Torry-Smith et al. 2003; Zhao 2007).

The main results of the analysis are shown in Figures 6.4, 6.5 and 6.6. In Figure 6.4 the distribution of the energy inputs to the different systems is presented. As can be observed substantial differences in energy inputs are found when comparing Case 2 with Cases 1 and 3. Inputs in Case 2 fluctuate between 57 and 67 GJ d^{-1} being 6 to 9 times higher as compared to the other cases. This is the result of evaporation which is responsible for 87-97% of energy inputs. As expected Case 1, which considers the highest reuse of outputs for all substrates types was found to be the one demanding lower inputs, i.e. 6.8 and 9.9 GJ $d^{-1,}$ however differences are not so big as compared to the scenario when solid amendment is composted and water treated, i.e. Case 3, where total energy inputs fluctuated between 9.1 and 16.3 GJ d^{-1}.

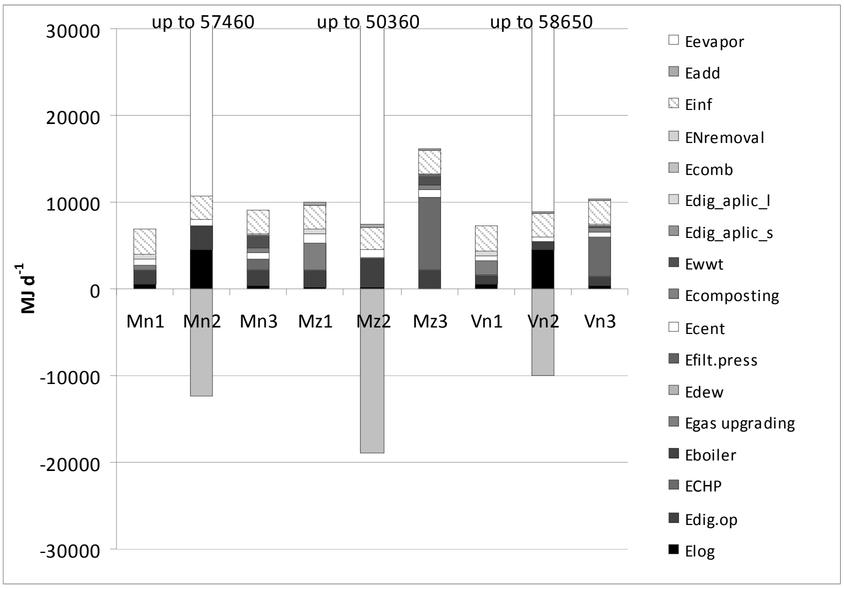


Figure 6.4 Energy input to different systems studied per category
Systems are described in Table 6.7

Regarding the distribution of the energy inputs, differences can be observed according to type of input and to the operations intrinsic to the specific cases analyzed.

In the manure scenarios 1 and 3 the indirect energy assigned to infrastructure constituted 31-41% of total energy inputs, whereas the energy input for digester operation was second in importance to 18-24% and being mainly affected by the energy use for heating the reactor. In the case of vinasses the energy needed for infrastructure was again first in importance with 27-38% of total energy inputs. Second were energy losses from conversion of the biogas to electricity and heat. Similarly, main losses from the maize systems were coming from heat lost in CHP unit and infrastructure; however heat losses were in this case first in importance.

Energy losses due to conversion of energy carriers can be very important in the case of highly energetic substrates as they are proportional to the methane produced from the substrate. Case 3 of the maize digestion exemplifies this issue, 8.4 GJ d^{-1} are lost in the conversion to electricity and heat in the CHP unit. Further when comparing Case 2 and 3 for the same substrate the energy losses from not reusing the heat produced can be as important as the sum of all other energy inputs provided evaporation is excluded, i.e. 18.2 GJ d^{-1}.

Combustion of the solid fraction of the centrifugated digestate showed to substantially contribute to the energy balance providing 10 to 19 GJ d^{-1} in the case of manure and energy maize, respectively.

The impact of transport in the case of liquid substrates is not relevant at 10 km but becomes important as distances are increased. To exemplify this, when transport distance of manure and vinasse reaches 100 km, it would constitute about 38% and 54% of energy inputs in the optimistic scenario, i.e. Case 1. The input needed for water treatment, N removal and composting appear to be of minor relevance. However it is important to recognize that the values considered do not include any energy allocated to infrastructure.

Brut energy output of the different systems fluctuated between 4.8 and 30.6 GJ d^{-1} depending on the type of substrate. The proportional impact of nutrient recirculation in the brut energy output was especially noticeable in the case of manure as shown in Figure 6.5. This is the result of both its lower energy content and higher nitrogen content as compared to maize. Water recovery showed not to have an important impact in the energy balance.

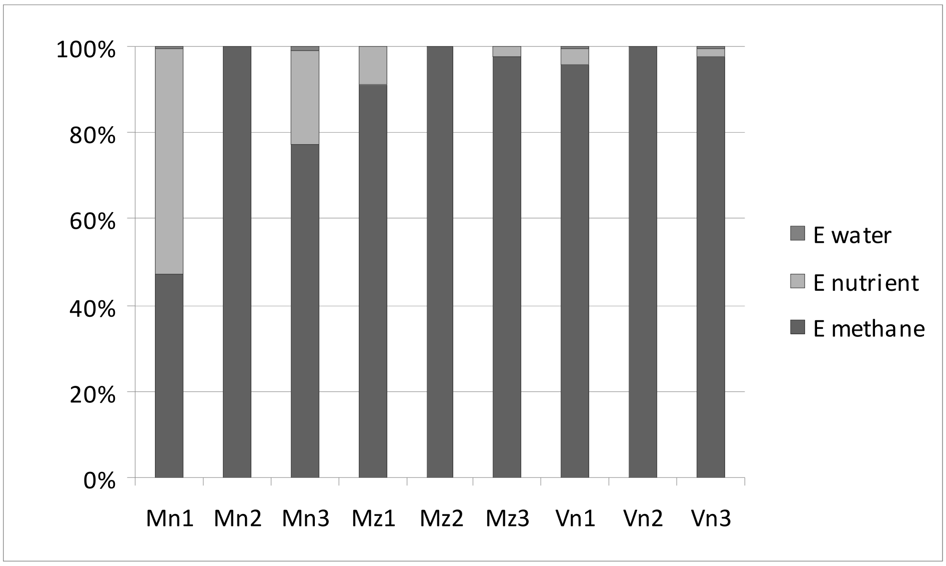


Figure 6.5 Distribution of brut energy outputs per system
Systems are described in Table 6.7

Figure 6.6 presents the summary of the energy balances of the different scenarios studied. It can be observed that manure digestion produces a net energy gain only in case 1 when nutrients and water in digestate are reused and biogas is upgraded for the gas grid or vehicular purposes. Maize systems show a net energy gain in Cases 1 and 3. It is important to recall that this is the only substrate requiring energy for biomass production which has been left out from the systems boundaries defined in this study. This issue will be revisited in the discussion. Vinasses also showed a net energy gain in two cases which although lower than maize net output were higher than manure. In the above all calculations were performed in MJ d^{-1}. However of interest is to analyze findings per ton material as it exemplifies the influence of TS and energy content of the substrate. As can be seen in Figure 6.7 the calculations in this case favor maize systems and the preference among scenarios do not change.

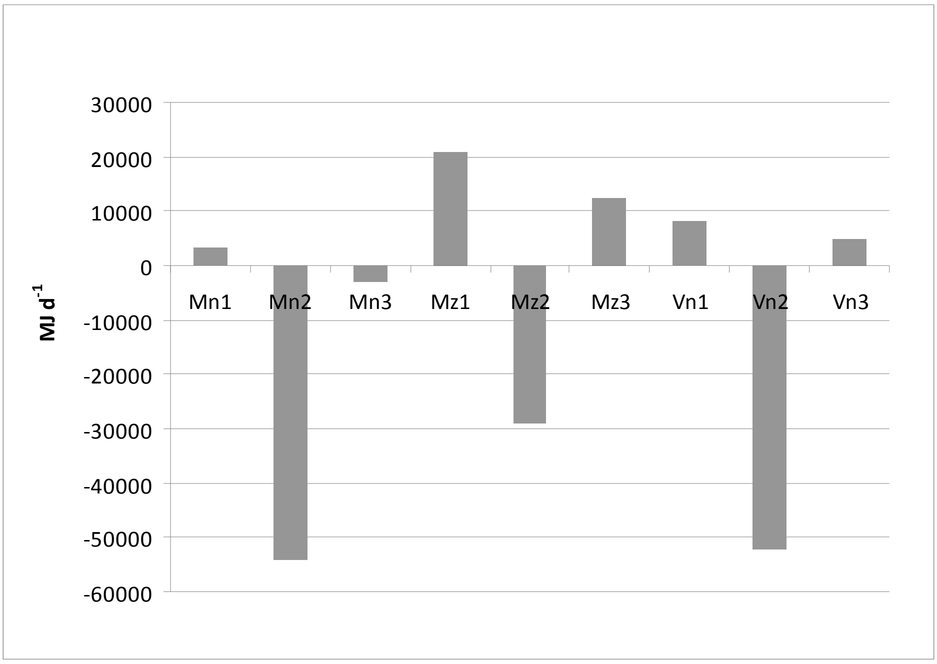


Figure 6.6 Energy balance of alternative AD systems in MJ per day
Systems are described in Table 6.7

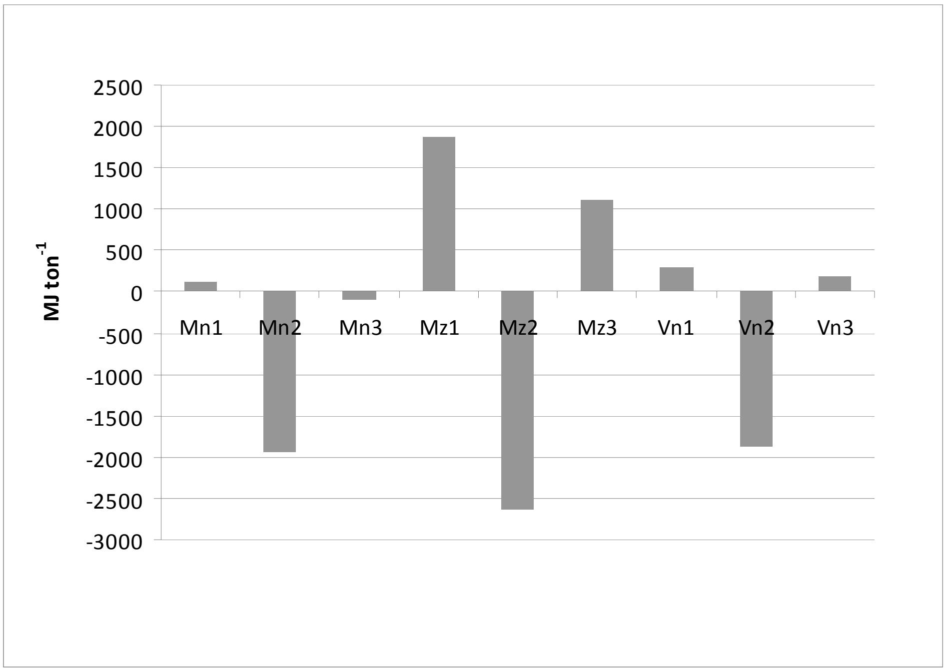


Figure 6.7 Energy balance of alternative ADD systems in MJ per ton raw material
Systems are described in Table 6.7

3 DISCUSSION

This study strived to depict the importance of the cascade conditions in the net energy gains from an anaerobic digestion system. It has been demonstrated that AD as such is a net energy producing technology since from all substrates at least one positive scenario could be found. On the other hand, boundary conditions and the demands from the outer system have also shown to influence the exploitation of the expected benefits of the technology.

Regarding the importance of the different energy inputs, it is clear that evaporation is prohibitive from an energy perspective. If evaporation is omitted from Case 2 and replaced by digestate application the energy balance would substantially improve as all systems will be able to produce energy gains provided the liquid digestate can be used in the close vicinity. For manure, maize and vinasse, 2.8, 20.8 and 5.9 GJ d^{-1} net energy gains can be obtained, respectively.

The importance of implementing AD as part of an agroindustrial cluster and/or decentralized facilities to optimize the recovery of its benefits is also stressed. The energy losses from liquid digestate reuse as affected by transport distances, and those coming from lack of heat reuse are both related to the existence of a surrounding environment that allow for closing cycles.

The indirect energy input for infrastructure showed to be remarkably important in most cases. This aspect certainly calls for the design of facilities less intensive in materials and energy. In developing countries the use of covered ponds is wide spread and under proper conditions of mixing and insulation can be seen as an important development in terms of energy savings, in addition to their obvious economic advantage.

Another important aspect to consider is the enlargement of system boundaries to include the energy used for biomass production as it allows for a fair comparison among systems having substrates of different origin as inputs. According to Gerin et al (2008) under conditions prevailing in Belgium 366 MJ ton^{-1} maize are needed as agricultural energy input. Considering this extra energy input, the net energy output of scenarios mz1 and mz3 changes from 20.7 and 12.4 GJ d^{-1} to 16.7 and 8.3 GJ d^{-1}. They will still be the highest as compared to the other substrates in the same scenario; however the vn1 scenario will deliver a slightly higher output than mz3. The previous suggest that the recovery of energy from residues can be more advantageous than producing crops for energy depending on external conditions. In proportional terms the energy needed for growing the crop represents 40-50% of the total energy inputs originally accounted or 15-16% of the total energy inputs after their addition to the energy balance.

Berglund and Borjesson (2006) compared the energy input/output ratio of different AD systems as related to the type of input, concluding that it will vary in between 20-40%. If omitting indirect inputs, i.e. infrastructure and additives, our findings for scenario 1 are in line with their finding, which is that is the manure, maize and vinasse system would use 40%, 36% and 28% of their energy output. Under these conditions, the energy use in heating the reactor gains relevance.

The energy value of nutrients and water also deserves further attention. Energy replacement value of nutrients showed to be of major importance in the case of manure whereas insignificant in the other cases. The case of water is discouraging from an energy perspective as despite its important mass amount, i.e. 90% of the digestate, its replacement value even using figures of energy intensive water purification system is still insignificant. Considering the scarcity of resources such as as phosphorus rock and clean water in certain regions, the use of the applied energy figures to value these resources seems inappropriate.

From the previous findings it seems possible to suggest the optimal conditions for fully profiting from the advantages of AD. An optimal scenario would be the combination of warm temperature conditions and close proximity to the input material, biogas direct use to avoid heat losses, low input in infrastructure, and the separate use of liquid and solid fraction of the digestate. Energy gains are maximized when liquid digestate is applied and solid digestate is combusted. From an environmental perspective other considerations need to be taken into account, including the air pollution from combustion, losses of nutrients to water and air from the liquid digestate and GHG emissions if not stabilized. From an agronomic perspective the nutrient content in the solid digestate and the need for soil conditioner are also to be considered.

Chapter 7

The added value of anaerobic digestion to cassava bioethanol production in Colombia: Energy, GHG, water and land implications

Abstract

A sustainability assessment of bioethanol (EtOH) production from cassava in Colombia was performed based on current practices and trends. The study assessed the energy, greenhouse gases (GHG), water and land use performance of alternative cassava cascades working at different scales, highlighting the implications of including the anaerobic digestion (AD) step. The centralized systems showed a poorer energy and GHG performance as compared to decentralized ones in part due to the artificial drying of cassava chips assumed for the centralized facility. If the centralized system would make use of solar drying, the Energy Balance of this system including AD will be the most positive, i.e.732 TJ yr^{-1}. Under solar drying of cassava chips systems with AD produced 3 to 5 times more energy than demanded. Such positive outcome is also present in the GHG emission savings found the same systems. The water balance output depends upon the water reuse within the ethanol industry which demands 21-23 l $lEtOH^{-1}$. In the AD scenarios assuming liquid flows are treated separately, complete water recovery is calculated to be feasible. Land use for cassava cultivation was calculated to be 0.27-0.35 ha $tEtOH^{-1}$ and is not affected by system design. The energy and water content of the material to digest, the options for digestate reuse and the recovery of the methane produced are major considerations substantially influencing the role of AD within cascade configurations.

Cassava bioethanol production in Colombia has to be approached with major caution acknowledging that the promotion of single product bioenergy production can be detrimental in terms of energy, GHG and water implications. This study shows how system design determines sustainability outcomes, the recovery of the energy contained in by-products being a crucial consideration.

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1 INTRODUCTION

Cassava is a tropical root crop mainly grown in Africa, Asia and Latin America. It is the forth staple food in the world after rice, wheat and maize being a basic component of the diet of a billion people (FAO 2004). Because it takes at least 8 months of warm weather to produce a harvestable root, cassava is mostly grown in tropical regions. In Latin America, about 19% of the world's cassava production takes place in about 16% of the world's cassava cultivated area (Ceballos 2002).

Traditionally, cassava is cultivated by small-scale farmers who use it as a food crop. However, cassava is also used as animal fodder, for industrial production of starch, gums, adhesives, and it is considered an attractive crop for the production of ethanol. In Colombia cassava main use has been domestic consumption (70.5%), other uses being fresh animal feed (18.4%), dry cassava for concentrated feed (4.1%), bitter starch (2.2%) and sweet starch (1.8%) (Balcazar and Mansilla 2004).

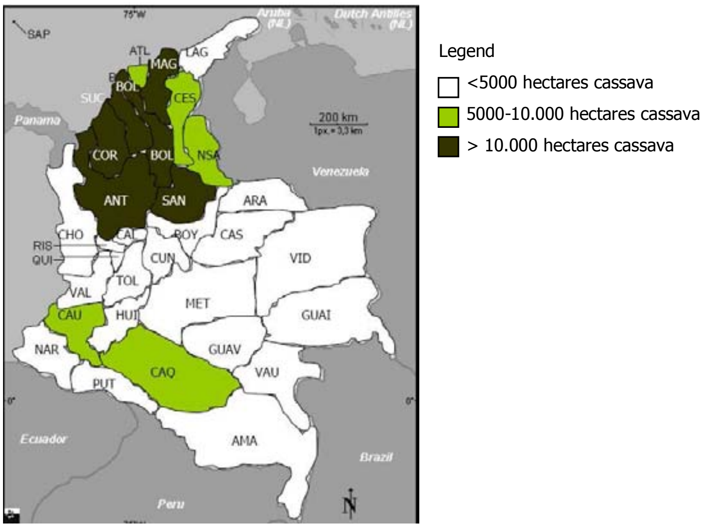


Figure 7.1 Cassava production in Colombia (Adapted from(Bajes Mora 1998))

The production of cassava in Colombia amounted to 2 million tons in 2005 equivalent to 8% of the total agricultural production of the country and 5% of Colombia's total agricultural land. An average yield of 11 ton ha^{-1} was reported for 2005 (IICA). Cassava is cultivated under various climates and soils, but the majority (about 70%) is cultivated in the northern coastal provinces (Figure 7.1).

Due to the fact that Colombia's most fertile and flat areas are used for the production of sugarcane and other crops destined for industrial use or export, food crops like cassava are generally grown on the Andean hillsides (Sonder et al. 2001). Whereas cassava traditionally has been planted by small farmers, having less than 5 ha of cassava per farm, and mostly intercropped with maize and yams, more recently, larger plantation-style plantings of more than 10 hectares of cassava per farm have been started in response to a sharp increase in demand from cassava processors (Gottret et al. 2002; Hillocks et al. 2002).

Since 2001, the Colombian government has been promoting biofuels through different laws and reforms. It established a 10% volume blend of bioethanol with gasoline in the main urban centers of the country along with the necessary technical requisites, tax exemptions and price regulations. The implementation of the law has been fast and as a result estimations by the Colombian Ministry of Agriculture and Rural Development indicate that by 2020, about 3.8

million liters ethanol will be produced per day as compared to the 900 thousand liters produced in 2006 (MADR 2006). The previous means that about 400 thousand has of land will be dedicated to ethanol production in 2020 vs. 40 thousand in 2006.

Cassava in Colombia has the second largest theoretical ethanol production potential per hectare if compared to other potential crops. In addition, other advantages of the crop have boosted its popularity as an ethanol feedstock, including its ability to grow well under marginal conditions where few other crops can survive, its tolerance to extreme soil pH, and, its resistance to the most important diseases and pests. Furthermore, cassava is a relatively labor intensive crop which makes it attractive to employment generation, an objective of the Colombian government. Because of the previous, cassava based bio-ethanol is expected to become an important provider of ethanol for the Colombian fuel mixing programme. Targets for bioethanol production from cassava mean about 280 thousand ha dedicated to ethanol in 2020 vs. 3 thousand in 2006. The bioethanol target for 2020 also means that the area needed for cassava production is expected to be 2.5 times that of 2005. As a result by 2020 cassava will be the major provider of bioethanol in the country after sugarcane (Henao Estrada 2008).

Because bioethanol is a renewable energy alternative to (partially) replace fossil fuels, many consider it to be a sustainable fuel. However, whether bio-ethanol is truly sustainable, is highly debated (Enguidanos et al. 2002; Niven 2005; Pimentel and Cecil 2007; Pimentel 2003; Shapouri et al. 2003) and depend upon several environmental, economic and societal considerations. Main issues of concern are the net energy balance of the whole production chain; the overall GHG mitigation potential; the competition for resources like land and water, which in turn potentially threaten food security and biodiversity; the large quantities of by-products generated which can lead to substantial pollution; the air pollutant emissions of ethanol enriched gasoline; the GHG emissions associated to land conversion, and numerous social and economic considerations including human rights, property rights, income distribution, governance and social structures, amongst others.

The incorporation of anaerobic digestion (AD) as a functional step into the production of bioethanol can potentially deliver valuable benefits that in turn could significantly improve the sustainability of bio-ethanol production (van Haandel 2005; Wilkie et al. 2000). The digestate coming from the AD process has high concentrations of nutrients and can be used as a fertiliser. The biogas, a mixture of methane, carbon dioxide and other trace gases, can be used as an energy source directly, or converted to electricity and heat, which in turn can be used in the bio-ethanol production process.

So far no detailed analysis of the environmental implications of bioethanol production from cassava in Colombia has been conducted. Furthermore, whereas other studies on bioethanol production from cassava in Thailand and China (Dai et al. 2006; Leng et al. 2008; Nguyen et al. 2007d) have included the anaerobic digestion step within the assumptions, no detailed description of the technological choices and analysis of its implications have been presented. The present study attempts to cover these knowledge gaps by analyzing the sustainability implications of bioethanol production from cassava in Colombia with two configurations, i.e. centralized and decentralized, emphasizing the role of AD to improve sustainability of currently planned bioethanol production systems.

The indicators covered by this study belong to the environmental sustainability compartment, including energy balance, GHG balance, water and land use. These indicators have been highlighted as most relevant in the analysis of environmental sustainability of bioenergy systems and/or biomass cascades (Cramer et al. 2007; Dornburg 2004; Pimentel and Cecil 2007; Searchinger 2008). In addition they are most likely to be impacted by the addition of the anaerobic digestion step (Baldassano and Soriano 2000; Borjesson and Berglund 2006; Borjesson and Berglund 2007; van Haandel 2005). Other aspects related to the social and economic performance of the studied systems are not undertaken as part of this study but are currently being researched as they are considered of upmost importance to make a definitive statement on the sustainability of bioethanol production from cassava in Colombia.

2 METHODOLOGY

2.1 Goal and scope definition

The goal of this study is to assess the energy performance, GHG emissions, water, and land use of alternative cassava cascades for bioethanol production working at different scales, highlighting the implications of having an anaerobic digestion step in the cascade. Complete balances were performed of cassava biomass, carbon, energy, nutrients and water following the flows and transformation processes in each system. The study comprises the raw materials production, their conversion into bioethanol and the end-use of by-products. Emphasis is placed in flows related to the cultivation and processing of the cassava, including relevant transportation. Carbon flows associated with the uptake and release of atmospheric carbon during photosynthesis and oxidation of the (intermediate) products as well as those related to change in land use are included in the calculations. N_2O emissions from fertilization are also covered. Flows related to the construction of the facilities and transport of the fuels for final use are not included because of the difficulty in their quantification plus their claimed minor contribution to ethanol energy balances(Shapouri et al. 2003). The systems boundary, main process units and flows are presented in Figure 7.2. For comparability of results the functional unit is the production of 100,000 liters fuel ethanol per day, which is about 6% of the expected ethanol production from cassava in Colombia for the year 2020.

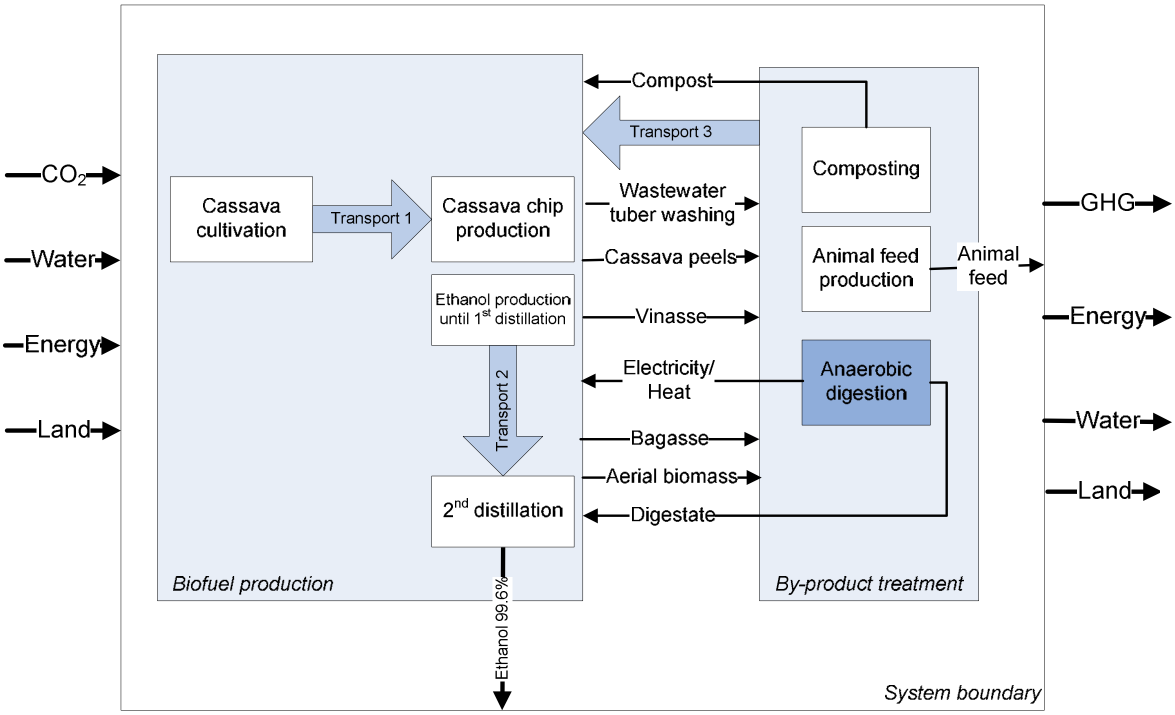


Figure 7.2 Overview of main elements in the systems studied
The division in ethanol distillation only takes places in decentralized systems

2.2 Data collection and validation

At the time this study was performed there were no cassava based bio-ethanol factories in operation in Colombia, therefore the definition and quantification of the systems are based on field visits, expert interviews, literature study and experimental results. Information on the amount and composition of by-products was obtained by running the ethanol production process at lab scale at the International Centre for Tropical Agriculture (CIAT) in Palmira, Colombia. The information was cross-validated with literature information on amounts and quality of by-products from cassava (Cereda and Takahashi 1996; Howeler 2001; Klinsukont et al. 1991; Wilkie et al. 2000). Information on the energy consumption of the ethanol production was obtained from expert interviews according to current design of the facilities, such information was cross validated with literature values (Dai et al. 2006; Leng et al. 2008; Nguyen et al. 2007a). Use of different fossil fuels was foreseen as part of the different systems. Direct energy consumption was calculated based on the Low Heating Value (LHV) as proposed by IPCC (1996). The values are specific for Colombia as reported by local scientific authorities (ACCEFYN 2003). Indirect energy was calculated as a percentage of the direct energy used, using values reported by Patzek (2004) and deCarvalho Macedo (2004). Data on GHG emissions from fossil fuels was obtained from the conversion of relevant activity rates to their emission equivalents using emission factors specific for Colombia calculated by local authorities following IPCC guidelines (ACCEFYN 1990; ACCEFYN 2003; UPME 2004). Energy content and emissions related to electricity coming from the grid are specific for Colombia where 75-80% of the electricity consumed is generated from hydropower. Energy and GHG emissions associated with agricultural inputs was obtained from different sources

(Fluck 1992; Kongshaug 1998; Maraseni et al. 2007) (Refer to Appendix 7.1, Tables A7.1.1 and A7.1.2 for energy and emission factors).

2.3 Systems definition

Four different cassava based bioenergy cascades are evaluated in this study. These systems were chosen to reflect current practices of cassava cultivation and current trends in cassava bioethanol production in Colombia in which two main types of systems are being implemented. These systems differ mainly in the centralization or not of production and processing band also show differences in the variety of cassava being cultivated and the regions were they are being promoted. In order to simplify the notation and guide the reader systems are called centralized (CS) and decentralized (DS). For each type of system an scenario without and with the anaerobic technology was defined. In the scenarios were AD is not implemented an alternative use of the by-products was defined for comparison purposes. In total four systems are analyzed, i.e. centralized bioethanol production without biogas production (CS), centralized bioethanol production with biogas production (CS+AD), decentralized bioethanol production without biogas production (DS), and a decentralized bioethanol production with biogas production (DS+AD) (See Table 7.1).

Table 7.1 Main systems characteristics

System	CS	CS+AD	DS	DS+AD
Location	Meta		Bolivar, Atlantic coast	
Average production size	6-8 ha		2 ha	
Soil quality	Sandy/clay loam. Extremely acid Low nutrient content		Sandy/clay loam. Rich in P and K	
Temperature	30°C		27°C	
Rainfall	2652 mm		1057mm	
Cassava variety	Roja (CM 4574-7)		MTAI8 (Rayong 60)	
Ethanol production	Centralized Single facility		Decentralized Separate facilities	
Type of energy used ethanol	Diesel (electricity) Fuel oil (distillation)		Hydropower (electricity) Coal (distillation)	
Byproducts treatment	Composting	Anaerobic digestion	Feed production	Anaerobic digestion
Labor	Mostly mechanized		Mainly manual	

CS: Centralized System; DS: Decentralized System; AD: Anaerobic Digestion

The centralized systems have been defined as fully mechanized ethanol production systems where both ethanol production and crop production are concentrated in one place. On the contrary, decentralized systems are defined as a number of small ethanol production and crop production sites, where operations are traditionally performed using a high level of manual labour as is the case in Colombia. In such systems, the distilling and dehydration steps do not take place in the same location. That is, at the microplant the ethanol is fermented and distilled until it reaches a 50% concentration and subsequently the resulting EtOH-water mixture is transported to be further distilled and dehydrated to 99.6% EtOH at a central factory processing the output of 50 microplants. This central step reduces investment costs and aids in standardizing the quality of the final product. Two out of four systems make use of anaerobic digestion technology (biogas production) to treat the by-products generated during the bio-ethanol production process including wastewater from root washing, peels, bagasse, vinasse and leaves/stalks. The other two systems make use of other technologies to add value to the by-products, i.e. composting and animal feed production for the centralized and decentralized system, respectively.

The centralized systems are projected in the department Meta in the eastern plains region (Llanos Orientales) of Colombia. Nowadays, the cassava cultivated area in the region accounts for 11.5% of the total in the country and the production is concentrated in medium size farmers (6-8 ha) (Gottret et al. 2002). Average temperature in Meta is 30°C, the average amount of rainfall is 2652 mm per year (IDEAM). Eastern plains are considered to have a good potential for centralized cassava cultivation because land is relatively flat and cassava is one of the few crops that can resist the prevalent extremely acid soil conditions. The nutrient content of the soil is very low, especially in P, K, Ca and Mg. (Howeler and Cadavid 1990). The cassava plantations are assumed to be located near the city of Puerto Lopez which is the actual location of the large scale cassava bioethanol plant currently under construction by the firm Petrotesting. Since connection to the grid is not in place in this system, the required electricity is coming from burning diesel and so is the energy needed for distillation. The decentralized systems are projected in the department Bolivar, in the Atlantic Coast. This region is selected for its tradition of small scale farming and cassava cultivation. In addition, the Colombian government has selected this region to establish several cassava based bio-ethanol plants. Bolivar is a hilly region with a hot climate, with an average temperature of 27ºC and an average rainfall of 1057 mm per year (IDEAM). Soils are sandy or clay loam and rich in P and K (Howeler and Cadavid 1990). It is estimated that the average area used for the cultivation of cassava per farmer in Bolivar is 2 ha (Hogevorst 2007). Electricity is available from the grid and coal is used for the distillation as verified on site.

In line with the different regional characteristics, two different cassava varieties are used in the centralized and decentralized systems. Roja (CM 4574-7) is used in the centralized systems and MTAI8 (Rayong 60) in the decentralized ones, having an average yield of 25.7 and 28.5 ton fresh roots ha^{-1} yr^{-1}, respectively. Both varieties have relatively high ethanol yields per tonne of fresh roots and are already used for industrial production in the selected regions. In addition, Roja is cultivated for the production of ethanol by Petrotesting, and MTAI8 has been identified as the best cassava variety for industrial applications in the Atlantic Coast (Ceballos et al. 2002).

3 PROCESS UNITS AND QUANTIFICATION OF SYSTEMS FLOWS

The analysis of the systems was performed considering the process units: cassava crop production, cassava chip production, ethanol production and by-products treatment, i.e, composting, animal feed or anaerobic digestion.

3.1 Cassava cultivation

It involves the activities of ploughing, planting, fertilizer application, pesticide application, irrigation, harvesting and packing activities within the farm. In the centralized systems, all processes are mechanised as far as possible. Planting of cassava is done semi-mechanically; tractors are used to prepare the soil. A mixture of chemical and biological herbicides and pesticides are used for weeding and disease control. As assessed in the field in average 5.5 kg ha^{-1} of herbicides (Alacror, Diuron and Glyphosate) are applied in the centralized system, whereas 2.8 kg ha^{-1} (Alacron and Diuron) are applied in the decentralized one. Despite these very high amounts applied, additional manual weeding is required. Pesticides are applied in the centralized and decentralized systems at 4.3 and 0.7 kg ha^{-1}, respectively (Arriaga Sierra 2008). Cassava harvesting is done using mechanical diggers to pull out the roots. Based on Ospina et al (2002b) the fuel consumption per hectare is calculated from the power specifications of the machinery a two-row model cassava planter PC-20 of 65 HP and a cassava harvester P900 of 90 HP, and considering an average fuel consumption of 2.75 HP-hrs per litre diesel fuel. The tractors operate at an efficiency of 6.2 and 6.5 ha d^{-1}.
Cassava production in the decentralized systems is performed in a traditional way as is the case in Bolivar department in Colombia. Planting, weeding and harvesting are all done manually by the farm owners and their relatives (field interviews). Herbicides are applied but pesticides are not. Irrigation is disregarded considering that the minimal amount of water required for cassava cultivation, i.e. 555 mm per year (Caraballo and Velasquez 2000), is exceeded by the rainfall in both regions. Fertilizer requirements are taken from the recommendations of Howeler and Cadavid (1990) considering differences per region. The amount applied was compared to the nutrient extraction as calculated following the study by Howeler (2001) and compensated in the case of potassium, as in the long-term its application is important to avoid depletion. The growing period is assumed to be 365 days, one crop rotation takes place once every three years and 10% of the fresh root harvest is assumed to be lost due to diseases. The labour requirements per hectare of cassava are based on Cock (1985), Perez Crespo (1991) and Ospina (2002c). A summary of inputs used in cassava cultivation is provided in Appendix 7.2, Table A7.2.1.

3.2 Cassava chips production.

Fresh cassava needs to be processed into cassava chips to prevent deterioration. Once cassava is harvested it is transported to the drying facility, where it is weighted, washed, peeled, chopped and dried. Per liter EtOH 8 liters of water are used for root washing (Klinsukont et al. 1991). Drying can be done naturally, taking advantage of solar energy, or artificially, which allows for the operation to be independent of seasonality. In the decentralized systems cassava is dried using solar energy. A sun drying plant covering an area of 2000 m^2 and working 20 weeks per year, can process 1440 ton fresh cassava. It requires a chopping machine working with a diesel motor of 6 kW and 1 man-day working force per ton fresh cassava (Ospina et al. 2002a). In the centralized systems cassava is dried artificially, by a system operating on diesel, consuming 121 l ton^{-1} fresh cassava. In addition, electricity is used for other operations at 78 kWh ton^{-1} fresh cassava (Arriaga Sierra 2008) (See Appendix 7.2, Table A7.2.2).

3.3 Ethanol production

The ethanol production starts by mixing the cassava chips with water and blending them into a homogenous pulp. Each tonne of cassava chips is mixed with 8 litres of water before entering the fermentation tanks. After the mixing and blending, the pulp passes through the hydrolysis and fermentation tanks. The fermented cassava pulp is filtered and the remaining liquid is then purified to 99.6% in distillation and dehydration units. In the centralized system, ethanol is produced in a modern facility using diesel for electricity generation. For the distillation, steam is produced using diesel fuel. In the decentralized system, the ethanol production process follows the design performed by researchers in CIAT, which aims to minimize investment costs, give opportunities to small holders and adapt to the available local resources. Electricity used is coming from the grid and distillation is performed using coal as fuel source. Energy inputs in ethanol conversion were assessed on site and are provided in Appendix 7.2, Table A7.2.3. Emissions associated to the material inputs into ethanol production other than fossil fuels were considered to be negligible (de Carvalho Macedo et al. 2004).

3.4 Transport

Three types of transport are considered, i.e. the transport of crop material, i.e. roots and aerial biomass, from the fields to the ethanol factories, the transport of crude ethanol from the microplants to the distillery in the case of the decentralized systems, and that from the distillery to the fields when compost or digestate is transported back. The average distance from the fields to the ethanol factory in the centralized system was calculated to be 50 km by assuming a circular distribution of the area needed to produce the 100,000 l EtOH d^{-1}. The cassava is transported in trucks with 10 ton capacity. In the decentralized system 113 farmers having an average farm size of 2 ha are needed to supply each microplant with the demanded cassava. They transport their product also in trucks with 10 ton capacity, the average distance to the microplant being 6 km. Partially distilled ethanol is transported 40 km from the microplant to the central dehydration facility by means of trucks having 6000 litres capacity. In all cases, diesel is used for transportation at an average efficiency of 2,5 km l^{-1} (Fluck 1992). The return of the trucks back to the fields requires the doubling of the calculated distance. When relevant that extra energy is used for the transport of soil amendments, i.e. compost or solid digestate.

3.5 By-products characterization and treatment options

Five main by-products are generated in the systems defined, namely cassava aerial biomass, i.e. leaves, petioles and part of stalks, wastewater from root washing, peels, bagasse and vinasse. It is assumed that 87.5% of the stalks produced are available, the rest being used as planting material for the next season (Lopez 2002). This biomass along with the leaves and petioles could be either left in the soil or given added value by means of a by-product recovery technology. Quantification and characterization of the flows is presented in Table 7.2. Amount and composition of peels, bagasse and vinasse were calculated according to laboratory experiments and cross-validated with pilot and full-scale facilities found in literature (Dai et al. 2006; Klinsukont et al. 1991; Nguyen et al. 2007b; Wilkie et al. 2000). Cassava peels and bagasse are produced in similar amounts, showing also similar solids and organic content. Vinasse is produced in great quantities 12-15 liters per liter EtOH (Klinsukont et al. 1991; Wilkie et al. 2000) and is a crucial residue to treat due to its undesirable characteristics for direct reuse or disposal including offensive high organic load and odor. The wastewater from root washing is also a substantial amount with a low Chemical Oxygen Demand (COD) and nutrient content (Klinsukont et al. 1991), which can be treated either for reuse at the ethanol facility or for final disposal in the environment.

Different alternatives could be used to add value to cassava by-products, in this study alternatives chosen for the systems without AD correspond with the current situation in Colombia. Figure 7.3 summarizes the conversion routes considered. In the CS composting of the main by-products of the ethanol industry is considered, whereas aerial biomass is left on the land. In the DS conversion of main by-products for animal feed production is implemented. In CS+AD all residues including aerial biomass are added value whereas in the DS+AD, aerial biomass is left on the land as it is produced in a different location from where ethanol conversion is taking place. In all cases, wastewater flows not treated by AD are assumed to be treated by aerobic treatment to meet discharge standards using intermediate rate trickling filters allowing concomitant nitrification with a loading of 0.24-0.48 kg BOD m^{-3} d^{-1} at 5 kW 10^{-3} m^{-3} (Tchobanoglous et al. 2004).

Table 7.2 By-product amount and characterization

By-product	Roja						MTAI8					
	Amount	TS	COD	N	P	K	Amount	TS	COD	N	P	K
	[ton ton EtOH^{-1}]	[g g^{-1}]	[g g^{-1}]	[mg g^{-1}]	[mg g^{-1}]	[mg g^{-1}]	[ton ton EtOH^{-1}]	[g g^{-1}]	[g g^{-1}]	[mg g^{-1}]	[mg g^{-1}]	[mg g^{-1}]
Peels [a]	1.8	0.300	0.252	0.00	0.02	0.13	1.5	0.300	0.252	0.00	0.02	0.13
Bagasse [b]	1.3	0.250	0.278	1.11	0.18	1.44	1.3	0.250	0.224	1.11	0.18	1.44
Vinasse [c]	17.5	0.027	0.029				17.5	0.027	0.025			
WWt [d]	11.5	0.001	0.001	0	0	0	9.4	0.001	0.001	0	0	0
Leaves, petioles, stalks [e]	4.3	0.20	0.26	7.2	0.7	4.4	3.09	0.20	0.26	7.2	0.7	4.4

[a] The quantity, TS and COD content of peels was determined in laboratory experiments. Nutrient composition from (Cereda and Takahashi 1996).

[b] The quantity, TS and COD content of bagasse was determined in laboratory experiments. Nutrient composition calculated from nutrient mass balance.

[c] The quantity of vinasse was assumed as13 l per lEtOH according to (Klinsukont et al. 1991; Wilkie et al. 2000). TS and COD content of vinasse were determined in laboratory experiments and concentrations recalculated considering the total amount. Nutrient composition calculated from nutrient mass balance.

[d] Amount and composition of wastewater from root washing according to (Klinsukont et al. 1991).

[e] The quantity of leaves, stalks and petioles was calculated considering the harvest index of the varieties selected and corresponds to the amount of this by-product after subtraction of 12.5% seed material. Nutrient composition was calculated according to the nutrient extraction expected from the cassava yield as reported by Howeler (Howeler 2001). TS and COD content were adapted from (Cereda and Takahashi 1996).

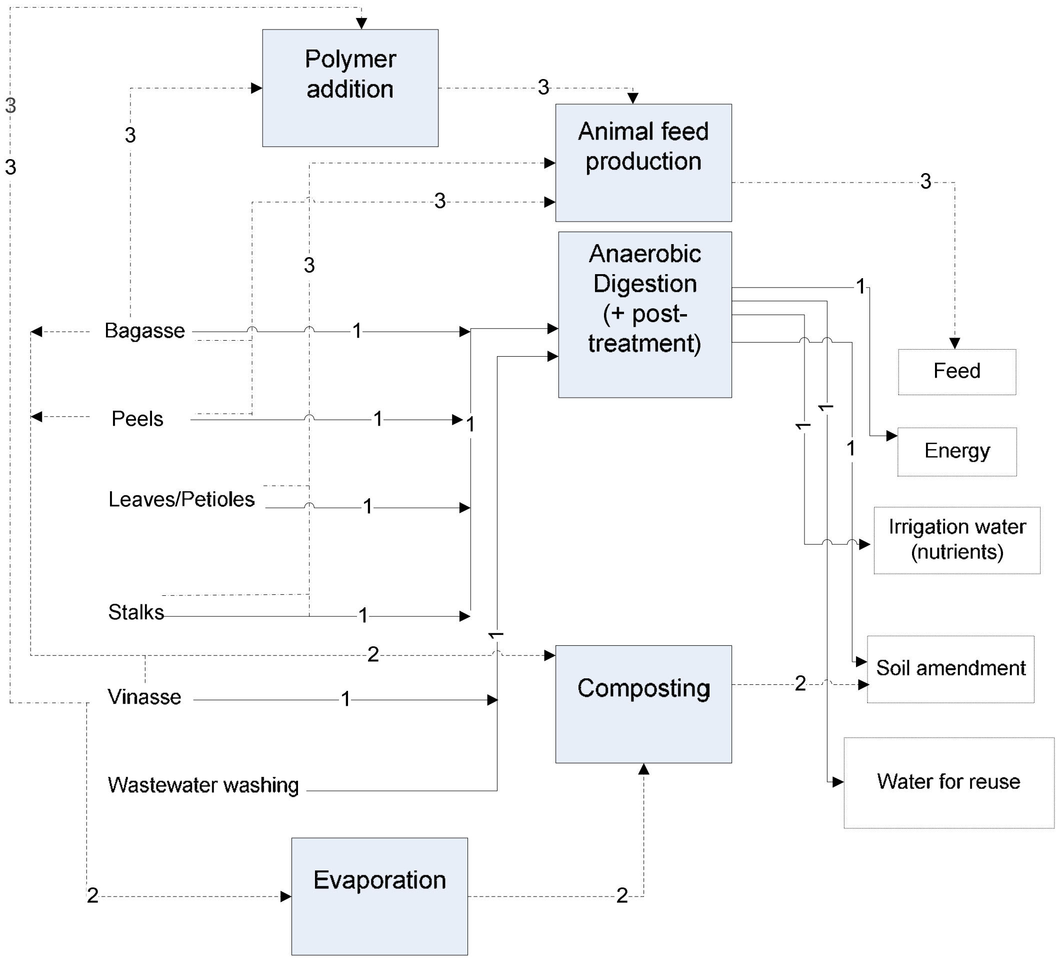


Figure 7.3 Overview of by-product treatment routes for residues from cassava ethanol production. The number refers to alternative conversion routes: 1. Anaerobic digestion, 2. Composting, 3. Animal feed

3.5.1 Composting

In the CS, peels, bagasse and vinasse are composted. Composting was chosen as the alternative for this system as it is current practice in sugarcane based bioethanol producing facilities in Colombia. Vinasse is evaporated to 35% Total Solids (TS) content in order to be incorporated into the composting process. The efficiency of the composting process in converting COD is assumed to be 50%, 4 ton of water being removed per ton COD converted. In addition it is considered that 35% of the N in the input is lost in the process, nitrous oxide emissions (N_2O as $CO_{2\ eq}$) being 5% of total N emitted (Borjesson and Berglund 2007). Energy consumption in the process is calculated considering 0.4 kg steam needed per liter water evaporated (Maroulis and Zaravacos 2003) and 32.5 kWh used per ton compost produced (Baldassano and Soriano 2000). GHG emissions are calculated as the sum of carbon dioxide, (CO_2) and methane (CH_4) as $CO_{2\ eq}$, which together accounts for the total amount of COD removed by the composting process. CH_4 emissions are calculated as 0.35% of the emissions of CO_2. The remaining COD corresponds to the long-term emissions of CO_2, which are calculated stochiometrically as 44/32 grams carbon dioxide produced per gram COD removed (Borjesson and Berglund 2007).

3.5.2 Animal feed production

In the DS residues from ethanol production are used for producing animal feed. Conventional animal feed production is an energy intensive process requiring about the same amount of energy as that for the ethanol process (Drosg et al. 2008). In Colombia decision makers are considering an approach in which the vinasse is pre-treated by adding polymers to concentrate it to 10%TS, afterwards centrifugation is applied to reach 25%TS. Nutritional blocks and nutritional salt bags for ruminant animals requiring 45% and 30% weight basis of concentrated vinasse and weighting 25 and 40 kg are produced, respectively. In both cases additional root flour, leaves and stalks flour, urea and mineral salts are required. A basket centrifuge using 105 kWh t TS^{-1} direct electricity and working at 90% solids efficiency is assumed to be used and polymers are dosed at 3 g per kg^{-1}. The energy demand for the preparation of the feed is 1.3 and 1.1 kWh per block/bag, respectively (Arriaga Sierra 2008).

3.5.3 Anaerobic digestion

The methane output for all digesters is calculated based on the COD content and the volume of the input flows considering a theoretical methane yield of 0.35 m^3 CH_4 kg^{-1} COD. The biogas is turned into electricity and heat using a combined heat/power-CHP unit expected to operate at 90% efficiency, i.e. 35% electricity and 55% heat (de Mes et al. 2003). Calculations of the net energy output were made considering electricity and heat produced are partially used in the anaerobic digestion facility for pretreatment, digester operation and digestate dewatering.
For the purpose of calculating electricity use and emissions different operations are included as part of the AD facility (Figure 7.4). For materials with more than 10%TS, pretreatment is needed for substrate homogenization, 33 MJ per ton by-product inputare coonsidered (Berglund and Borjesson 2006). The use of electricity for the operation of the biogas plant is assumed to be 66 MJ per ton raw material (Berglund and Borjesson 2006) considering in all cases single stage continuous mesophilic digesters managing more than 10 ton raw material per year. Due to constant high temperature conditions in the studied areas and the high temperature of vinasse, i.e. 72-80 ^{o}C (Nandy et al. 2002), it is not required to use the produced heat from the CHP for the operation of the digester at mesophilic temperature. Reuse of the digestate is a crucial consideration when evaluating the incorporation of anaerobic digestion in the bioenergy chain. Digestate offers many advantages as part of an agricultural production system including the high content of mineralized nutrients, its content of organic matter which can help improve soil structure and its reported weed suppression capacity (Berglund 2006; Lehtomaki and Bjornsson 2006). Nonetheless energy needs associated with its transportation and spreading, and the emissions taking place during storage and spreading also need to be considered.

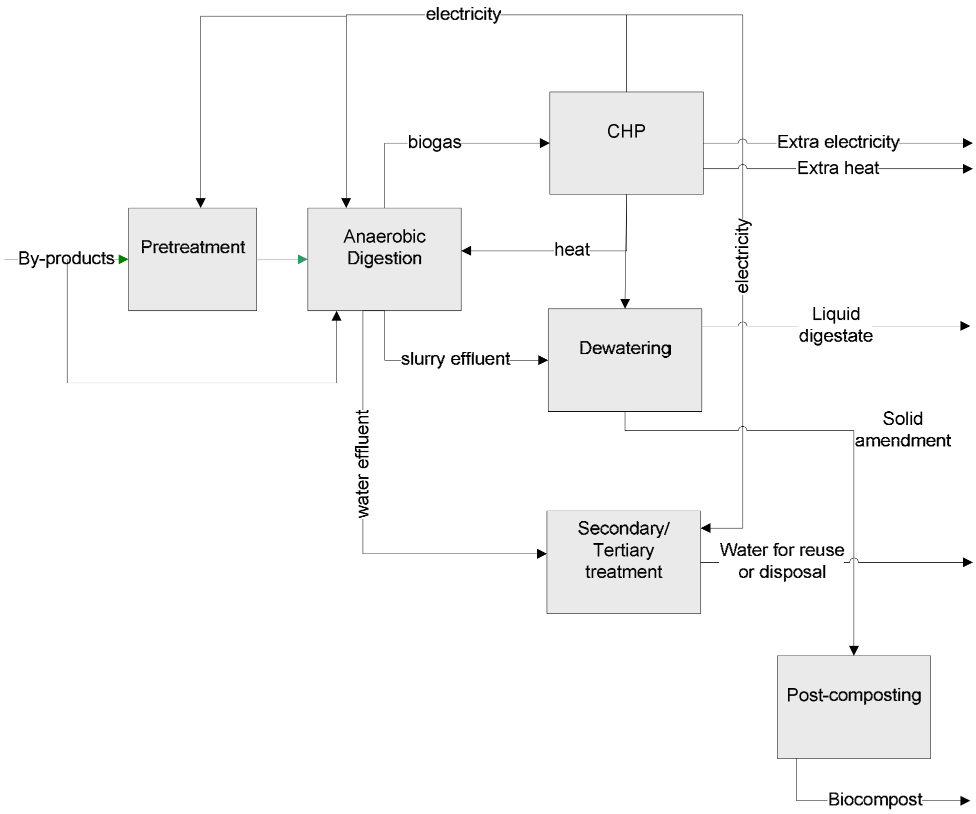


Figure 7.4 Operations included as part of AD facility
Sub-units are included in the analysis according to the type of facility evaluated

The amount of digestate produced is calculated by assuming a 25% TS removal during the AD process (De Vries 2007) whereas its COD content is calculated by subtracting the COD used for methane generation from the total influent. All nutrients coming from the input materials are preserved in the digestate. Based on previous research on digestate properties of manure-maize codigestion it is assumed that 50%, 50%, 70% and 30% of COD, N, P and K, respectively, remain in the liquid digestate (De Vries 2007). Energy needs for dewatering are assumed to be 10 MJ kg^{-1}, while requirements for loading and spreading were calculated to be 0.63 and 0.52 liters diesel per ton liquid and solid digestate, respectively (Berglund and Borjesson 2006). The energy need for transport of the digestate were calculated following the same assumptions previously outlined (See 3.4). When relevant, the (empty) transport provided by the trucks delivering cassava to the ethanol facilities was substrated from the energy demand for digestate transport differentiating liquid and solid flows.

Following the previous considerations, AD scenarios were designed (Table 7.3) departing from the amount and characteristics of the different flows, i.e. TS, nutrient content and energy potential, and the possibilities for reuse of the digestate. The alternative digestion of leaves and stalks was considered as well as the separate treatment of wastewater from washing tubers. In all alternatives digestate is dewatered, the resulting solids are composted for further stabilization and the liquid digestate is left for reuse in cassava fields.

Table 7.3 Evaluation of anaerobic treatment options considering different available flows and characteristics

	CS+AD						DS+AD							
	Alt1	Alt 2		Alt 3		Alt 4	Alt 1		Alt 2			Alt3		
Input	All	Bg, Pls, AeBio	Vi, WWt	Vi, Bg, Pls, AeBio	W Wt	All excl. AeBio	Vm, Bg, Pls,W Wt	Vd	Vi, WWt	Bg, Pls	Vd	Vi, WWt	Bg, Pls, AeBio	Vd
AD treatm	PF/C STR	PF	UASB +TF	PF/CS TR	TF	PF	PF	UASB + TF	UASB+ TF	PF	UASB+ TF	UASB+ TF	PF	UASB+ TF
Digestate end use	Fld	Fld	Et. plt	Fld	Et. plt	Fld	Fld	Dch	Et.plt	Fld	Dch	Et. plt	Fld	Dch
Digestate handling	Dw	Dw	n.a.	Dw	n.a.	Dw	Dw	n.a.	n.a.	Dw	n.a.	n.a.	Dw	n.a.
End product	Lq.Fr , Sl.A	Lq.Fr, Sl.A	Wr	Lq.Fr, Sl.A	Wr	Lq.Fr, Sl.A	Lq.Fr, Sl.A	W	Wr	Lq.Fr, Sl.A	W	Wr	Lq.Fr, Sl.A	W
Q [m^3 d^{-1}]	2,865	579	1,377	1,956	909	2,526	2,237	100	4,980	1,277	100	466	1,277	100
COD [ton COD d^{-1}]	193	152	39	191	1.0	104	86	2.5	125	32	1.7	117	32	1.7
BEO-AD [TJ yr^{-1}][a]	633	629		629		340	291		288			498		
NEO-AD [TJ yr^{-1}][b]	492	**539**		458		227	226		198			**364**		
E Eff [%Brut energy]	78%	86%		73%		67%	78%		69%			73%		

Bg: Bagasse; Pls: Peels; AeBio: Aerial Biomass; Vi: Vinasse total: Vm: Vinasse microplant; Vd: Vinasse distillery; WWt: Wastewater washing tubers; PF: Plug Flow or CSTR: Continuously Stirred Reactor; UASB: Upflow Anaerobic Blanket; TF: Trickling Filter; Fld: Field; Et.plt: Ethanol plant; Dch: Discharge; Dw: Dewatering; Lq.Fr: Liquid fertilizer; Sl.A: Solid Amendment; Wr: Water for reuse; W: water; BEO-AD: Brut Energy Output AD units; NEO-AD: Net Energy Output AD units; E Eff: Energy Efficiency.

[a] Considering 90% COD conversion efficiency into methane and 90% conversion efficiency from the CHP unit (35% electricity, 55% heat). Based on (Cuzin et al. 1992; Mai 2006; van Haandel 2005).

[b] Brut energy output minus energy consumed in transport of raw materials, pretreatment of materials with TS>10%, electricity use by the digester, digestate dewatering, solid digestate composting, digestate transport, digestate spreading and aerobic post-treatment of the effluents. Assumptions explained in the text.

In the CS+AD, four alternatives are evaluated. In alternative 1 and 2 the digestion of all by-products is considered, including leaves and stalks, meaning that extra transport and handling is required. Whereas in alternative 1 all flows are codigested, in alternative 2 solid and liquid flows are digested apart. In alternative 3 the digestion of all by-products except wastewater from washing tubers is assumed. In this case such wastewater is aerobically treated to meet reuse standards within the ethanol plant. Alternative 4 considers the digestion of all by-products except aerial biomass. In the DS+AD three alternatives are considered. In alternative 1 wastewater from washing tubers, peel, bagasse and vinasse are mixed and digested together. Alternatives 2 and 3 consider the separate digestion of solid and liquid by products in the microplant. In the first case only industrial by-products are treated whereas alternative 3 considers as well the digestion of leaves and stalks. In all alternatives the extra vinasse produced in the central distillation-dehydration facility is treated in a UASB reactor and further polished by means of trickling filters.

As shown in Figure 7.5, among the different sub-units considered in the alternatives evaluated, the electricity for running the biogas plant is the most energy consuming activity, followed by the energy needed for aerobic polishing of the wastewater when necessary. From comparing CS1 and CS4, it is concluded that it is energy profitable to use the aerial biomass for biogas production and subsequently disposing it in land as the double amount of energy can be produced. Further, when comparing CS2 and CS3 it is noticed that it is profitable to separately digest the solid and liquid flows and to avoid the anaerobic treatment of the water from tuber washing due to its low energy content. Hence alternative CS2 is selected as it is the one producing more energy, the most energy efficient and the one providing more possibilities for water reuse in the ethanol facility. In the case of the decentralized systems, alternative 3 considering the digestion of aerial biomass is also the most energy profitable, its energy efficiency being comparable to that of digesting only the industrial by-products.

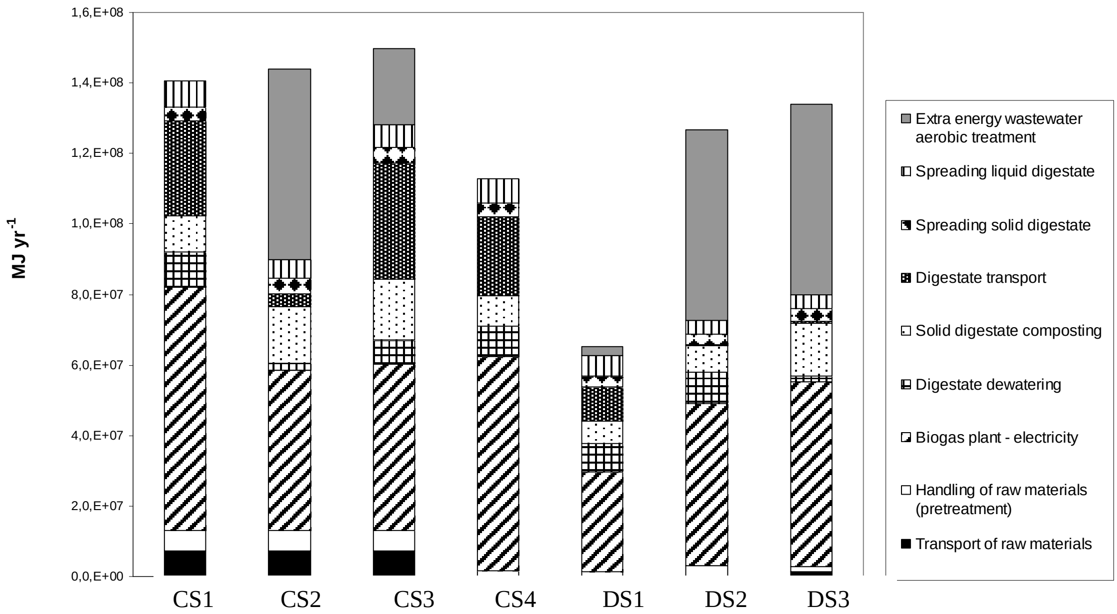


Figure 7.5 Energy used by the different anaerobic digestion alternatives evaluated

4 SYSTEMS PERFORMANCE

4.1 Energy performance

The energy performance was evaluated by means of different indicators, i.e. Energy Balance ($E_{balance}$), Net Energy Ratio (NER), the Net Renewable Energy Ratio (NRER) and Energy Efficiency (EEff). Whereas the $E_{balance}$ indicates the net energy produced by the systems after subtraction of all energy inputs, the NER reports such value as a fraction of the total energy input. Similarly to the NER, the NRER reports a ratio but referring only to the non-renewable energy input as an estimation of the fossil replacement value of the system. The EEff represents the percentage of energy from the cassava plant (root and leaves and stacks) that is recovered in 'usable' energy (ethanol, electricity, heat), being a measurement of resource use efficiency (See Equations 7.1- 7.4).

$$E_{balance} = E_{output} - E_{input} \tag{7.1}$$

$$NER = \frac{E_{output} - E_{input}}{E_{input}} \tag{7.2}$$

$$NRER = \frac{E_{output} - E_{fossilinput}}{E_{fossilinput}} \tag{7.3}$$

$$BEff = \frac{E_{output}}{E_{input\ biomass}} \tag{7.4}$$

As can be seen in Table 7.4, the CS demands 1809 TJ yr^{-1} extra energy, meaning a negative NER of -0.70, which means 70% more energy than produced is needed for such a system. The conversion of by-products by AD notoriously improves the energy balance leading to 10% more energy produced than demanded in the CS+AD. In both centralized systems ethanol conversion is the most energy consuming step. In the CS ethanol conversion demands 70% of the total energy input, whereas only 6% of the energy is demanded by cassava cultivation, and an extra 23% of the energy demand goes to the composting process in the system without AD. Among ethanol conversion activities, artificial drying of the cassava represents most of the direct energy input, i.e. 74% in the CS. Given this large contribution, alternatives are explored in the sensitivity analysis. In the CS+AD the energy output from AD is able to cover most ethanol conversion energy inputs. In addition savings are produced due to the avoidance of composting giving a total difference in the energy balance of 1,899 TJ yr^{-1}.

Decentralized systems are substantially less energy intensive as compared to the centralized ones due to the use of solar drying instead or the artificial process. The system with AD has a positive $E_{balance}$ producing 637 TJ yr^{-1}. The system producing animal feed appears approximately energy neutral, i.e. -82 TJ yr^{-1}, nevertheless in this system the energy needed for the additives to the animal feed has not been considered therefore indirect energy inputs are expected to be higher.

The NRER in all systems is equal or very similar to the NER, meaning that energy inputs other than fossil fuels make an insignificant contribution to the systems.

Table 7.4 Energy performance of alternative bioethanol production systems from cassava

		CS TJ yr^{-1}	CS+AD TJ yr^{-1}	DS TJ yr^{-1}	DS+AD TJ yr^{-1}
Cassava cultivation	Direct	44	59	3	12
	Indirect	120	117	141	43
	Total	163	166	144	55
Ethanol conversion	Direct	1515	403	550	39
	Indirect	300	80	19	2
	Total	1,816	482	569	40
Transport (cassava and ethanol)	Direct	15	15	29	29
	Indirect	3	3	6	6
	Total	18	18	35	35
Byproduct conversion	Direct	470	0	52	0
	Indirect	111	0	49	0
	Total	581	0	101	0
Byproduct transport	Direct	0	11	1	2
	Indirect	0	2	0	0
	Total	0	13	2	1
Total Direct Energy In		2,044	488	637	81
Total Indirect Energy In		534	210	214	50
TOTAL ENERGY INPUT		**2,578**	**698**	**851**	**131**
Ethanol		769	769	769	769
Extra electricity (from AD)		0	0	0	0
Extra heat (from AD)		0	0	0	0
TOTAL ENERGY OUTPUT		**769**	**769**	**769**	**769**
$E_{balance}$	*TJ yr^{-1}*	*-1,809*	*90*	*-82*	*637*
NER		*-0.70*	*0.13*	*-0.10*	*4.85*
NRER		*-0.69*	*0.13*	*0.05*	*4.85*

Figure 7.6 presents the results of the energy efficiency analysis. Around 75% of the energy fixated by the cassava plant is found in the cassava tubers, the rest is present in the aerial biomass. In the CS only 48% of the energy in cassava is recovered as useful energy output, i.e. ethanol, whereas in the CS+AD a total energy efficiency of 92% is found, 41% of the energy being recovered in the form of electricity and heat from the biogas produced. In the DS also 48% of the energy is recovered as usable energy, i.e. ethanol. The energy contained in the leaves and stalks, peels, vinasse and bagasse is recovered as animal feed, for an extra 40% of the total energy input. Similarly in the DS+AD a total 89% of the energy in cassava is recovered as usable energy.

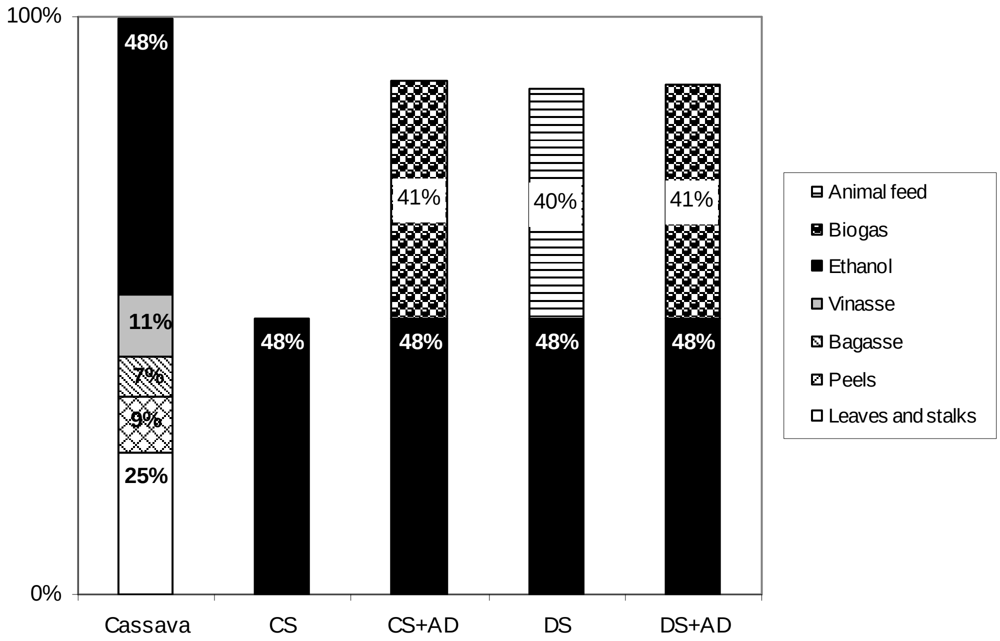


Figure 7.6 Energy efficiency of alternative bioethanol production systems from cassava

4.2 GHG balance

GHG emissions were calculated and grouped in four categories. In category 1 flows related to the uptake of atmospheric carbon by photosynthesis and release by oxidation in the different industrial processes and final use of the products was included, as well as flows related to the application of nitrogen in fertilizers and amendments in cassava cultivation. In category 2 all flows related to the use of fossil fuels in the different processes were accounted whereas category 3 corresponds to an estimation of emissions related to change in land use. Category 4 corresponds to the avoided emissions due to the positive energy outcomes of the systems studied, i.e. ethanol, electricity and heat. The total GHG balance is calculated following equation 7.5.

$$GHG = GHG_{cat1} + GHG_{cat2} + GHG_{cat3} - GHG_{cat4} \qquad (7.5)$$

As can be seen in Table 7.5, the GHG emissions from category 2, i.e. ethanol production, are the most important in all systems except in the DS+AD where the emissions from category 1 are most prominent. In all cases net emissions from category 1 exceed the carbon capture by the cassava plant meaning GHG emissions of 33,345 to 63,372 tCO_{2eq} yr^{-1} for the different systems, equivalent to 18%, 31%, 40% and 78% of total emissions in the CS, CS+AD, DS and DS+AD, respectively. The reason for the higher prominence of category 1 emissions in the decentralized systems is the lower amount of fixated CO_2 due to the lower yield of the cassava variety as compared to the centralized ones.

Table 7.5 Direct and indirect GHG emissions of alternative bioethanol production systems from cassava

	CS $tCO_{2eq}\ yr^{-1}$	**CS+AD** $tCO_{2eq}\ yr^{-1}$	**DS** $tCO_{2eq}\ yr^{-1}$	**DS+AD** $tCO_{2eq}\ yr^{-1}$
Uptake of atmospheric carbon [a]	-196,733	-196,733	-167,469	-167,469
Released during ethanol production [b]	55,093	55,093	55,093	55,093
Released during composting [c]	25,760	0	0	0
Remaining in compost [d]	25,760	0	8,201	0
Released from WWT [e]	566	566	4,163	648
Released from biodigestion and burning [f]	0	62,835	0	50,061
Released during biogas production [g]	0	10,291	0	8,008
Remaining in digestate [d]	0	6,845	1	5,395
Release during ethanol combustion [h]	54,593	54,593	54,593	54,593
Remaining in leaves and stalks [i]	32,279	3,431	2,468	2,468
Remaining in animal feed [e]	0	0	65,502	0
N_2O fertilizer [j]	16,191	15,786	34,788	10,535
N_2O and CH_4 compost [k]	12,065	0	0	0
N_2O digestate [j]	7,934	20,639	0	25,162
N_2O leaves and stalks [j]	18,877	0	0	18,877
Total Category 1	**52,383**	**33,345**	**57,339**	**63,372**
Use of fossil fuels in cassava cultivation	7,733	8,580	495	495
Use of fossil fuels cassava transport	1,362	2,017	2,100	2,100
Use of fossil fuels ethanol production	155,764	41,379	55,726	3,704
Use of fossil fuels for crude ethanol transport	0	0	564	564
Use of fossil fuels extra transport and spreading digestate	0	1,487	0	814
Use of fossil fuels for compost	46,055	0	0	0
Use of fossil fuels for animal feed production	0	0	516	0
Use of fossil fuels for wastewater treatment	5,817	2,968	12,470	0
Use of fossil fuels in inputs for cassava production (fertilizer, pesticides, herbicides)	7,077	7,305	6,419	1,983
Use of fossil fuels in inputs for animal feed production [l]	0	0	41	0
Total Category 2 [m]	**223,808**	**63,375**	**78,330**	**9,659**
Total Category 3: Emissions from change in land use [n]	**10,551**	**10,551**	**8,201**	**8,201**
Avoided emissions from gasoline [o]	**91,992**	**91,992**	**91,992**	**91,992**
Avoided emissions from electricity (extra AD) [p]	**0**	**0**	**0**	**0**
Avoided emissions from heat (extra AD) [p]	**0**	**0**	**0**	**0**
Total Category 4	**91,992**	**91,992**	**91,992**	**91,992**
TOTAL	**194,751**	**15,639**	**51,878**	**10,760**
Total ($kgCO_{2\,eq}\ l_{EtOH}^{-1}$)	**5.3**	**0.4**	**1.4**	**-0.3**

[a] Calculated considering the physic-chemical composition of cassava root and leaves as reported by (Cereda and Takahashi 1996), its COD equivalence (Angelidaki and Sanders 2004) and the Total Organic Carbon-COD ratio (TOC/COD) for the different physico-chemical compounds. An average 0.15 gC g VS^{-1} and 0.09 gC g VS^{-1} was calculated for cassava root and cassava leaves (also used for stalks), respectively. When considering the total VS harvested per Ha per year a total CO_2 fixation of 18.4 and 19.5 tCO_2 $ha^{-1}yr^{-1}$ is calculated for the Roja and MTAI8 varieties, which is in agreement with total Carbon contained in the different cassava (by)products of the studied systems.
[b] Stochiometrically per mol ethanol one mol of CO_2 is produced per mol ethanol.
[c] Considering 50% of COD is lost during the composting process and assuming a TOC/COD ratio of 2.67 (for carbohydrates) and molar weight ratio CO_2/C of 44/12.
[d] Corresponds to the emissions equivalent to the COD remaining in compost or digestate assuming a TOC/COD ratio of 2.67 and molar weight ratio CO_2/C of 44/12. Whereas in the case of compost and digestate this COD is expected to be (partly) incorporated as organic matter in soil, it is included in calculations to close the mass balance related to photosynthesis and oxidation of cassava (by) products. All emissions are assumed to be in the form of CO_2.
[e] CO_2 emitted calculated from COD content following similar calculation as explained in d.
[f] Biogas is assumed to have a 40% content of CO_2 . In addition, stochiometrically one mol methane is combusted into one mol CO_2 in the CHP unit.
[g] Includes unintended methane emissions during biogas production, i.e 2% of total CH_4 (Borjesson and Berglund 2007), emissions from digestate storage(5% COD in liquid digestate) and emissions from post-composting of solid digestate (15% COD in solid digestate).
[h] Stochiometrically 2 moles CO_2 are produced per mol EtOH combusted.
[i] Corresponds to the theoretical CO_2 emissions from remaining COD in leaves and stalks. Calculated considering a TOC/COD ratio of 2.67 (for carbohydrates) and molar weight ratio CO_2/C of 44/12. Whereas this COD is expected to be (partly) incorporated as organic matter in soil, it is included in calculations to close the mass balance related to photosynthesis and oxidation of cassava (by) products.
[j] Calculated considering 1.25% of applied N escapes into the air as N_2O, 30% of applied N escapes from the field and 2.5% of that quantity is converted to N_2O in the surface water, 10% of applied N escapes as NH_3 into the air and 1% of that becomes N_2O. Hence a total 2.10% of applied N is lost as N_2O. From (Patzek 2004) according to EIA 2002 and IPCC 1996.
[k] Total N emissions are 35% of N content in original material, N_2O calculated as 5% of total N emissions. CH_4 emissions from the applied compost are accounted, assuming 0.35% of the total emissions of carbon dioxide(Borjesson and Berglund 2007).
[l] Calculated based on a polymer consumption of 300g per liter vinasse and an assumed emission of 0.8 metric ton carbon equivalent per ton mined bentonite, value corresponding to clay mining according to EPA (EPA 2006)
[m] Calculated considering fossil fuel consumption and emissions as reported in the text and summarized in appendixes 7.1 and 7.2.
[n] According to Searchinger et al (Searchinger 2008), 20.5 and 224.5 ton C per ha grassland and tropical forest are emitted when changing their use, respectively. A modest 25% land use change from land assumed to be previously natural grassland was considered in these calculations; they were amortized over 30 years.
[o] Avoided emissions were calculated according to the direct and indirect emissions for the gasoline that the ethanol produced is replacing.
[p] Since all outputs from the AD process are used within the system, no additional emissions are avoided for exporting the products.

The impact of land use change in the GHG balance of the systems is accounted in category 3 by assuming a conservative change in land use of 25% of land originally used as natural grassland. Those emissions are calculated and amortized over 30 years using emission data reported by Searchinger et al (2008). The contribution of such emissions represents only 4-10% of total emissions in the studied systems. Overall, the CS delivers net GHG emissions of 5.3 $kgCO_{2\ eq}$ l_{EtOH}^{-1} while the DS emits 1.4 $kgCO_{2eq}$ l_{EtOH}^{-1}. Notoriously both systems with AD present an almost even GHG balance the CS+AD emitting 0.4 $kgCO_{2\ eq}$ $l_{EtOH}^{-1}$and the DS+AD producing GHG savings of -0.3 $kgCO_{2\ eq}$ l_{EtOH}^{-1}. Systems taking advantage of the energy in the biogas produce only 20 and 36% of the emissions of the systems without AD during the ethanol production process, such difference being the result of the origin of the energy used, i.e. coal and diesel instead of biogas.

4.3 Water balance

According to our estimation, 27-31 liter water per liter ethanol are used in the cassava production systems without accounting the water needed for steam production. Of these, 21-23 liter are provided for the ethanol production itself , i.e. water for washing tubers and pulping, whereas the rest is incorporated in the cassava biomass. Hence the net water use without accounting the rain water incorporated in biomass is 776,340-836,839 ton yr^{-1}.
The water incorporated in the systems leaves them in different flows as shown in Figure 7.7.

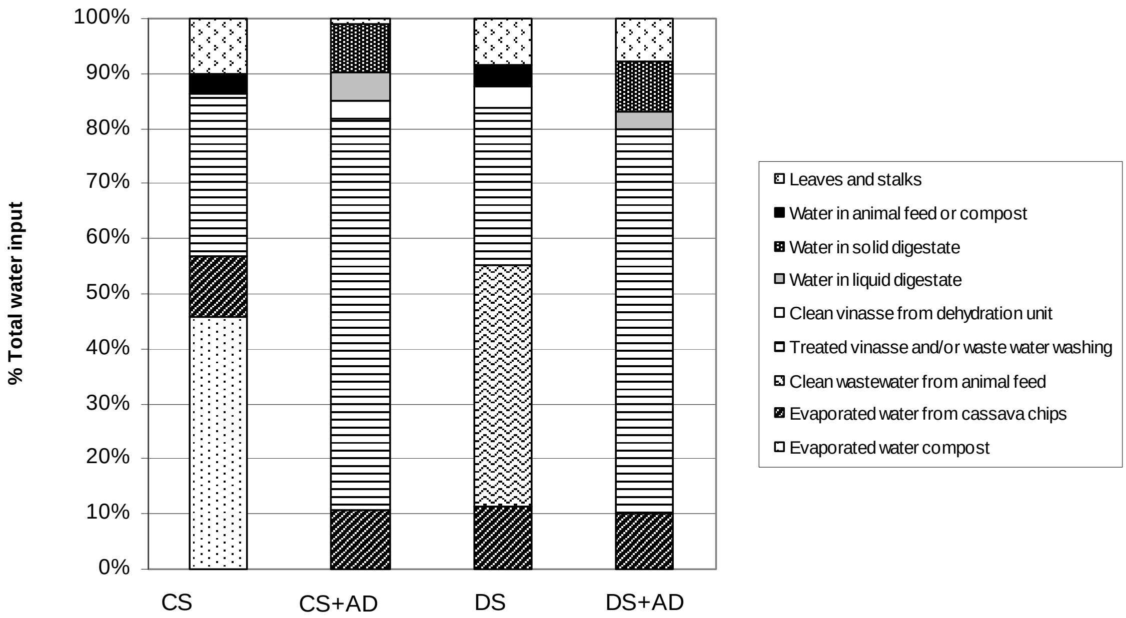


Figure 7.7 Distribution of water inputs in alternative bioethanol production systems from cassava

In the Figure 100% refers to the total water incorporated in the systems, including the water present in the cassava tuber and that used in ethanol production, i.e. 1,002,579 and 1,116,088 ton yr^{-1} for the decentralized and centralized systems, respectively.

Water used in cleaning the cassava tubers constitutes about 30% of the water output, and in all systems is treated and reused within the ethanol process providing important water savings. If considering total water input and reuse, all systems except the CS would show substantial water savings. In the CS, 46% of the water incorporated in the system is evaporated during the compost production process. Similarly, 44% of the water output leaving the DS is coming from the animal feed production. This flow could be in principle reused within the ethanol process. In the AD systems, the digestion of by-products generates a substantial amount of water savings, i.e. 70% of the total water output. In addition, 12 and 14% of the water input is left in the digestate which needs to be adequately disposed in the fields to take advantage of the nutrients they contain.

Overall, significant differences in net water use result in the different systems, the CS being a highly water demanding one, i.e. 505,502 ton yr^{-1}, in contrast with a water saving system in the CS+AD, i.e.-19,193 ton yr^{-1}. In both DS systems similar water consumption results equivalent to 10% of that in the CS, i.e. 53,756 - 55,784 ton yr^{-1}.

4.4 Land use and soil quality

Including rotation and losses 13,092-16,844 ha yr^{-1} of arable land are needed in the centralized and decentralized systems. 60% of this amount corresponds to the area cultivated with cassava. The previous means that per ton ethanol produced 0.27-0.35 ha need to be cultivated with cassava. Solar drying of the cassava chips as performed in the decentralized systems also demand land, about 1.4 m^2 ton^{-1} fresh cassava (Ospina et al. 2002a). However when calculating the total amount of land required for the decentralized systems, such amount is insignificant as compared to the cultivated land, i.e.31 ha yr^{-1}.

With regards to soil quality, three of the different scenarios analyzed consider the return of by-products to land in the form of compost or solid/liquid digestate which implies the reincorporation of valuable material for building up soil structure and fertilization. When such by-products are applied on the land cultivated with cassava, an application ratio of 6, 14 and 16 ton ha^{-1} yr^{-1} compost/solid digestate results in the CS, CS+AD and DS+AD respectively, whereas in the case of liquid digestate 6 and 5 ton ha^{-1} yr^{-1} are to be applied in the CS+AD and DS+AD, respectively.

Total nutrient recirculation achieved in the different systems is 37%, 42%, -181% and 73% for the CS, CS+AD, DS and DS+AD, respectively. In the CS+AD, AD allows for higher recirculation of nutrients as composting is limited by the nitrogen losses during the process. The animal feed scenario implies the export of the nutrients outside the system boundaries including those present in the leaves for which fertilization is originally not provided. The previous yields as a result a negative nutrient balance.

4.5 Overall performance of the studied systems

Table 7.6 presents the comparison of the energy, GHG, water and land use performance of the four systems analyzed.

Table 7.6 Overall comparison of alternative bioethanol production systems from cassava

		CS	CS+AD	DS	DS+AD
Energy balance	TJ yr^{-1}	-1809	90	-82	637
GHG	kg CO_{2eq} l_{EtOH}^{-1}	5.3	0.4	1.4	-0.3
Water [b]	ton yr^{-1}	505,502	-19,193	55,784	53,756
Land	ha yr^{-1}	16,844	16,844	13,123	13,123

[a] Value in brackets corresponds to the calculated GHG balance when extra heat is reused for cassava chip drying.
[b] Calculated as total water use (washing tubers and pulping) minus water reuse within the ethanol industry (from recirculation of water for washing tubers and the treated vinasse in the dehydration facility). Water reuse on the fields not accounted as irrigation is not demanded.

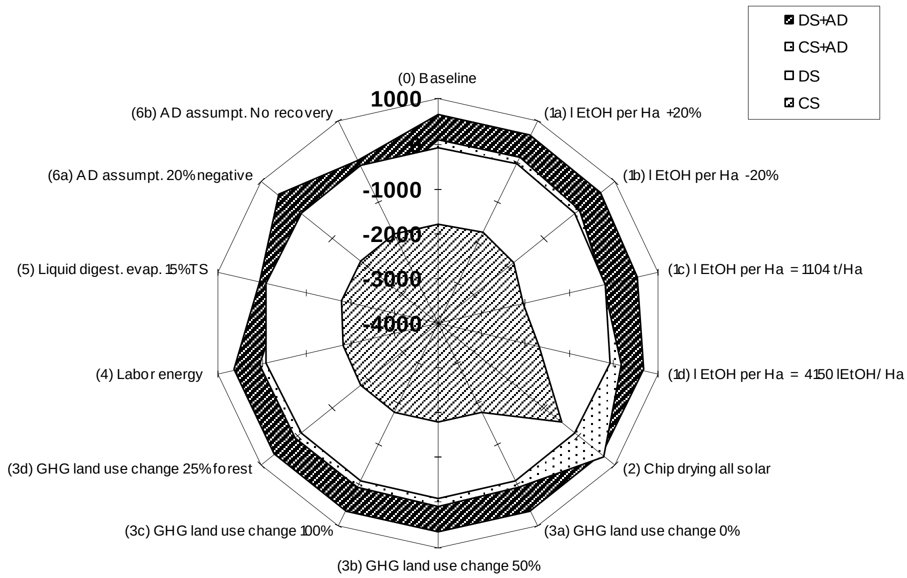
Centralized systems show a poorer energy and GHG performance as compared to decentralized ones. In addition, systems with AD show a better energy balance and GHG performance as compared to their counterpart. The CS+AD produce water savings, whereas the two decentralized systems consume limited amounts of water. All systems behave similarly in terms of land use, the variability shown related to the yield of the two cassava varieties studied. Nutrient recirculation as performed in the AD systems in the form of concentrated effluents made possible savings of 42-73% in imported fertilizers.

5 DISCUSSION

5.1 Sensitivity analysis

From the results of this study it is clear that some of the main assumptions have a considerable impact in the performance of the systems. Therefore within the sensitivity analysis some of them are revisited. The previous further clarifies the effect of systems design and the implications of main assumed activity rates and energy and emission factors in the overall performance. The following are the revised assumptions and their impact in the output of the different systems. In Figure 7.8 the output of the sensitivity analysis is graphically exposed.

(1) *Assumed EtOH yield per ha*. Ethanol yields considered in this study were 3,648 and 4,694 l_{EtOH} ha^{-1} cassava, for the centralized and decentralized systems, respectively. These yields were calculated from the average yields expected from the cassava varieties and their ethanol yield under laboratory conditions. It is however important to recognize that there are significant yield fluctuations among trials of the same variety in different regions. For example trials of MTAI8 in years 2001-2002 fluctuated between 17.9-45.7 ton ha^{-1}. In addition average cassava yield in Colombia is much lower than figures assumed, i.e. 11.04 ton ha^{-1} in 2005 (IICA). As can be observed in Figure 7.8, when assuming the average Colombian cassava yield, the CS and DS systems diminish their net energy output by 267-296 TJ yr^{-1} and 120-133 TJ yr^{-1}, respectively. As a result the CS+AD will deliver a negative energy balance. Assuming the same ethanol yield per ha in all systems, i.e. 4,150 l EtOH ha^{-1} calculated from an average yield of 27.1 ton cassava root ha^{-1} and an average ethanol yield of 192 l EtOH ton^{-1} peeled root, does not affect the classification of the systems in terms of their energy outcome as the decentralized systems are still favored over the centralized ones. The GHG balance is less sensitive to changes in yield assumptions, however decreasing the yield to average Colombian yield will cause the systems with AD turn into net emitters of GHG, i.e. 2.4 and 1 kg CO_{2eq} l_{EtOH}^{-1} for the CS+AD and DS+AD, respectively. Land use is majorly affected by the cassava yield, a low yield of 11 ton cassava tuber ha^{-1} means more than 100% increment in land use in all systems.



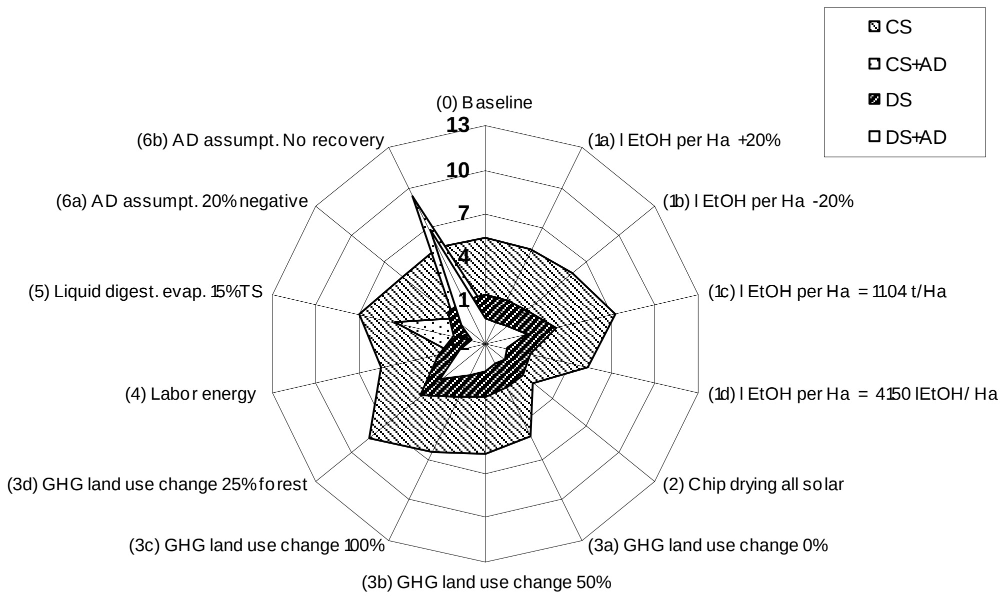


Figure 7.8 Sensitivity analysis of alternative scenarios of cassava bioethanol production (Above $E_{balance}$ in TJ yr^{-1} and below $GHG_{balance}$ in kg CO_{2eq} per l_{EtOH}^{-1})

(2) *Use of solar energy for drying cassava chips in the CS systems.* It was clear from the energy balance results that the artificial drying process has considerable negative consequences in the energy performance of the CS. In Colombia infrastructure for cassava drying is currently only (partially) available in the decentralized systems.

However, if considering that the land use demand is mimnimum as compared to the area needed for cultivation, in principle solar drying could also be feasible in the centralized systems. Revisiting this assumption is important for comparison purposes as studies conducted for other countries have also assumed the use of solar drying (Dai et al. 2006; Leng et al. 2008; Nguyen and Gheewala 2008; Nguyen et al. 2007c). If the centralized system would make use of solar drying, the CS+AD will deliver the best energy outcome, i.e. $E_{balance}$ of 732 TJ yr^{-1}, whereas the net energy losses in the CS will become only 27% of the ones originally assessed. The systems with AD will still be the only ones delivering a positive energy outcome producing 3.4 and 4.8 times more energy than demanded in the centralized and decentralized system, respectively. Such positive outcome will also influence the GHG emissions, the CS would produce only 2.2 vs. 6.8 kg CO_{2eq} l_{EtOH}^{-1} previously assessed, whereas the CS+AD will generate net GHG emissions savings, i.e.-1.7 kg CO_{2eq} l_{EtOH}^{-1}.

(3) *GHG emissions from land use change.* The total area of cassava cultivated in Colombia in 2005 was 180,600 ha (IICA) and only 3,000 ha were dedicated to ethanol production in 2006 (Henao Estrada 2008). Current targets for ethanol production from cassava in 2010 are of 110,000 ha cultivated and if considering losses and rotation the total amount of land needed would be in the order of 183,700 ha. This is almost the same total amount of land dedicated to cassava cultivation in 2005 which in its majority was dedicated to direct food consumption. Hence, if trying to minimize competition with food, land should come from other sources. In this study it has been assumed that 25% of the land used is coming from natural grassland; however this could very well be an underestimation. If land used for cassava cultivation would come entirely from natural pastureland extra GHG of 0.87 and 0.67 kg CO_{2eq} l_{EtOH}^{-1} would be produced in the centralized and decentralized systems, respectively. However if only 25% of the total area would replace tropical forest instead of natural pastureland, emissions will increment in 2.88 and 2.24 kg CO_{2eq} l_{EtOH}^{-1} in the centralized and decentralized systems, respectively. These figures show the importance of properly assessing the land use changes and their origin.

(4) *Labor accountability within energy balance.* Previous studies (Dai et al. 2006; Nguyen et al. 2007d; Pimentel 2003) have considered the energy embodied in human labor as part of the energy inputs into the ethanol systems. Although the addition of this flow is contestable because of its different nature in relation to other energy flows, it is a fact that energy embedded in labor is also indirectly coming from fossil energy. An energy consumption of 2.3 MJ h^{-1} is frequently used for this type of calculations although higher energy consumption has also been calculated, i.e.12.1 MJ h^{-1} in (Nguyen et al. 2007d). In this study total energy coming from labor is substantially different in centralized and decentralized systems; hence an estimation of the extra energy invested in labor is revised considering 2.3 MJ h^{-1}energy consumption. The inclusion of labor within the energy calculations means extra 13 and 17 TJ yr^{-1} energy use in the centralized and decentralized systems, respectively, meaning between 1 and 20% differences in the $E_{balance}$.

(5) *Liquid digestate reuse and irrigation water demand.* It is important to recognize that the positive performance of the AD systems is closely related to choice for separate treatment of liquid and solids flows. Apart from allowing substantial water reuse within the ethanol industry such choice implies considerable energy savings and avoidance of GHG emissions related to liquid digestate handling. An alternative to the separate digestion could be the mixed digestion of liquid and solid flows. However as there is a limited possibility for irrigation due to the limited water demand of cassava and the rainfall availability in the studied regions, the (partial) evaporation of this digestate to concentrate the nutrients for agricultural reuse could be required. To exemplify the implications of such a choice, calculations were performed for a system digesting all cassava by-products assuming centrifugation followed by liquid digestate evaporation from 5 to 15%TS with an energy use of 0.93 GJ ton^{-1} water evaporated (Maroulis and Zaravacos 2003). Following the previous assumptions extra 605 TJ yr^{-1} will be demanded which is equivalent to the total energy use of the CS+AD.

(6) *Change in assumptions anaerobic digestion.* Energy recovery from AD can fluctuate depending on system design and operation. In addition, due to the high global warming potential of CH_4, assumptions on its losses are critical. A negative AD scenario of 20% more emissions, 20% more energy use and 70% energy recovery was evaluated. The change in assumptions substantially impact the outcome of the systems, the NER substantially diminishes i.e. from 0.10 to -0.07 and from 4.85 to 2.17, in the CS+AD and DS+AD, respectively. The GHG balance is less affected emissions in the AD systems increasing by 0.3-0.4 $kgCO_{2\,eq}\ l_{EtOH}^{-1}$. The overall outcome will remain the same, the AD systems being more energy and GHG profitable than their counter parts. Further the extreme case of no methane recovery is considered. In such a case, the $E_{balance}$ will diminish by 884 and 609 TJ yr^{-1} in the CS+AD and DS+AD, respectively, whereas GHG emissions will increment in 8.9 and 7.1 kg $CO_{2eq}\ l_{EtOH}^{-1}$. The benefits of AD will remain in terms of energy as the technology is significantly less energy consuming than the compost scenario and slightly better than the animal feed production processes. However GHG emissions will significantly outweigh the other scenarios, making the AD option not appealing anymore.

5.2 About the role of AD in cassava bioethanol production

So far the importance of AD for the environmental sustainability of bioethanol systems has been verified n terms of energy, GHG, water and land use. Further the improvement in biomass resource use efficiency has been highlighted (See Figure 7.6).

The energy produced by AD is enough to compensate for the energy demanded by the ethanol production process. In fact when solar drying is assumed for all systems, both systems having AD would produce 3.4 and 4.8 times more energy than consumed and will be net GHG sinks in contrast with the alternative systems.

The role of AD in this study was clarified by defining different design options and further contesting assumptions within the sensitivity analysis. The energy outcome of the AD process has been shown to be always positive, i.e. above 67% for the different configurations (Table

7.3). The importance of the type of influent to be digested is evident. On one hand, the energy benefits of digesting aerial biomass outweighed the energy costs of its loading and spreading by more than double in the centralized system. On the other hand, the digestion of the diluted wastewater from root washing showed to decrease the net energy output of the system. The type of influent to digest need to be carefully examined not only in view of its energy content but also taking into account the reuse of the digestate output. Ethanol production is a water intensive activity producing major wastewater effluents, whereas cassava is not a water demanding crop, building water loops within the system is therefore a major challenge. The (partial) evaporation of the digestate showed to outweigh the energy output of the CS+AD making evident the susceptibility of the AD system to digestate considerations. Although the outcome of the systems involving AD showed to be sensitive to the 20% change in assumptions, overall it did not influence the conclusions about the performance of the studied systems. The digestion of cassava by-products without energy and GHG recovery would be extremely negative for the GHG balance, however AD options will remain more energy profitable than the animal feed or composting ones.

Overall, our findings support previous studies suggesting that the performance of biogas system are highly dependent on systems design (Berglund 2006; Borjesson and Berglund 2006) especially relevant are the amounts and liquid content of the substrates, the recovery of the biogas and the digestate final disposal all of them in close relation to the imposed characteristics of the original industrial and agricultural system. The Energy and GHG balance will remain advantageous as long as digestate can be safely disposed and methane produced is effectively recovered and used.

5.3 Comparison with previous studies

The Net Energy Value (NEV) of ethanol is defined as the energy output per liter ethanol produced. NEV of ethanol production from cassava in China and Thailand has been calculated as 7.48 and 9.95 MJ l_{EtOH}^{-1} considering the partial anaerobic digestion of residues (Dai et al. 2006; Nguyen et al. 2007d). In this study, NEV as indicator has not been employed since it refers to a specific product output, i.e. ethanol, whereas our focus is on the overall system performance. Nonetheless, for comparison purposes such value is now calculated for the different systems. Our results deliver values between -49.6 and +17.5 MJ l_{EtOH}^{-1}. The assumption of artificial cassava drying explains the major part of the differences. If assuming solar drying for all systems and appropriate allocation for the system producing animal feed, as in the mentioned studies, -13.21, 1.9, 8.4 and 17.5 MJ l_{EtOH}^{-1} are produced by the CS, CS+AD, DS and DS+AD, respectively (See allocation procedure in Appendix 7.3). Remaining differences among studies are related to the inclusion of labor, transport, denaturing and distribution of ethanol, and the digestion of only vinasses in the studies for China and Thailand. Other differences could come from the quantification of indirect energy use and the type and origin of the primary energy in the different countries.

In their review on bio-ethanol environmental assessments, von Blottniz and Curran (2007) conclude that there is now strong evidence that all bioethanol production is mildly to strongly beneficial from a GHG emission and fossil fuel conservation perspective. The present study however highlights the susceptibility of this kind of research to systems boundaries and assumptions, in line with findings of previous studies of bioethanol production from different crops. Shapouri (2003) presented a comparison of different studies in which the NEV of corn ethanol fluctuates between -9.35 and 8.53 MJ l_{EtOH}^{-1} and the differences were related to assumptions about yields, ethanol conversion technologies, fertilizer manufacturing efficiency, fertilizer application rates, co product evaluation, and the number of energy inputs included in the calculations. Bastianoni and Marchettini (1996) also show differences in energy and GHG outcomes of three case studies of bioethanol produced from sugarcane in different regions.

5.4 Other sustainability considerations

This study constitutes a first approximation to the environmental sustainability of cassava bioethanol production in Colombia and the role of AD. It is desirable to refine it once bioethanol plants are in operation and to extend it to the quantification and analysis of other environmental impacts like erosion, acidification, eutrophication, and human and ecological toxicity, aspects which have been highlighted by different authors (Niven 2005; Sonder et al. 2001; von Blottnitz and Curran 2007). Furthermore, the amount of cassava required to meet the target of bioethanol production from cassava in Colombia imply risks which need to be carefully addressed to avoid threatening of food security and biodiversity. Social and economic implications of the systems are not undertaken as part of this study but are currently being addressed as they are crucial to make a definitive statement on the sustainability of bioethanol production from cassava in Colombia.

6 Conclusions

Bioethanol production from cassava in Colombia has been shown to deliver substantially different environmental outcomes depending on the system design. The Energy balance, GHG balance and water balances fluctuated in a wide range, i.e.-1809 to 637 TJ yr^{-1}, -0.3-5.3 kg CO_{2eq} l_{EtOH}^{-1}, -19193-505,502 ton yr^{-1}, respectively. Further, it was made evident that without the energy recovery provided by AD, the production of bioethanol from cassava in Colombia is not sustainable from an energy and GHG perspective. In the centralized systems it is not desirable to implement artificial drying of cassava since it is an enormously energy consuming activity. The decentralized systems showed that both animal feed production and anaerobic digestion can be feasible from an energy and GHG balance perspective although benefits from AD will be remarkably higher.

The energy outcome of the AD process has been shown to be always greater than its energy input for the different configurations evaluated, i.e. above 67%. The energy and water content of the material to digest, the use of aerial biomass, the options for digestate reuse and the recovery of the methane produced are major considerations substantially influencing the role of AD within cascade configurations.

Cassava bioethanol production in Colombia and other countries has to be then approached with major caution; general conclusions are not desirable as they hide the substantial differences in outcome coming from the system design and context conditions. The analysis and design of bioethanol production has to be approached from a systems perspective in which by-products are added value in an energy rational way if the systems are to be called ‘renewable’ and beneficial from an ‘environmental’ perspective.

APPENDIX 7.1 ENERGY AND GHG EMISSION FACTORS

Table A7.1.1 Energy content, indirect energy and GHG emissions assumptions for fuels

	Energy content [a] [$MJ\ kg^{-1}$]	Indirect energy [b] [% direct energy]	Direct GHG emissions [c] [$kg\ CO_{2\ eq}\ MJ^{-1}$]	Indirect GHG emissions [$kg\ CO_{2\ eq}\ MJ^{-1}$]
Diesel	42.67	20%	0.07392	0.013 [d]
Gasoline	42.44	19%	0.07457	0.0001 [d]
Coal	25.23	1%	0.09725	0.012 [d]
Fuel oil	40.6	20%	0.07795	0.013 [d]
Natural gas	40.24	14%	0.05510	0.010 [d]
Electricity	n.a.	101% [e]	n.a.	0.133 [f]
Ethanol	26.7 [g]	n.a. [i]	0.071	n.a. [i]
Methane	49.92 [h]	n.a. [i]	n.a. [i]	n.a. [i]

n.a. not applicable

[a] The Low Heating Value or Net Caloric Value is used in all cases as proposed by IPCC (1996). Values are specific for Colombian case as reported by local scientific authorities (ACCEFYN 2003).

[b] Indirect energy refers to the percentage of the extra energy needed for the manufacturing of the fuel. With the exception of electricity, values from Patzek (2004) are used which consider the exergy of all natural resources consumed in all the steps of the production process of the fuels.

[c] Direct GHG emissions refer to emissions from fuel combustion. Values used are specific for Colombian case as calculated by local scientific authorities (ACCEFYN 2003) following IPCC methodology (IPCC 1996). For the calculation of the emission factors a λ value of 1.25 has been assumed for liquid fuels and 1.1 in the case of natural gas.

[d] Fugitive emission during the production, transport, refining and storage of petroleum, coal and natural gas in Colombia, calculated based on data reported in (ACCEFYN 1990).

[e] Calculated based on total electricity produced and total fossil energy used for electricity production in Colombia from (ACCEFYN 1990).

[f] Value specific for the Colombian case as calculated by the Colombian scientific authorities following international guidelines (UPME 2004).

[g] From (Patzek 2004).

[h] Value calculated considering the combustion energy of methane at 298 ^oK, i.e. 55.438 $kJ\ g^{-1}$ and its density, i.e. 0.65 $kg\ m^{-3}$. The value was further corrected to be expressed as LHV by assuming a 10% lower value related to the HHV (IPCC 1996).

[i] These values are calculated in detail for the scenarios analyzed in this study based on system configuration.

Table A7.1.2 Indirect energy and GHG emissions from agricultural inputs

	Indirect energy		Indirect GHG emissions [b]	
N	60 [a]	[$GJ\ ton\ N^{-1}$]	2.13 [d]	[$ton\ CO_{2eq}\ ton\ N^{-1}$]
P	4.2 [a]	[$GJ\ ton\ TSP^{-1}$]	0.28 [d]	[$ton\ CO_{2eq}\ ton\ TSP^{-1}$]
K	4.0 [a]	[$GJ\ ton\ KCl^{-1}$]	0.27 [d]	[$ton\ CO_{2eq}\ ton\ KCl^{-1}$]
Herbicide	274 [b]	[$GJ\ ton^{-1}$]	22.5 [e]	[$ton\ CO_{2eq}\ ton^{-1}$]
Pesticide	215 [c]	[$GJ\ ton^{-1}$]	24.2 [e]	[$ton\ CO_{2eq}\ ton^{-1}$]

[a] Energy consumption for manufacturing of fertilizers in Europe using old technology as reported by Kongshaug (1998).

[b] Average energy used in the manufacturing of Alaclor and Diuron (Fluck 1992).

[c] Average energy used in the manufacturing of different pesticides (Fluck 1992).

[d] GHG emissions during manufacturing of fertilizers in Europe using old technology as reported by Kongshaug (1998).

[e] From (Maraseni et al. 2007).

APPENDIX 7.2 ACTIVITY RATES DURING CASSAVA CULTIVATION AND PROCESSING

Table A7.2.1 Direct energy, material and labor inputs in cassava cultivation

Item	Unit	CS and CS+AD	DS and DA+AD
Fertilizer [a]			
N	[kg ha^{-1}]	70	100
P	[kg ha^{-1}]	60	0
K	[kg ha^{-1}]	75	50
Herbicide	[kg ha^{-1}]	5.5	2.8
Pesticide	[kg ha^{-1}]	4.3	0.7
Water (other than rainfall)	[kg ha^{-1}]	0	0
Total Labor	[Worker-days ha^{-1}]	71.5	108.5
Land preparation	[Worker-days ha^{-1}]	10	25
Planting	[Worker-days ha^{-1}]	0.5	9.5
Weeding	[Worker-days ha^{-1}]	47	44
Harvesting and packing	[Worker-days ha^{-1}]	14	30
Farm machinery [c]			
Land preparation	[l diesel ha^{-1}]	7.3	0
Fertilizer/pesticide application	[l diesel ha^{-1}]	7.3(*2)	7.3
Planting	[l diesel ha^{-1}]	25	0
Harvesting and packing	[l diesel ha^{-1}]	34	0

[a] (Howeler and Cadavid 1990) [b] Considering (Cock 1985) and (Ospina et al. 2002b) [c] Calculated based on specifications presented by Ospina et al (2002b) for a two-row model cassava planterPC-20 and a cassava harvester P900.

Table A7.2.2 Direct energy and material inputs in cassava chips production

Operation	Fuel [l diesel ton $^{-1}$ fresh cassava]	Labor [man-day ton $^{-1}$ fresh cassava]	Water [l l EtOH^{-1}]
Washing [a]	0	0	8
Weight and chopping	0.9	2	0
Solar drying	0	0.38	0
-Spread cassava pieces	0	0.19	0
-Turn cassava pieces	0	0.19	0
Artificial drying	121	n.a.	0
Recollecting, packing and storing	n.a.	0.38	0

[a] Energy consumed is considered negligible (Fluck 1992)

Table A7.2.3. Direct energy inputs in cassava ethanol production

Energy type	Unit	Centralized system	Decentralized system
Electricity use	[kWh lEtOH $^{-1}$]	0.240	0.109
Energy for electricity	[l diesel lEtOH^{-1}]	0.049	n.a.
Energy use for distillation	[l fuel oil lEtOH^{-1}]	0.26	n.a.
	[kg coal lEtOH^{-1}]	n.a.	0.58

APPENDIX 7.3 ALLOCATION

Appropriate allocation of flows to the different outputs of a system has been highlighted as a crucial step in the case of systems delivering different outputs (Dornburg 2004). Only one of the systems analyzed in this study deliver apart from the ethanol produced, a valuable market product, animal feed. Other products like electricity, heat, compost and digestates are reincorporated within the system and therefore do not need to be considered within the allocation calculations. Still allocation is important for comparison purposes with other studies and is therefore considered in this section. Allocation is usually performed according to market values or replacement values, previous studies on bioethanol production from cassava have shown that both methods deliver similar results (Dai et al. 2006; Leng et al. 2008). A replacement allocation has been chosen in which the energy credits are assumed to be equal to the energy value of a substitute product that the animal feed produced can replace. From the mass balance calculations of this study we calculated a total energy content of animal feed of 54,566 ton COD yr^{-1}. Considering an energy equivalence of 12.5 MJ kg^{-1} COD and a replacement ratio of 0.95, corresponding to the average value of corn and soybean meal, the total energy to be replaced would be 648 TJ yr^{-1}. Considering that 769 TJ yr^{-1} ethanol are produced, a total 46% of the total energy consumption in the systems should be allocated to the animal feed production, i.e. 648/(648+769). From the previous, 54% of total energy inputs in the DS should be allocated to ethanol, that is 462 TJ yr^{-1}, which turns positive the NER of the DS scenario to 8.41.

Chapter 8

Unfolding possibilities for anaerobic digestion within the framework Colombian biofuel policy

Abstract

The current situation of perceived fossil fuel scarcity coupled with increasing energy demand has brought about increased interest in biofuels as a means to increase energy security and boost agricultural development in developing countries. Colombia is a tropical developing country that exemplifies this panorama. Since year 2001 consistent efforts have been taking place for the partial substitution of fossil fuels for transporation purpose which have meant that bioethanol and biodiesel are produced nowadays from agricultural feedstocks including sugarcane, panelacane, cassava and oil palm. The implementation of the policy has triggered concerns regarding land use, food security and resource use efficiency. In this Chapter, the role of anaerobic digestion to add value to the existing biofuel cascades in Colombia is analyzed. Benefits of the anaerobic digestion technology are calculated in terms of energy, land, nutrients and water savings under different scenarios of by-product reuse.

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1 INTRODUCTION

The use of biomass for energy production has been exacerbated in recent years. The rapid population growth and the increase in energy demand in both industrialized and especially in developing countries have induced such tendency. Perceived fossil fuel scarcity and geopolitical tension has lead to energy instability and high prices fluctuation which in turn has imposed serious energy security risks to countries heavily dependent on energy from third parties and also to those depending on their own finite energy sources (Dufey 2006). As a result, and in order to decrease their vulnerability, many countries have adopted energy strategies that increase their self-sufficiency, and diversify their energy sources. Furthermore, the implementation of international agreements for the reduction of greenhouse gas (GHG) emissions has fostered the urgency to produce and use environmentally sound energy sources.

The possibility of creating energy out of biomass in a competitive way is seen as an opportunity to tackle the presented situation. Biomass is a renewable form of energy, regarded as more easily accessible than fossil energy sources which may be exploited using less capital-intensive technologies. By using biomass for energy purposes it is also expected that commodity prices volatility is reduced as commodity surpluses reduce and conditions are created for a value-added agriculture (Dufey 2006). Furthermore producing biomass for energy can provide a setting for industries to be brought into rural areas, which in turn can potentially create jobs and return money into rural systems and create opportunities for local, regional, and national energy self-sufficiency.

However and despite the presented opportunities, important criticism dealing with food security risks and the possible danger to biodiversity due to unplanned expansion of the agricultural frontier has been raised. Biofuels are expected to increase the already intense competition for land between agriculture, forest and urban uses (Dufey 2006). Such expansion of agricultural land, triggered by energy production based on biomass can further stimulate conflict over lands rights and force migration for rural dwellers.

Colombia is a tropical developing country that exemplifies such panorama. The already existing expertise in the production of crops with an interesting energy potential like sugarcane and oil palm, the dependence on fossil fuels for the transport sector, the existence of isolated rural areas with no electricity access and the necessity of making the rural sector a viable one in a situation of instability and unemployment are important considerations that have raised interest in bioenergy production out of crops and agroresidues as an appealing option.

Since year 2001, Colombian government has been working on developing new alternatives for energy production. In that, it has developed and implemented a strategy on biofuels triggered among others by the following. Firstly, there has been an important international and national call to diminish dependency on fossil fuels not only because of its detrimental effects upon the environment but also due to its changing prices. Secondly, and in line with the previous argument, due to the wide range of energy sources existing in Colombia, the country has considered strategic to diversify its energy supply (UPME 2003). This would not only mean less vulnerability to changing prices and natural phenomena but also a diverse portfolio of energy products that guarantees national self-sufficiency and better fit the international energy market. Lastly, the production of biofuels becomes an additional alternative to strengthen agriculture based economies.

Policies have been developed to enlarge the energy portfolio, main focus being the fostering of the production and use of biofuels. Legal instruments and regulations have been set to procure the gradual use of bioethanol and biodiesel for transportation purposes fixing blending targets, which are already operating since 2006 and 2008, respectively. Sugarcane, panelacane, oil palm and cassava are the crops receiving major attention to fulfil the created demand. The endeavour has been largely supported by the Government and by sugarcane and oil palm agroindustries. These actors have presented biofuels as economically feasible and as environmentally sound alternatives able to foster rural development. The previous has not been received without major criticism regarding the best use to give to biomass including the energy efficiencies achieved, and the risks entailed for food security and equitable distribution of outcomes.

Regarding environmental concerns, it is argued that the expansion of the agriculture frontier will inevitably have a negative effect on biodiversity, particularly in the pacific region where oil palm plantations have already altered the rich biodiversity and the natural landscape. Criticism dealing with data on GHG balances and energy balances presented by Colombia government are also the case as data availability is limited and in many occasions data from other countries are used (Leon and Gallini 2008).

Apprehensions on the social implications of biofuel expansion are also the case. The economies of scale that prevail in the biofuel industry are seen as a risk to benefits sharing. It is argued that such business logic will magnify land property concentration by benefiting large producers of sugarcane and oil palm. In addition, it is still not very clear to what extent the opportunities expected in the rural areas will be realized. There is no clarity regarding the seasonality and intensity of employment and the amount of direct jobs that will be created. Further and due to the particularities of the instability of Colombian situation there are also important concerns dealing with forced displacement of rural inhabitants. In Chocó region, for example, displacement cases exerted by paramilitary groups linked to oil palm business have been denounced (Leon and Gallini 2008). Important concerns related with food security are also existent.

Whereas producing crops specifically for energy purposes demands land, energy and other resources, opportunities lie in the use of residues for bioenergy production which include not only their energy potential but also the avoidance of environmental and social problems.

Anaerobic digestion is a flexible technology allowing adding value to biomass resources of different quality by turning them into a valuable energy carrier, i.e. methane, and a residual by-product, i.e. digestate, containing nutrients and organic compounds that potentially can be recirculated back to land. So far the Colombian government has not paid attention to the possibilities that the anaerobic digestion technology can offer to increase energy security and add value to residual biomass and crop material.

This study strives for unfolding some of the possibilities that anaerobic digestion could offer to add value to different biomass cascades under the current panorama of biofuel legislation and considering the realities of land use and food security in the country. To do so, firstly the overall context is described by outlining the trends in energy demand, food demand and land use in the country. In the following, current agricultural and energy legislation is examined. Thereafter the specific situation of the main crops that are being promoted as biofuels in Colombia is described. Finally, calculations are performed on the possibilities that AD could offer as part of different biomass cascades departing from the same crops. Comparison is made on the basis of the energy and food/feed output of the different cascades and legislation guidelines are given focusing on the trade-offs on the use of biomass for different type of bioenergy carriers and other competing claims.

2 POPULATION, ENERGY AND FOOD IN COLOMBIA: DEMANDS AND PROJECTIONS

2.1 General population trends

The world population is rapidly growing. According to United Nations, worlds' population will pass from 6.5 billion in 2005 to 7.7 billion in 2020 and 9.1 billion in 2050. Such increases will be accompanied with a radical shift in terms of urban/rural population. In 2050, 70% of world's population is expected to be urban (UN 2007a). The increase and change in population pattern will inevitably have a direct impact on energy and food requirements.

The Colombian population is expected to pass from 46 million in 2007 to 61.8 million in 2050, meaning a 34% increase. In terms of distribution, current urban population equivalent to 74% in 2007 is expected to shift to 86% in 2050 (UN 2007a). For the year 2020 the Colombian population is expected to be 51 million inhabitants. The population growth rate in the country is however expected to diminish particularly after 2010 when low fecundity rates and higher life expectancy will predominate (DANE 2007).

2.2 Energy demand and energy security

Together with population growth, and partly due to it, energy demand is expected to grow. In addition, according to the projections of the Colombian Planning Unit for Energy and Mining (UPME), energy demand will grow as the result of steady economical growth that might increase per capita income and per capita energy consumption as well as the energy demand from the industrial and commercial sectors.

In 2002, total energy demand in Colombia was 890 PJ. For 2020, the energy demand in Colombia is estimated to reach 1,528 PJ implying an annual growth of 3.0%. The per capita consumption is expected to increase from 20.5 GJ per inhabitant in 2002 to 25.5 GJ in 2020.

Energy consumption in Colombia is dominated by fossil fuels. In 2002, 45% of the primary energy consumption in the country came from petroleum derivatives, 21% from wood and bagasse, 14% from hydroelectricity, 11% from natural gas and 9% from coal. Important changes have occurred, though. For instance, in the residential sector the use of traditional energy sources as wood has declined, mainly due to the expansion of LPG in rural areas. The participation of wood in the energy use declined from 69% in 1990 to 17.4% in 2005. In the same period, the participation of natural gas passed from 0.5% to 22%, and that of LPG from 6.1% to 16.6% in the residential sector, whereas the share of electricity passed from 8.3% to 38.8% due to the enlargement of the network. In urban areas, the substitution process also took place. Natural Gas replaced almost completely the use of LPG.

In the long term, Colombian Planning Unit for Energy and Mining (UPME) expects a sharp increase in the demand of petroleum derivatives and steady but slower increase in the use of natural gas and electricity which demand is expected to double in 20 years (UPME 2003)(Table 8.1).

Table 8.1 Projected energy demand 2002-2020 in PJ yr^{-1}

Energy form	2002	2006	2010	2015	2020
Coal	81.8	101.0	110.0	124.4	143.9
Natural gas	98.6	114.3	136.5	165.0	197.2
Electricity	122.3	136.9	160.1	190.4	237.8
Biomass	184.8	190.6	205.4	227.6	256.0
Petroleum derivatives	403.6	439.0	449.4	589.8	694.5
Total	890.8	938.2	1,112.8	1,301.4	1,529.5

Source: UPME (2003)

The transport sector, which demanded 39% of total final energy in the year 2006, is expected to have a relatively small growth rate in coming years due to governmental projects for urban massive transportation and tighter restrictions for private vehicle use within cities. In addition, a steadily substitution of gasoline by diesel is projected due to the lower prices of the later (UPME 2003). Figure 8.1 depicts the projection in the demand of gasoline and diesel up to year 2025 according to UPME (2006) and based on the economical growth expected by Colombian Planning Department (DNP).

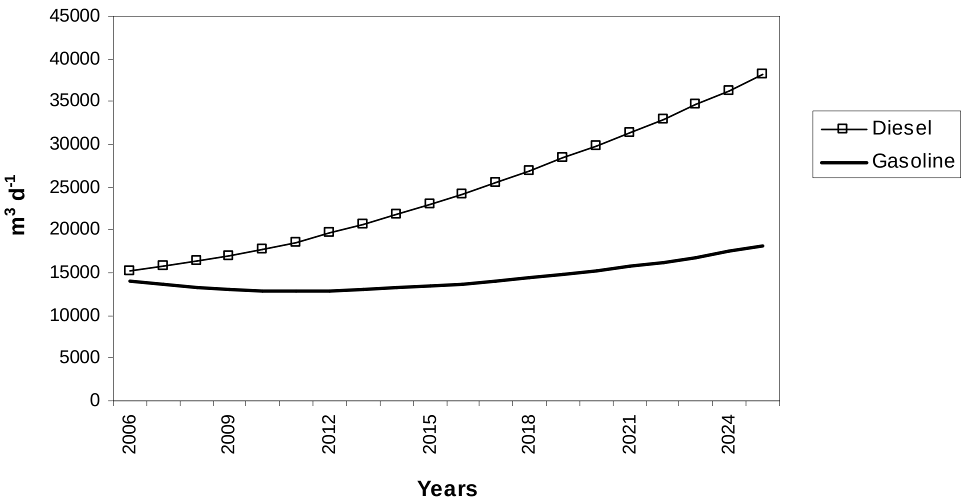

Figure 8.1 Projected diesel and gasoline consumption in Colombia
Adapted from (UPME 2006)

Natural gas consumption has been stimulated in the country in the last decade and in the future the expansion of gas into rural and a periphery area of the cities is expected to continue (UPME 2006). The expansion in the use of gas is receiving major incentives due to the country's available reserves and new explorations being performed. The consumption is expected to double by year 2020 especially in the thermal and industrial sectors. Domestic consumption is not expected to grow drastically after 2009 due to the progressive saturation of the market since its expansion started (Figure 8.2).

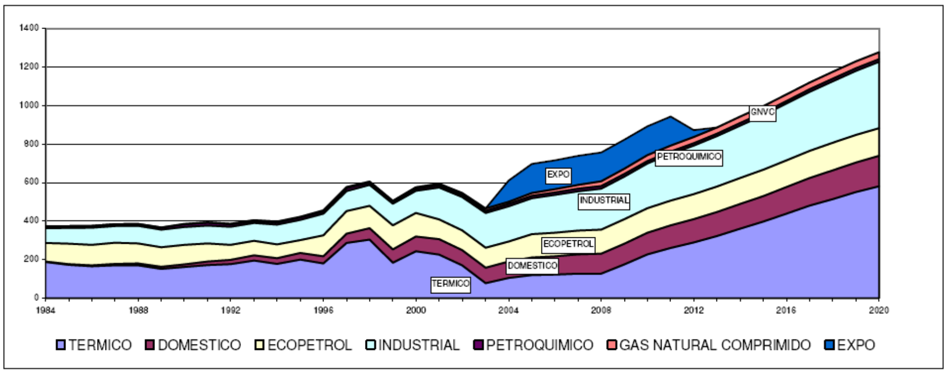

Figure 8.2 Expected increase in the consumption of natural gas in Colombia. (UPME 2003)

The lack of energy provision is an important factor delaying development in the country. Remote areas not connected to the National Interconnected System for electricity provision account for around 65% of total national area. This area is spread among 22 departments (out of the existing 32) and inhabited by about 1.5 million people, i.e. 4% of the total population, of which 88% live in rural areas. Average population density in these areas is low, i.e. 2 inhabitants km^{-2}, making their connection to the electricity system not economically viable (Antolinez Olarte 2001).

Apart from the importance of energy for internal economic development, the energy sector is of main importance for the Colombian economy, as the country exports a substantial amount of its exploited energy resources. In 2001 for example, the contribution of the energy sector to the national balance of trade was 42%, those exports representing 56% of the total 3,098 PJ energy produced in the country (UPME 2003). In 2007, Colombia exported about half of its oil production, the bulk of those exports went to the United States (EIA 2009).

A large portion of the energy export is derived from coal. Colombia is the fifth largest exporter of coal in the world and possesses the second largest coal reserve in South America after Brazil (EIA 2009). Import of primary energy is marginal. Nonetheless, due to lack of sufficient refinery capacity some diesel and gasoline is imported. In 2006, about 16% of the total demand was supplied with imported diesel (UPME 2006).

2.3 Food demand and food security

The increasing population in Colombia coupled with changing food patterns shifting towards a high caloric diet, will also mean an increase in food requirements in the future. At the beginning of the 90's Colombians were consuming 2,440 kcal $person^{-1}$ d^{-1} whereas at the end of the same decade average food consumption increased to 2580 kcal person^{-1} d^{-1}. By 2005, food consumption increased to 2,670 kcal person^{-1} d^{-1}, an increase that took place in a decade of poor economical development (FAO 2006).

The food security debate in Colombia in relation to biofuels is gaining increased attention although the debate is still poor in considering all the issues at stake, i.e. food use; food availability and food access. Substantial increases in prices of imported products like corn (80%) and wheat (90%), and national products as panela, sugar and cassava have been reported since the introduction of biofuels (Leon and Gallini 2008). However, it has not been clearly established to what extent such increase is due to biofuel production as such. A study from CEPAL and FAO suggests that production of biofuels in Latin America will not jeopardize food security given the quantity of land available in the region and its capacity for food production. Yet, the same study emphasizes that it depends on the extent of benefit sharing and underlines the importance of small scale production (Leon and Gallini 2008).

The increase in prices of the mentioned commodities all of them important in the Colombian Household Market Basket, can aggravate current hunger conditions in the country. In Colombia 41% of households suffer food insecurity and according to the UN, between 2003 and 2005 Colombia had a moderate level of undernourishment equivalent to 10% of the total population which is higher than the average in South America and the Caribbean. Further, 11 million inhabitants, i.e. almost 25% of the population, go to sleep every night in hunger or having eaten just one meal during the day, and more than 20% of children below 5 years are under-nourished. All this depicts a risky situation that could be potentially magnified by the impact of biofuels production on the commodity market.

3 LAND USE AND CROP PRODUCTION IN COLOMBIA

3.1 Generalities

Colombia has a total area of 1,141,748 km^2 and is divided in five geographic regions, namely: Andean region, Caribbean region, Amazonian region, Orinoquia region (grassland plains) and Pacific region (Figure 8.3). The highest concentration of inhabitants, industries, services and agriculture takes place in the Andean and Caribbean regions. Not surprisingly, these areas are the most transformed of the country with just some patches (mostly protected) of original vegetation cover still remaining. In contrast, the Pacific, Amazonian and Orinoquia regions are much less populated and still contain important areas of undisturbed ecosystems. The population centres in these areas, with the exceptions of major cities, are small and scattered towns or villages accessibly either by airplane and/or river.

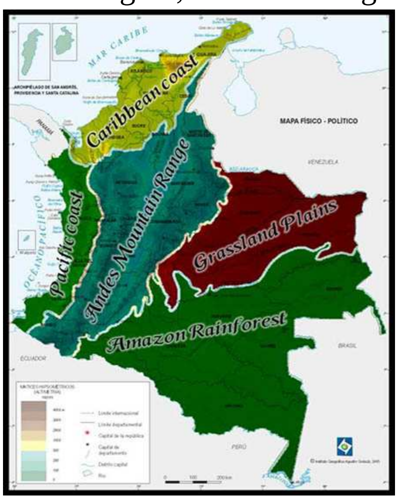

Figure 8.3 Colombian geographic regions

Due to size, geographic location, and topography, Colombia is a country with multiple agro-environmental conditions. Such variety has facilitated the specialization of regions in the production of certain crops. In the mostly dry and hot Caribbean lowlands, for instance, the main crops cultivated are maize, sorghum, barley, wheat, cassava, plantain, cotton and oil palm. Livestock, both for meat and milk production has also high relevance. In the Andean region, altitude has been the major denominator and coffee the most traditional crop. The most favourable spots for agriculture in this region are the well irrigated interandean valleys, although agriculture could take place anywhere below 3,000 meters above sea level (masl). Nonetheless, due to the variety of temperatures and soil conditions many crops are cultivated: rice in the interandean valleys, sugarcane in the low interandean valleys and in mountain slopes between 1,000 masl and 1,800 masl, potato in mild slopes between 2000 and 3000 masl, fruit trees all over the region and plantain in areas below 2,000 masl. Livestock occurs mainly for milk production. The eastern plains located in the Orinoquia region, especially those adjacent to the Andes are also lands targeted for agricultural activities. Sharing to some extent the agro-environmental conditions of the Caribbean region, these plains are used for the production of rice, maize, oil palm and plantain.

Colombian cropland has not varied drastically in the past 10 years. In 2002, approximately 4% of Colombian territory, i.e. roughly 4 million ha, was used for food/feed production (cropland) although it is estimated that 10 million ha are available and suitable for this purpose (Reyes 2007). Out of cropland area, 60% was arable land for annual crops and 40% permanent crops (WRI 2003). 23% was irrigated land. The production of food/feed is predominantly concentrated in the Andean and Caribbean regions, although a small but representative area is also located in the grassland plains.

In contrast to the small area used for crop production, currently 26% of Colombian territory is used for extensive livestock production (ASOCANA 2008) some areas having very low livestock densities, i.e. 0.5 animal ha^{-1}. According to Reyes (2007) 4.2×10^7 ha are used in extensive livestock although just 1×10^7 ha have conditions for such use.

In the year 2000, 47% of the total country was forest land, represented in 50 million ha of natural forest and 1.4×10^5 ha of planted forest (WRI 2003). The major concentration of forest can be found in the Pacific and Amazonian region.

Currently, approximately 10% of the Colombian territory is officially protected. Besides the national system of national parks, protected land also occurs through regional, municipal, and civil initiatives. Total area protected is 1.15×10^7 ha spread over all five Colombian Regions (PNC).

3.2 Cropland

In 2005, 4 million has of land were cultivated in Colombia, equivalent to 25 million ton of products per year, out of which 65% were perennial crops and 35% non-perennial ones. Ten crops account for 80% of the agricultural production and area cultivated, their individual contribution presented in Figure 8.4. In terms of economic production, sugar and panela from sugar cane (17%), followed by fruits (13%), plantain (12%), potatoes (11%), rice (10%) and cassava (8%) are the most important crops, whereas in terms of area coffee is the most important product (19%), followed by maize (15%), rice (12%), sugar cane (10%) and plantain (10%) (MADR 2005b).

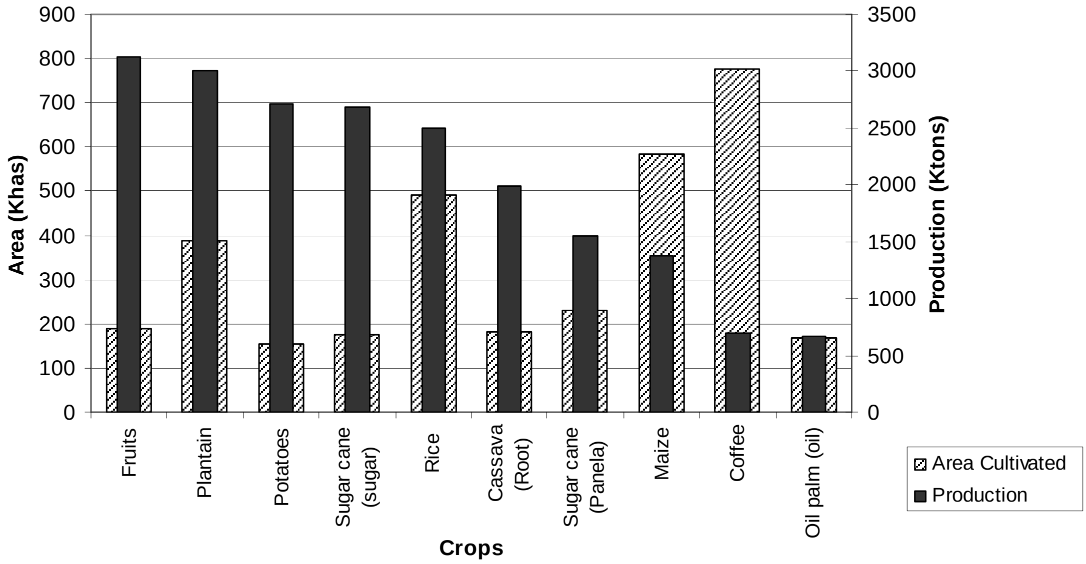

Figure 8.4 Main Colombian crops according to production and area cultivated (MADR 2005b)

Regarding concentration and scales, rice, sugarcane, oil palm and coffee are crops cultivated in rather localized areas leading to the establishment of agro-industrial clusters. Rice and coffee industry grew mainly in the Andean region, whereas sugarcane settled largely in the Pacific region. Other crops such as panelacane, cassava, plantain and maize are widely cultivated throughout the country and very much related to peasant economies and less developed post-harvest processing. Table 8.2 presents the details on the markets patterns and uses of the main crops.

Table 8.2 Main characteristics on markets and consumption patterns of main agricultural crops in Colombia

- *Fruits*: 5.1% positive growth. Fresh orange (70%), also fresh lemon and concentrates. Export.
- *Plantain*: Produced mainly for internal consumption. Only 6.3% out of the total production is exported. Plantain production has been largely a sector of traditional peasant economy, based on small producers and high geographical dispersion.
- *Potato:* Produced mainly for internal consumption (98% of the production). Approximately 8% of the production is aimed at industrial processing, the rest is consumed fresh. Potato is obtained mainly by small farmers (90% of total producers) with basic farming technologies.
- *Sugarcane (sugar):* Agriculture sector highly productive and technified with comparatively high and growing yields. High geographical concentration of the

production and the processing.

- *Panelacane:* Produced for internal market. Sector of traditional peasant economy based mainly on small producers and high geographical dispersion.
- *Rice:* The agroindustrial chain of rice in Colombia is mainly constituted by rice growers and rice mills. The large proportion of the production is obtained from medium to large plots.
- *Cassava:* Produced mainly for internal consumption (70%) and associated to peasant economies and highly dispersed throughout the country.
- *Maize:* Negative growth in the last decade (-0.3% per year). Imports come from USA (88%), Argentina and Ecuador.
- *Coffee:* For many years the most important product of Colombian economy. 85% of the production is exported. In recent years it has lost participation in the international market and also as contributor of Colombia GDP.
- *Oil Palm:* Agriculture sector highly productive and technified. High geographical concentration of the production in four clusters of production.

a. In Colombia sugarcane is used both for the production of sugar and the production of panela, denominated by FAO: non centrifuged sugar. Provided the big differences in yield, technology, farming systems, a distinction is made between sugarcane and panelacane.

Seven out of the ten crops listed above have potential for the production of biofuels. Provided currently technology, cassava, potato, sugar cane, panelacane, oil palm, cassava and maize are suitable for the production of either bioethanol or biodiesel. The extent to which such crops are able to be effectively used for the production of bioenergy varies, though. It depends, among others, on environmental restrictions, productivity, institutional and organizational arrangements, technology and economic feasibility.

4 ENERGY AND AGRICULTURAL POLICY IN COLOMBIA

4.1 Agricultural policy

Agriculture has been a crucial element of Colombian economy, its boost originating in the tobacco and coffee industries in the nineteenth century. Since then, it has become a key for the provision of food both for domestic consumption and as a source of export revenue. In the 60’s, with the industrialization of the country, the sector started to grow slower than the rest of the economy, nonetheless by the 80’s it continued as the foundation of the economy accounting for nearly 21% of GDP in 1987 and nearly 68% of all export revenue in 1986 (USDA 1988).

Economic reforms in the 90’s ended with protective measures for particular sectors, which led to a weakening in the production of some traditional crops like corn, cotton, and cassava. Still by the year 2000, agriculture accounted for roughly 19% of GDP, employing 30 % of the population and accounting for 17.4 % of exports (NE 2009).

In spite of the small growth in the past decades and a long stagnation of the area planted, Colombia is predominantly a self-sufficient nation in terms of food and agriculture. Further, the country is a net exporter of agricultural products (Figure 8.5).

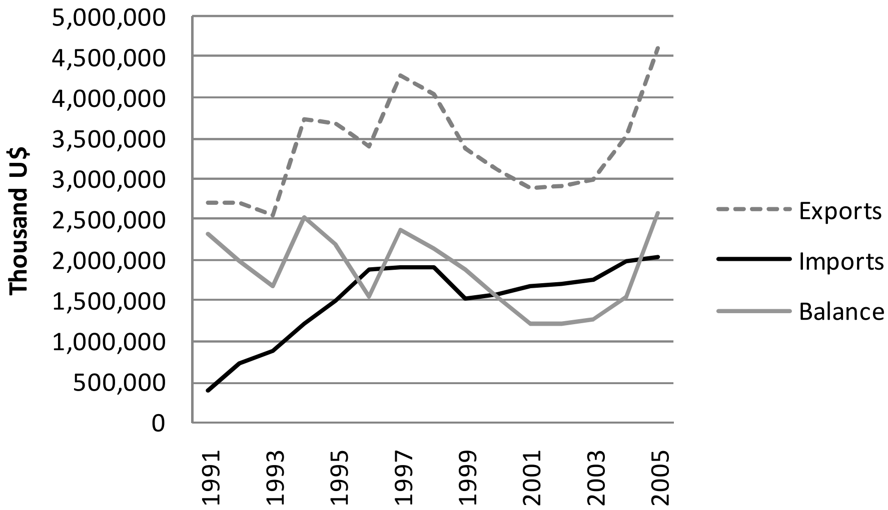

Figure 8.5 Agricultural Commercial Balance
(MADR 2005a)

Current Colombian policies on Agriculture are very much based on the following fundamentals: (i) globalization of the economies is an irreversible process that determines to large extent national actions, (ii) promotion of productive activities should be based upon the achievement and maintenance of competitiveness and (iii) within this new context, the relation between private and public sectors should be adjusted.

From the previous, current agricultural policies are oriented towards the creation of a competitive sector where added value is of primary importance. Thus, in the agriculture sector in Colombia new policies are taking place stressing the relevance of market competition, the reduction of trade fees, and the slow withdrawal of government from actions dealing with price control, supply regulation, imports licenses and other control and regulation instruments. In the *current scheme global and macroeconomics policies prevail over those related with the sectors* (Mendoza 1999). Specific strategies fostered by the Ministry of Agriculture are depicted in Table 8.3.

Table 8.3 Policy Strategies of the Colombian Ministry of Agriculture

▪ *Initiation of new markets for agricultural product, guaranteeing its competitiveness*. For the implementation of this strategy, the government has been working on internationalization of the economy via bilateral and multilateral international agreements with the US, Andean Community and the European Union among others. To guarantee its success, this strategy has been accompanied by a program for the modernization and specialization of agricultural production.
▪ *Improvement of the sanitarian status.* In order to assure the entrance of national agriculture production to new markets, efforts have been deployed to strengthen the Sanitarian and

Fitosanitarian measurements.

- *Access to financial resources.* Efforts are devoted to facilitate the access to loans for small farmers, strengthening the microcredit lines offered by the National Loan System for Agriculture. At the same time, the system itself has been revised to improve services and widen options.

- *Rationalization and decrease of production costs:* In order to increase yields, reduce production costs and make use of Colombian comparative advantages in agriculture, the government has fostered research, technological transfer and innovation through the strengthening of research institutions.

- *Modernization of the support instruments*: This strategy is aimed at creating and strengthening instruments for reducing the risk involved in agricultural production and improving the sanitarian management of crops.

- *Social ordering of property*: This strategy aims at redistributing land making rural inhabitants also owners. The priority is to distribute land back to peasant families and those displaced by conflict and to promote once again rural development fostering rural entrepreneurship, rural housing, gender programs and land adaptation amongst others.

- *Promotion of biofuels*: In order to open a new market for agriculture, the government has fostered biofuels production and consumption in the country. Demand of feedstock for biofuels production is expected to enhance crop's prices and increases farmers' income. Besides, it promotes new rural employment and the pacific occupation of the territory.

4.2 Energy policy

Historically, Colombia has oriented its energy policy towards the exploitation of its numerous non-renewable resources, i.e. oil, natural gas, coal, as its national budget largely depends upon the revenues generated by these exports.

Main targets of the Colombian government in the energy sector are compiled in the National Energy Plan which is aimed at six main targets: (i) Maintain or increase the contribution of the energy sector to the National Payment Balance, (ii) Consolidate the sector competitiveness in the different markets, (iii) Strengthen the use of natural gas as an energy source, (iv) Enlarge and guarantee the supply of energy with price efficiency and product quality, (v) Favour regional and local development, and (vi) Incorporate new technologies.

In order to materialize the production and consumption of biofuels, Colombia has worked on an Integral National Plan on Energy (UPME 2003) and on legal instruments and regulations. The core issue in what refers to biofuels has been the gradual increase in the use of bioethanol and biodiesel for transportation purposes. Bioethanol is intended to be used blended with conventional gasoline whereas biodiesel is expected to be used similarly but by heavy load vehicles. The main policy documents setting the track for biofuels in Colombia are presented in Table 8.4.

Having as orienting guides the previous policy documents, the government developed an important number of laws and regulations to set up production and consumption of biofuels in the country. For the case of bioethanol, the most important is Law 693 (2001) which established the general norms and objectives regarding carburant alcohols in Colombia. Later on, in 2002, Law 788 established the first economical incentives for production of biofuels by exonerating bioethanol from certain taxes. In the case of biodiesel, law and regulations emerged more recently. The main legal instrument is Law 939 of 2004 that stimulates the production and commercialization of diesel from vegetal and animal sources. Besides, it concedes tax exemption to perennial crops as cocoa, rubber, critics, fruits and oil palm.

Table 8.4 Policy documents stimulating biofuel production in Colombia

- *National Developmental Plan*, which aims at the optimization of national oil refineries and the expansion of natural gas as vehicular fuel (DNP 2002).
- *National Energy Plan*, which went further by setting the ground for the implementation on non-hydrated ethanol as oxygenating compound for gasoline, the use of biodiesel as blending compound for conventional diesel and specially by mandating the government to issue the adequate regulations to bring into reality such initiative (UPME 2003).
- *CONPES Document* (National Council on Social and Economy Policy): Planning document for the formulation of a policy to prevent and control air contamination
- *Transport Sector Strategic Plan 2003 – 2006*, which aimed among others at using clean fuels as natural gas and bioethanol for transport (MTRANSPORTE 2003).
- *National Policy on Cleaner Production*, which promoted the incorporation of cleaner technologies in all Colombian productive sector (MMA 1997).

Colombian Biofuel Program

The Biofuel Program in Colombia is constituted by two differentiated subprograms, namely Carburant Alcohol Program (Bioethanol) and Biodiesel Program (MME 2006). The first one received most of the attention during various years, especially as part of the agenda of the sugar sector. Not surprisingly, bioethanol is the most developed subprogram with a comprehensive set of regulations and a considerable production capacity installed. More recently, efforts were devoted to the biodiesel program through the developing of guiding regulations, incentives and production projects.

The main objective of the program is to diversify Colombian energy portfolio keeping as ultimate goals: (i) Environmental Sustainability, (ii) Maintenance and development of agriculture based employment, (ii) Energy self-sufficiency, (iv) Agroindustrial development , and; (v) Fuels quality improvement as a result of the biofuels/conventional fuel blending (MME 2006).

The target for bioethanol use in Colombia establishes a progressive use of E10 blend (10%ethanol – 90% conventional gasoline) throughout the country. Southwest of Colombia was expected to start bioethanol consumption in 2005, the centre of the country in 2006, northeast of Colombia since 2007 and Antioquia and Atlantic Coast since 2009. Target for biodiesel use in Colombia is the consumption of B5 (5% biodiesel – 95% conventional diesel) starting in the Atlantic coast in January 2008 and expanding to the rest of the country since May 2008. Besides, a target on the international ethanol market has also been set in the framework of the free trade treaty with the United States, i.e. TLC.

Although delays in the implementation of both subprograms have occurred, the strategy set by Colombian government has already resulted in important outcomes. Following the regulation established five sugarcane-based and one cassava based (experimental) bioethanol plants are currently operating with an overall production of 1,070,000 l d^{-1}. At least eight sites based on crops such as cassava, panelacane and sugar beet are constructed or projected (Fedebiocombustibles, 2007). The country became in 2006 the second producer of bioethanol in Latin America, and currently 70% of national potential ethanol demand is already supplied.

Table 8.5 shows the projected bioethanol production per feedstock from 2006 until 2020 as well as the projected bioethanol consumption considering two possible scenarios, i.e. a modest scenario with a permanent E10 blending, and an aggressive scenario using increasing blending percentages according to Fedebiocombustibles (2007), that is: E10 for 2006, E15 for 2010, E25 for 2015 and E25 for 2020. The calculation of bioethanol consumption is made using gasoline projections from (UPME 2006) as presented in Figure 8.1.

Table 8.5 Projected bioethanol production and consumption in Colombia

	2006		2010		2015		2020	
	[l d^{-1}]	% total production	[l d^{-1}]	% total production	[l d^{-1}]	% total demand	[l d^{-1}]	% total demand
Sugarcane	858,082	97.7%	1,469,863	51.8%	1,469,863	47.2%	1,469,863	38.7%
Cassava	20,000	2.3%	632,500	22.3%	907,500	29.2%	1,595,000	42%
Panela	0	0%	733,300	25.9%	733,300	27.8%	733,300	19.3%
Total production	878,082		2,835,663		3,110,663		3,798,163	
Total Consumption -Modest scenario*	1,411,920		1,326,060		1,340,370		1,523,220	
Total Consumption - Aggressive scenario**	1,411,920		1,924,695		3,350,925		3,808,050	

Source:Adapted by the authors based on data from Colombian Ministry of Agriculture as presented in (Proexport 2008; UPME 2006).
* Permanent E10 blending
** E10 for 2006 , E15 for 2010, E25 for 2015 and E25 for 2020

As can be observed in the table, sugarcane is called to take major protagonism during the introduction of the bioethanol program, whereas later on cassava and panela increase their share, cassava becoming the major bioethanol provider in 2020.

Biodiesel production started in November 2007, the first plant inaugurated has a capacity of 50,000 ton yr^{-1}. Since January 2008 B5 consumption started in some regions of the country and in April 2008 a new plant started to operate adding a production capacity of 36,000 ton yr^{-1}. Currently approximately 20% of national biodiesel demand is being covered. Table 8.6 shows projected biodiesel production from 2008 until 2020, and the projected biodiesel consumption under two scenarios, i.e. a modest scenario with a permanent B5 blending and an aggressive scenario using increasing blending percentages that is: B5 for 2008, B10 for 2010, B20 for 2015 and B20 for 2020 (Reyes 2007). The calculation of biodiesel consumption is made using data from Figure 8.1 (Projected diesel and gasoline consumption in Colombia).

Table 8.6 Projected biodiesel production and consumption

	2008	**2010**	**2015**	**2020**
National production [ton yr^{-1}]	610,000	724,382	1,478,786	2,763,892
Total Consumption [ton yr^{-1}] Modest scenario*	254,306	277,651	359,605	465,897
Total Consumption [ton yr^{-1}] Aggressive scenario**	254,366	555,302	1,438,420	1,863,589

Source: Adapted by the authors from (Reyes 2007; UPME 2006)
* Permanent B5 Blending. ** B5 for 2008, B10 for 2010, B20 for 2015 and B20 for 2020

5 CURRENT AGRICULTURAL COMMODITIES USED FOR BIOFUEL PRODUCTION

In Colombia, five crops are used (or planned to be used) for the production of biofuels: sugarcane, panelacane, cassava, sugar beet and oil palm. All of them - but sugar beet - are among the major crops in Colombia both in terms of volume and area. Their usage as raw material for biofuel production is the result of various factors. Firstly, all are well established and largely known crops rich either in starch, sugar or oil. In the case of well organized industries, as sugarcane and oil palm, their use is part of a business strategy aimed at diversifying their portfolio of products and reducing their exposure to prices fluctuations. The selection of panelacane and cassava, traditionally peasant economy crops, obeys to a private-public strategy with multiple aims. Some of the drivers are: to supply regional fuel markets, to create new niches for the allocation of peasant economy crops, to strengthen poorly developed rural economies and to ameliorate panela price after its crisis resulting from overproduction among others. The following sections look in detail into the resource base per crop and its potential/existing response for biofuels production

5.1 Sugarcane

The production of sugarcane in Colombia is based in the neighbouring departments of Valle del Cauca, Cauca, Risaralda and Caldas. In this region, for more than a century, the industry of sugar has evolved into a geographical concentrated, organized, developed and highly productive agro-industrial sector that supplies refined sugar and other derivates to national and international markets. This regional cluster is constituted by 13 sugarcane mills and more than 1500 sugarcane growers gathered in three main growers associations.
As seen in Table 8.7, sugarcane area has been growing slightly in recent years, although yields and productivity has decreased after reaching a peak in year 2003.

Table 8.7 Sugarcane: extension and productivity 2003-2007

	Unit	Year 2003	2004	2005	2006	2007
Area	[ha]	168,633	172,241	176,367	181,336	184,866
Yield	[ton cane ha^{-1}]	127.9	127.9	122.8	120.6	113.3
Productivity	[ton sugar ha^{-1}]	13.3	13.1	13.2	13.2	12.8

Source: (ASOCANA 2008; MADR 2005d)

Nearly 79% of sugarcane plantations are located in a stretch of land along the Cauca river in the department of Valle del Cauca. Such concentration is the result of agro-environmental conditions that permit harvesting and milling all year around. Out of the total production of sugar, 60% is exported and 40% in consumed nationally. Within the Colombian market, 53% is aimed at human consumption and 47% for industrial use (ASOCANA 2008).

The industry is supported not only by a strong gremial organization (Asocaña) that represents the interests of the sector but also by a research institute (Cenicaña) fully devoted to research on sugarcane, a trading organization that canalized all the commercial efforts avoiding unnecessary competition between the mills and a technical exchange institution (Tecnicaña) that promotes technological solutions for the industry.

The areas where the plantations take place are highly transformed lands devoted to agriculture. Land used is managed in diverse ways. In 1998 the distribution was as follows: Land property of sugar agroindustries (24.8%); Land rental contracts (22.9%), provision (52.3% - land used by its owner to produce sugarcane) (MADR 2005d).

Since year 2006, five ethanol refineries located in equal number of industrial sugar mills are operating. Such refineries have a joint production capacity of 1,050,000 l d^{-1}. Under current circumstances, and according to *Grupo Manuelita*, 70 to 75 liters of ethanol are produced per ton of sugarcane and approximately 9000 liters are obtained per ha per year. To fulfil installed capacity approximately 5,300,000 ton sugarcane are needed per year for which approximately 43450 has are used.

Currently the production of bioethanol is replacing the production of refined sugar formerly sold in international markets at non-preferential prices. According to a report from the National Controller Authority, the sugar-based industry is intended to transfer 120,000ha traditionally used for the production of exportable sugar to the bioethanol business due to the high volatility of prices in the international sugar market and the losses provoked in recent years.

Sugar cane residues are produced either as postharvest residues or as the result of its processing into final products. Harvesting the sugar cane will leave as by-product the trash, i.e. tops, dry and green leaves, which are usually burned in the fields directly after harvesting. Processing into ethanol will yield the residues bagasse (solid resulting after juice extraction), and vinasses (waste water from the fermentation process) remain.

Trash accounts for approx. 140 kg DM per ton of sugarcane stalk (De Carvalho Macedo et al. 2001), whereas bagasse yield ranges from 135-175 kg DM ton^{-1}. In the ethanol producing industry 12-15 liters vinasses per liter ethanol are produced(van Haandel 2005).

A major concern of the sugar and ethanol industry has been finding economic opportunities for solving the problems related with the disposal of its by-products (Rosillo-Calle and Cortez

1998). Possibilities for reusing bagasse include co-generation of electricity, production of building materials, animal feed, paperboard and additional ethanol (Pandey et al. 2000; Rosillo-Calle and Cortez 1998). Vinasses are partially spread on the fields and are in general the cause of major environmental problems (Wilkie et al. 2000).

5.2 Panelacane

Panela are blocks of non centrifuged sugar produced from sugarcane. In contrast with sugarcane produced for sugar, the production of sugarcane for panela, i.e. panelacane, is not concentrated in one area in Colombia. On the contrary, as it is largely a peasant economy crop, panelacane is dispersedly planted throughout the Andean region in mild to steep slope areas. It is cultivated virtually in all departments of the Andean region, although most of the areas planted and the production is concentrated in four departments, i.e. Cundinamarca (24% of total area, 15% of total production), Santander (9%, 20%), Antioquia (16%, 10%), and Boyacá (8%, 17%).

While sugarcane is produced for the sugar based industry, panelacane is cultivated almost exclusively for the production of panela and small quantities of cane honey (almost marginal). The crop importance relies on the fact that many rural families depend on it for their subsistence. The sector is highly vulnerable according to the Ministry of Agriculture and Rural Development, as most of it is made up by micro and small productive units hardly able to face a systematic effort of modernization (MADR 2005c).

The socio-economical relevance of the panelacane sector in rural Colombia can be summarized as follows: (i) There are approximately 70,000 agricultural-based family units active in the production of panelacane, (ii) About 15,000 artisan-mills convert panelacane into panela and cane honey, (iii) The panelacane sector creates annually more that 25 million rural daily wage jobs. The panelacane sector is the second largest generator of rural employment after coffee, (iv) Nearly 350,000 rural people are involved in the activity, representing about 12% of the economically active rural population (MADR 2005c).

Due to the wide spectrum of places, conditions and farm arrangements, the production of panelacane is very heterogeneous. Only five percent of the production is realised in big scale exploitations in areas larger than 50 ha (Valle del Cauca). Under these conditions, production is eminently commercial and the main labor arrangement is the salary. In other regions, predominantly in Boyacá and Santander, exploitations range from 20 to 30 ha and the capacity of panela production range from 100 and 300 kg h^{-1}. In these regions, there is commercial integration with the market although traditional economic arrangements as *"aparceria"*, i.e. the rental of the production capacity in exchange for a percentage of the profits, still persist. It is also in these regions coinciding with the highest yields where panelacane biofuel projects are being stimulated. In other departments as Antioquia and Cundinamarca most of the panelacane is cultivated in small areas not exceeding 20 ha and obeying to peasant economies. This segment is the most representative of Colombian panela agroindustry. Finally, a last portion of the production is obtained in "micro" productive units not larger than 5 ha with poor infrastructure and technology.

As seen in Table 8.8 yields are considerably smaller than those of sugarcane (see Table 8.7). In average, 71.7 ton of panelacane are obtained per hectare per year. In addition, variation in yields between areas and departments is large.

Table 8.8 Panelacane: Area and productivity 2001 – 2005

		Year				
	Unit	2001	2002	2003	2004	2005
Area	ha	222204	243118	246057	249384	243866
Yield	Ton panelacane ha^{-1}	69	70	72	73	75
Productivity	Ton panela ha^{-1}	6.46	6.53	6.73	6.80	6.95

Source: (MADR 2005c)

The area cultivated with panelacane has grown in past years whereas yield has only slightly increased. This is not a surprise as, in contrast with sugarcane, there is not investment in new cultivation or harvesting technologies to make the sector more productive. Hence additional opportunities in the market are rather fulfilled via enlargement of the area planted and not through yield improvement.

In recent years, per capita consumption of panela in Colombia has decreased partly due to the competition of sugar, synthetic sweeteners and artificial beverages. Thus, the sector has faced dropping prices due to oversupply and the expectations created by the production of biofuels. All this setting has brought about one of the most difficult crises for the panela sector due to overproduction and lack of organization for commercializing the product.

Lately, panelacane also received attention as a feedstock for bioethanol production. However whereas ethanol yields are exactly the same as for sugarcane, i.e. 70 to 75 l ton^{-1}, yields differences already portrayed are a major challenge.

5.3 Cassava

Cassava is of utmost importance for food security in Africa, Asia and Latin America(Gottret et al. 2002). According to FAO (2004), it is the fourth basic product in importance in the diet of more than 1000 million people in the world after rice, wheat and maize. Cassava is obtained in very diverse climates and soils and tolerates biotic and abiotic stress. Due to this, it is a very attractive crop for marginal lands being hardly found intensively cultivated in large areas (Arriaga Sierra 2008).

Cassava is widely cultivated in Colombia. For many years, it has been crucial in peasant’s economy as one the main subsistence crops in areas of the Caribbean region. It is cultivated in association or rotation with other crops as beans, yam and peas (Arriaga Sierra 2008).

Due to the great importance of cassava in the rural economy, it has been the point of reference of programs and strategies of different institutions aimed at strengthening employment and developmental condition in rural areas. It is seen as an alternative for strengthening rural economies. It has had peaks of production during the early 80´s and the 90´s due to attention given to agroindustrial processing of roots.

Although the crop is distributed all over Colombia, it is mainly concentrated in the Atlantic coast, i.e. 42% for year 1999. As shown in Table 8.9, the area cultivated as well as yield grew slightly from 2002 to 2005. Average yields in Colombia are slightly smaller than those obtained in other Latin-American countries as Costa Rica and Brazil where average yields were 15 and 13.6 ton ha^{-1} in 2005. As new technologies are implemented, especially for the production of bioethanol, productivity should increase.

Table 8.9 Cassava: Area and productivities 2001-2005

		Year				
	unit	2001	2002	2003	2004	2005
Area	[ha]	190,200	172,100	176,000	177,600	180,600
Yield	[ton roots ha^{-1}]	10.41	10.34	10.60	11.04	11.04

Although the production of cassava has changed, i.e. from a peasant economy crop to a market oriented one, and the crop has received a lot of attention from the government and research institutions as CIAT (Centro Internacional de Agricultura Tropical), it is still valid to describe the production of cassava as mentioned by (Bajes Mora 1998) as follows: (i) the crop is produced mainly by smallholder in terrains with an average size of 1.4 ha. This is especially valid for the production in the Atlantic coast. (ii) There are a high number of producers predominantly small in size, (iii) Poor technology developments, (iv) Great yield variation across the country and even within regions.

Besides being a source of basic nourishment, i.e. 70% being used fresh for domestic consumption, cassava is a product with high potential for production and alternative use considering its possibilities for obtaining processed products. In Colombia two general markets exist for cassava: fresh and processed. The fresh market is the most important one and comprises a fresh root segment, pre-processed roots and snacks (Balcazar and Mansilla 2004). The processed market could be further divided in three, namely food industry (production of flour, production of sweet starch, production of bitter starch) animal feed and non-food purposes (modified starch, organic acid, polysaccharides, solvents and pharmaceutical.

Lately, cassava has received a lot of attention as a feedstock for bioethanol production. Due to its starch content, cassava bioethanol projects are on the move in Colombia.

The yields of anhydrous ethanol varied depending on the starch content in fresh cassava roots. Cassava rich in starch (30%) could produce 280 l EtOH ton^{-1} while cassava with 20% starch reaches yields of 180-190 l EtOH ton^{-1}. According to the Colombian Ministry of Agriculture ethanol yields from cassava per year should reach 4500 l EtOH $ha^{-1}yr^{-1}$. Considering ethanol yields of 190 l ton^{-1} such target implies raising cassava root yields to at least 23.5 ton ha^{-1} yr^{-1}.

Main by-products generated by the ethanol production industry from cassava are cassava aerial biomass, i.e. leaves, petioles and part of stalks, wastewater from root washing, peels, bagasse and vinasse. Approximately 87.5% of the stalks produced are available, the rest being used as planting material for the next season (Lopez 2002). Leaves and petioles are either left in land or added value for animal feed production. Cassava peels and bagasse are produced in similar amount showing as well similar solids and organic content. Vinasse is produced in great quantities 12-15 l $lEtOH^{-1}$ (Klinsukont et al. 1991; Wilkie et al. 2000) and is a crucial residue to treat due to its undesirable characteristics for direct reuse or disposal including offensive high organic load and odor. The wastewater from root washing is also a substantial amount with a low polluting load and nutrient content.

5.4 Oil palm

As in the case of sugarcane, the oil palm sector in Colombia is characterized by a strong gremial organization. The main gremial structure is the National Federation of Oil Palm Growers (Fedepalma) which represents the interests of the sector and provides supports services to growers. Through *Fedepalma*, the oil palm sector in Colombia relies on other organizations aimed at providing different services: *Cenipalma* is in charge of research and technology transfer in issues dealing with extraction, palm oil uses and cropping, *Acepalma* is the trading organization for the palm oil and other derivates obtained (80% of exports occurred via Acepalma), and *Propalma* is a promoter of agroindustrial projects to strengthen the sector.

The crop was introduced in Colombia in 1932. Nowadays, the country is the first oil palm producer in Latin-America whereas worldwide is the fifth producer, although very far away in volume and area from Malaysia, Indonesia and Nigeria.

In Colombia production and processing of oil palm is concentrated in four regions. The north region, the east region in the outskirts of the Andean mountains, the central region along the Magdalena River valley and the southern tip of the department of Cesar, Norte de Santander and Santander (Fedepalma 2009).

In year 2007, there were about 316402 has cultivated, out of which 201,040 ha were productive plantations and 115,362 ha were plantations in development (See Table 8.10). The sector is composed by 4,500 oil palm growers and 51 oil palm extraction sites. The area planted has had an important growth in recent years, partly due to the governmental impulse given to the crop via tax exemption. From 2000 to 2004, 94,601 new hectares of oil palm where cultivated, representing a 62.9% increase. Such increase took place before the biodiesel debate became active at governmental institutions.

Table 8.10 Oil palm: Extension and productivities 2001-2005

		Year				
	unit	2003	2004	2005	2006	2007
Area in production	[ha]	146,790	153,216	163,770	177,852	201,040
Area in development	[ha]	60,011	85,710	106,256	114,717	115,362
Total area planted	[ha]	206,801	238,926	270,026	292,562	316,402
Palm oil produced	[ton]	526,634	630,388	672,597	715,687	732,445

Average oil efficiency in Colombia is 3.7 ton of palm oil ha^{-1}. For year 2007, approximately 730 kton of palm oil were produced. Of the total oil production, 35% was exported, 58.5% was allocated in the national oil and fat industry and 6.5% was supplied to the animal feed and soap industries.

In recent years, and as part of the biofuels program, oil palm has been the center of attention for biodiesel production. According to the Ministry of Agriculture, 5,500 l $ha^{-1}yr^{-1}$ are expected to be obtained.

Out of one ton of palm oil approximately one ton of biodiesel is obtained. Different residues are produced in the process including leaves and trunks, empty fruit bunches (EFB), palm oil mill effluent (POME), fibres and palm kernel cake (PKC). Leaves and trunks are lignocellulosic materials, not high in nutrient content, which are mainly used as soil amendment, to protect new plants and for construction. About 75 ton DM are generated when renewal pruning is performed, their incorporation in the soil is associated with increase in yields. EFB are fibrous residues rich in nutrients and organic matter, produced at about 6-7 ton $ha^{-1}yr^{-1}$. Due to their high Si and K content and relatively high humidity, i.e. 50-70%, they are not commonly employed for combustion. Instead, they are usually transported back from the extraction plant and incorporated into the fields as soil amendment. POME is the viscous brown residual water from the oil extraction which comprises the sterilizer condensate, separator sludge and hydrocyclone waste. For a well-controlled conventional mill, about 0.9, 0.1 and 1.5 m^3 of each are generated per ton of crude palm oil produced (Borja et al 1996). Approximately 120 kg fiber are produced per ton fruit bunch process. Despite their humidity content, 30-40%, they are a very important source of energy for oil palm mills due to their high volatile solids, low carbon and high oxygen content. Finally the PKC, resulting together with the fiber from the extraction process, has a high calorific value and is commonly used as animal feed supplement (MAVDT 1998).

5.5 Comparative review: Agriculture chains with energy potential

As seen in the sections before, agricultural chains with energy potential in Colombia vary importantly on their characteristics. While some are very organized sectors, others are less structured ones. Crop location changes from crop to crop, as well as the type of farmers. All these variations determine the conditions for the production of biofuels to succeed. In Table 8.11 main features characterizing biofuel production are summarized per feedstock.

As seen so far, it is rather evident to understand how biofuels production have had such a rapid absorption in the sugarcane and oil palm industries where high yields, centralization of decision making, concentration of land and rapid technological adjusting among other predominate.

Cassava and panelacane are the contrasting case. Despite of both having adequate ethanol yields in terms of l EtOH ton^{-1} when average crop yields for both crops are considered the ethanol yields in terms of l EtOH ha^{-1} are low, particularly for cassava. This, together with the low level of organization of the sectors, places them in disadvantage with respect to sugarcane as feedstocks for bioethanol. Because of the previous, it is very much expected that biofuels projects based on these two feedstocks will occur in regions where there is a moderate to high level of concentration of the crop (at least regionally) and where crop yields per ha are the highest. In the case of panelacane, such conditions, as explain before, predominate in regions as Santander and Boyacá in exploitations ranging from 20 to 30 ha and with yields similar to those of sugarcane. In the case of cassava, the use of special industrial varieties is most likely to occur.

Table 8.11 summarizes main differences between biofuel feedstocks. Energy yields per ha per year are calculated using as reference the average crop yields in Colombia instead of the ideal target yields used by governmental or private organizations for their estimations. Therefore, it is important to note that for the case of cassava and panelacane results are particularly low in comparison to those targeted by the Ministry of Agriculture which are for panela 9,000 l ha^{-1} yr^{-1} and for cassava 4,500 l ha^{-1} yr^{-1}.

Table 8.12 summarizes land requirements based on projected bioethanol and biodiesel planned production. Percentages indicate the proportion of the national demand that would be covered from the planned production under both modest and aggressive blending scenarios (Tables 8.5 and 8.6).

For bioethanol, results portray lack of supply in the first year followed by an important increase of production from 2010 which will largely cover the national demand under the modest blending scenario. When considering the aggressive blending scenario a lack of supply would be expected in 2015. It is important to note how cassava gains importance over the years as bioethanol feedstock passing from a small participation in year 2006 to a predominant one in 2020. Withstanding to observe is the fact that if such increase in cassava takes place in reality, the area planted will need to grow substantially or current areas should divert its production to biofuels. Table 8.12 also shows that in the modest scenario, overproduction results which might be targeted to international markets. Under the aggressive scenario, exports are still likely to occur as overproduction takes place after year 2010. Regardless of the scenario, the growth in the total area planted for bioethanol purposes will be immense, having a tenfold enlargement from year 2006 to 2020, and being particularly important in the case of cassava in which case the area needed for bioethanol purposes is 1.6 times the current area planted for food purposes. In the case of sugarcane and panelacane growth will be more moderate.

In the case of biodiesel, oil palm area planted should grow substantially to be able to cover the needs of production. A fivefold growth by 2020 with respect to the area needed in 2003 for biodiesel production is expected. When comparing with national demand in both, the modest and aggressive scenarios, overproduction is expected. The previous underlines the importance of exports for the biodiesel projects. The excess of supply is evident when looking at the modest scenario which since first years deliver more than the national demand and reaches an immense 577% in year 2020. When looking at the aggressive blending scenario, percentages are more moderate.

Table 8.11 Summary of agricultural chains with bioenergy potential

Generalities						Area and yields				
Feedstock	**Type of production**	**Concentration**	**Type of stakeholder**	**Vulnerability**	**Capital tenure**	**Total area 2003 [ha]**	**Average crop yields # [ton ha^{-1}]**	**Target crop yields## [ton ha^{-1}]**	**Energy yields # [l ton^{-1}]**	**Energy yields## [l ha^{-1} yr^{-1}]**
Sugarcane	Medium to large plantations, highly mechanized and technified and associated with agroindustrial clusters	Highly concentrated (Cauca Valley)	Medium to big producers, high level or organization.	Dependant on national and international markets	Concentration of property and/or land control	168,633	122	120	72	8,784
Cassava	Peasant economy crop. Poorly mechanized.	Dispersed	Mostly small farmers. Low level of organization.	Highly dependent on local market	Non concentrated property	176,000	11.04	26	190	2,097
Panela cane	Peasant economy crop. Poorly mechanized and associated with artisanal processing	Dispersed	Mostly small farmers. Low level of organization	Highly dependent on local market	Non concentrated property	246,057	69	120	72	4,968
Oil palm (Crude Palm Oil)	Medium to large plantations, highly mechanized and technified and associated with agroindustrial clusters	Concentrated in four production poles	Medium to big producer, high level of organization	Dependant on national and international markets	Concentration of property and/or land control	146,790	3.71	3.71	1,193	4,426

\# Average yield refers to average productivities in Colombia for year 2005

\## Target yields refer to yields assumed by the Colombian government for their estimations

Table 8.12 Land requirements and expected covered demand for biofuel production in Colombia (Modest and aggressive scenarios as shown in Tables 8.5 and 8.6)

Bioethanol

	2003	2006			2010			2015			2020		
	Total area planted [ha]	Area [ha]	National demand covered modest scenario	National demand covered aggressive scenario	Area [ha]	National demand covered modest scenario	National demand covered aggressive scenario	Area [ha]	National demand covered modest scenario	National demand covered aggressive scenario	Area [ha]	National demand covered modest scenario	National demand covered aggressive scenario
Sugarcane	168,633	35,605	60.8%	60.8%	60,990.2	114.6%	76.4%	60,990	109.7%	43.9%	60,990	96.5%	38.6%
Cassava	176,000	3,481	1.4%	1.4%	110,091.8	49.3%	32.9%	157,958	67.7%	27.1%	277,623	104.7%	41.9%
Panelacane	246,057	0	0%	0.0%	53,876	57.1%	38.1%	53,876	54.7%	21.9%	53,876	48.1%	19.3%
Total production	590,690	39,086	62.2%	62.2%	224,958	221.0%	147.3%	272,824	232.07%	92.8%	392,489	249.4%	99.7%

Biodiesel

	2003	2008			2010			2015			2020		
	Total area planted [ha]	Area [ha]	National demand covered modest scenario	National demand covered aggressive scenario	Area [ha]	National demand covered modest scenario	National demand covered aggressive scenario	Area [ha]	National demand covered modest scenario	National demand covered aggressive scenario	Area [ha]	National demand covered modest scenario	National demand covered aggressive scenario
Oil palm	146,790	156,616	233%	233%	185,983	254%	127%	379,674	400%	100%	709,622	577%	144%

6 THE ROLE OF ANAEROBIC DIGESTION IN EXISTING BIOFUEL CASCADES IN COLOMBIA: ENERGY, LAND, WATER AND NITROGEN IMPLICATIONS

In this section the potential role of AD in Colombia is broadly approached by comparing the energy balances and efficiencies for different bioenergy cascades departing from the crops being currently promoted for biofuel production in Colombia. Within the system boundaries the biomass production unit, the biomass processing unit and AD unit are considered (Figure 8.6).

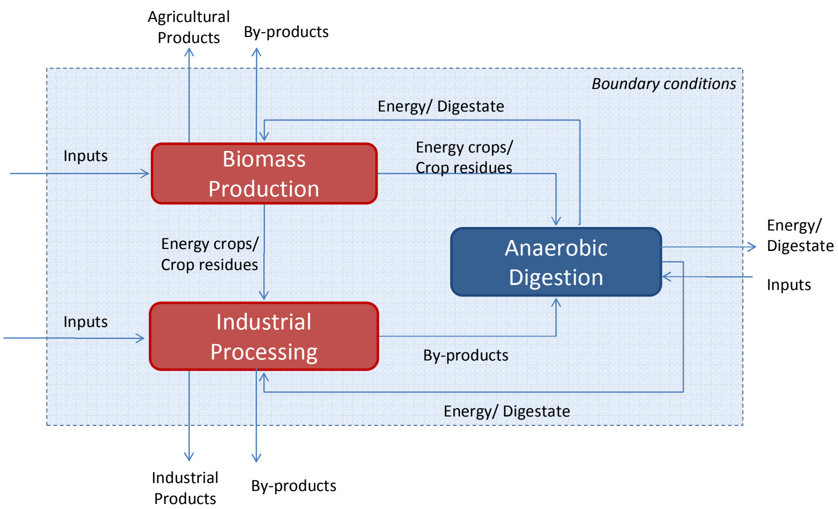

Figure 8.6 System definition used for cascade analysis

The analysis departs from the calculation of the energy balances and energy efficiencies of the existing processes without accounting for any use to the by-products. Such scenario is then compared with alternative scenarios where by-products are added value using AD and with the hypothetical situation where the whole crop is used for bioenergy purposes. Table 8.13 present the cascades analyzed for each biofuel commodity.

Table 8.13 Cascades analyzed for each commodity

		Flows digested			
	General Description	**Sugarcane**	**Panelacane**	**Cassava**	**Oil palm**
A	Biofuel	None	None	None	None
B	Biofuel+AD industrial by-products	Vinasse+Bagasse	Vinasse+Bagasse	Vinasse+Bagasse	POME+Fruit residue+Glycerine
C	Biofuel+AD industrial by-products and biomass by-products	Vinasse+Bagasse +Trash	Vinasse+Bagasse +Trash	Vinasse+Bagasse+ Leaves and stalks	POME+Fruit residue+Glycerine+Lea ves
D	Methane from full plant	Full plant	Full plant	Full plant	Full plant

All flows have been calculated in terms of mass, nitrogen and energy. Nitrogen and mass flows are converted to energy equivalents considering in the first case average energy content of 60 MJ ton^{-1} N fertilizer, and in the second case lower calorific values (LCV) of each of the biomass fractions. Due to the recent development of the biofuel industry data availability specific for Colombia is very limited. Cassava data is taken from the case study performed in this thesis. Biomass yields for sugarcane, panelacane and oil palm correspond to average 2003-2007 in Colombia as shown in previous sections. Biofuel yields are those reported by Colombian authorities, i.e. target crop yields presented in Table 8.11. By-product yields and composition are specific for Colombia in the case of cassava (Chapter 7 of this thesis) and oil palm (MAVDT 1998) and assumed for the Brazilian case in the case of sugarcane and panelacane (van Haandel 2005). Data on energy consumption for biomass and biofuel production is specific for Colombia only in the cassava case (from Chapter 7 of this thesis) whereas in the case of sugarcane, panelacane and oil palm data was taken from the study by Brehmer (2008b) in which optimal conversion efficiencies are assumed, i.e. Brazilian case for sugarcane and Malaysian case for oil palm. For the calculation of the added value of AD, digestibility of different flows were assumed from different studies, i.e. for sugarcane (van Haandel 2005), for oil palm (Atil 2005; Borja et al. 1996) and for cassava Chapter 7 of this thesis. The digestibility of the whole plant as necessary for the calculation of scenario D, was assumed to be that of the by-products as in cascade C plus 90% of the energy content in the biofuel being replaced. In all cases a 15% energy use of the AD system with respect to total methane output was considered assuming no energy is used for heating the reactor (Berglund and Borjesson 2006). Main assumptions for the calculations performed are presented in Table 8.14 whereas Figures 8.7 and 8.8 summarize the results of the assessment on the value of anaerobic digestion for recovering the energy contained in by-products of the biofuel industry.

As can be observed great differences are found among the cascades studied. In all cases a negative net energy outcome is found in systems A, which is the result of accounting not only for the energy inputs for biomass production and industrial processing, but also for the energy embedded in by-products.

The contribution of by-products appears crucial constituting 41-68% of the sum of all energy flows. Energy in by-products including field residues constitute 51%-71% of the total energy content in the crop. Industrial by-products constitute a lower share of the crop energy as compared to residues from crop production except in the case of oil palm. The proportion of the energy content present in the aerial biomass as compared to the total energy fixated by the plant is 26%, 7%, and 34% for cassava, oil palm and sugarcane, respectively. In the case of oil palm, the energy content of the trunks which are replaced every 25 years has not been considered. Due to the energy importance of by-products, when they are added value as in cascades B and C, much higher net energy outputs are produced. The energy content in aerial biomass appears especially relevant when comparing cascades B and C. As can be observed, the net energy output of sugarcane, panelacane and oil palm become positive only when this flow is included.

Table 8.14 Main assumptions employed for energy calculations

	Unit	Bioethanol from sugarcane	Bioethanol from panelacane	Bioethanol from cassava	Biodiesel from oil palm
Energy use for biomass production	[GJ ha^{-1} yr^{-1}]	9.5	5.5	9.2	16.0
-Farming	[GJ ha^{-1} yr^{-1}]	3	1.7	3	2.2
-Fertilizer	[GJ ha^{-1} yr^{-1}]	4.6	2.7	4.1	13.1
-Other inputs #	[GJ ha^{-1} yr^{-1}]	1.9	1.1	2.4	0.7
Energy use for industrial processing	[GJ ton biofuel^{-1}]	6.9	6.9	11.1	13.9
-Electricity	[GJ ton biofuel^{-1}]	1.5	1.5	1.8	0.4
-Thermal	[GJ ton biofuel^{-1}]	5.2	5.2	9.3	9.3
- Other inputs ##	[GJ ton biofuel^{-1}]	0.25	0.25	0.25	4.2
Biofuel productivity	[GJ ha^{-1} yr^{-1}]	189.1	109.2	93.8	157.9
By-product output					
-Green biomass**	[ton ton^{-1} agric product]	0.33(70%)*	0.33 (70%)	4.3 (70%)	1.1 (70%)
-Vinasse/POME	[ton ton biofuel^{-1}]	19.1 (80%)	19.1 (80%)	17.5 (90%)	2.5 (90%)
-Bagasse/Fb+EFB+PKC	[ton ton biofuel^{-1}]	5.1 (50%)	5.1 (50%)	3.1 (50%)	3.3 (50%)
-Glycerine	[ton ton biofuel^{-1}]	-	-	-	0.10 (90%)

Considers only pesticides. ## Energy in additives.*In parenthesis assumed anaerobic digestibility. ** Green biomass corresponds to trash in sugarcane, leaves and stalks in cassava and leaves in oil palm.
POME; Palm Oil Mill Effluent; EFB: Empty Fruit Bunches; PKC: Palm Kernel Cake.

Similar energy outcomes to cascade C are produced when the total plant is assumed to be digested, i.e. cascade D. In this case energy outcome fluctuates between 90 and 210 GJ ha^{-1} yr^{-1}. Cassava, panela cane and oil palm deliver similar results whereas sugarcane offers the highest energy outcome. Due to the limited digestibility assumed for aerial biomass and lignocellulosic residues like bagasse, the energy content left in by-products from AD is still significant as shown in Figure 8.8. If this energy is to be harvested via combustion for example, the net energy output of cascades B in the case of oil palm, sugarcane and panelacane becomes positive whereas cascades C and D can almost double their energy output.

It is also important to notice that the by-products from AD still have a substantial energy content which could be further recovered for example via combustion as proposed by van Haandel (2005) for the sugarcane case.

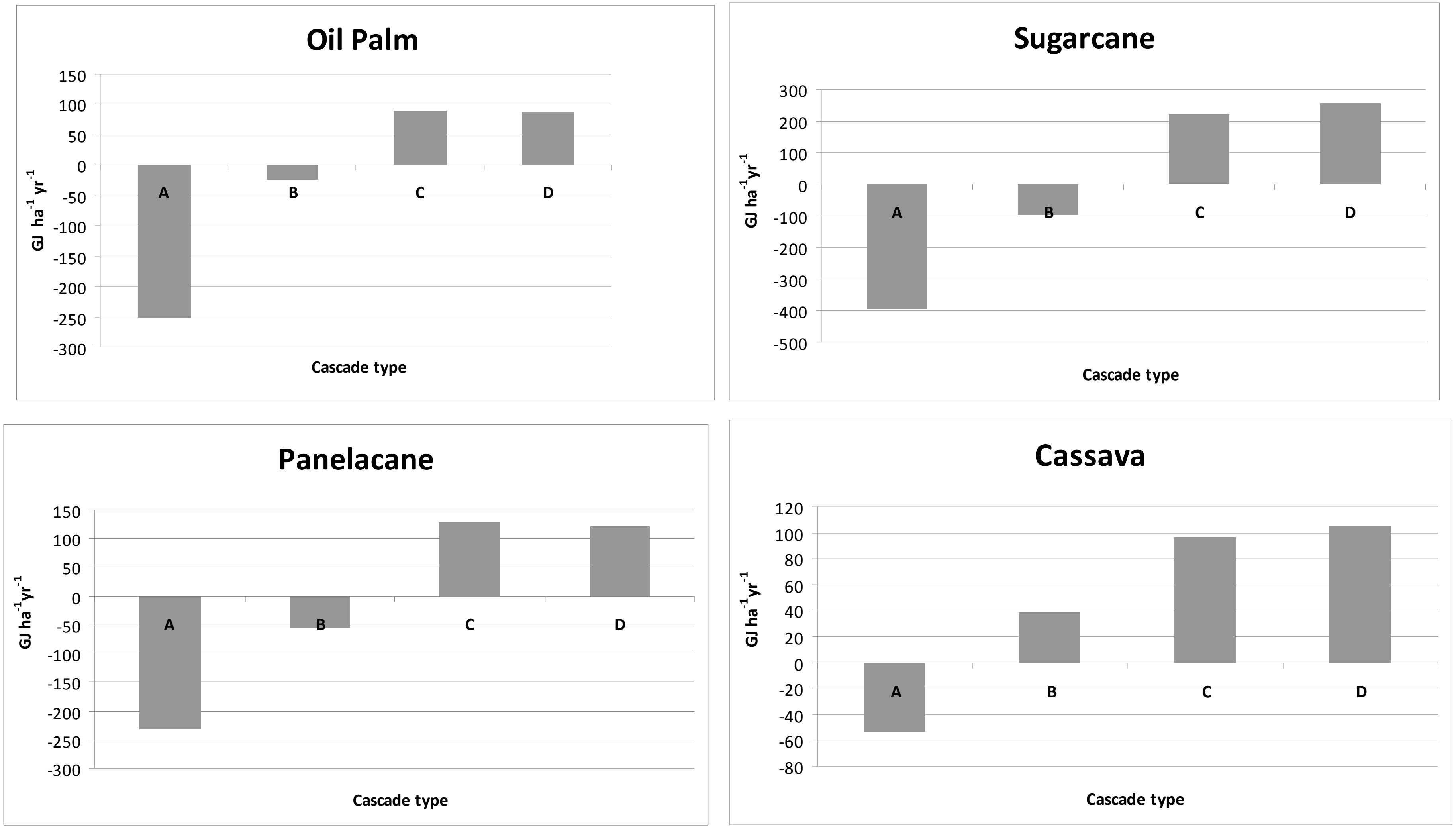

Figure 8.7 Energy outcomes of four alternatives cascades based on the current Colombian biofuel commodities with and without anaerobic recovery of the by-products (Cascade types according to Table 8.13).

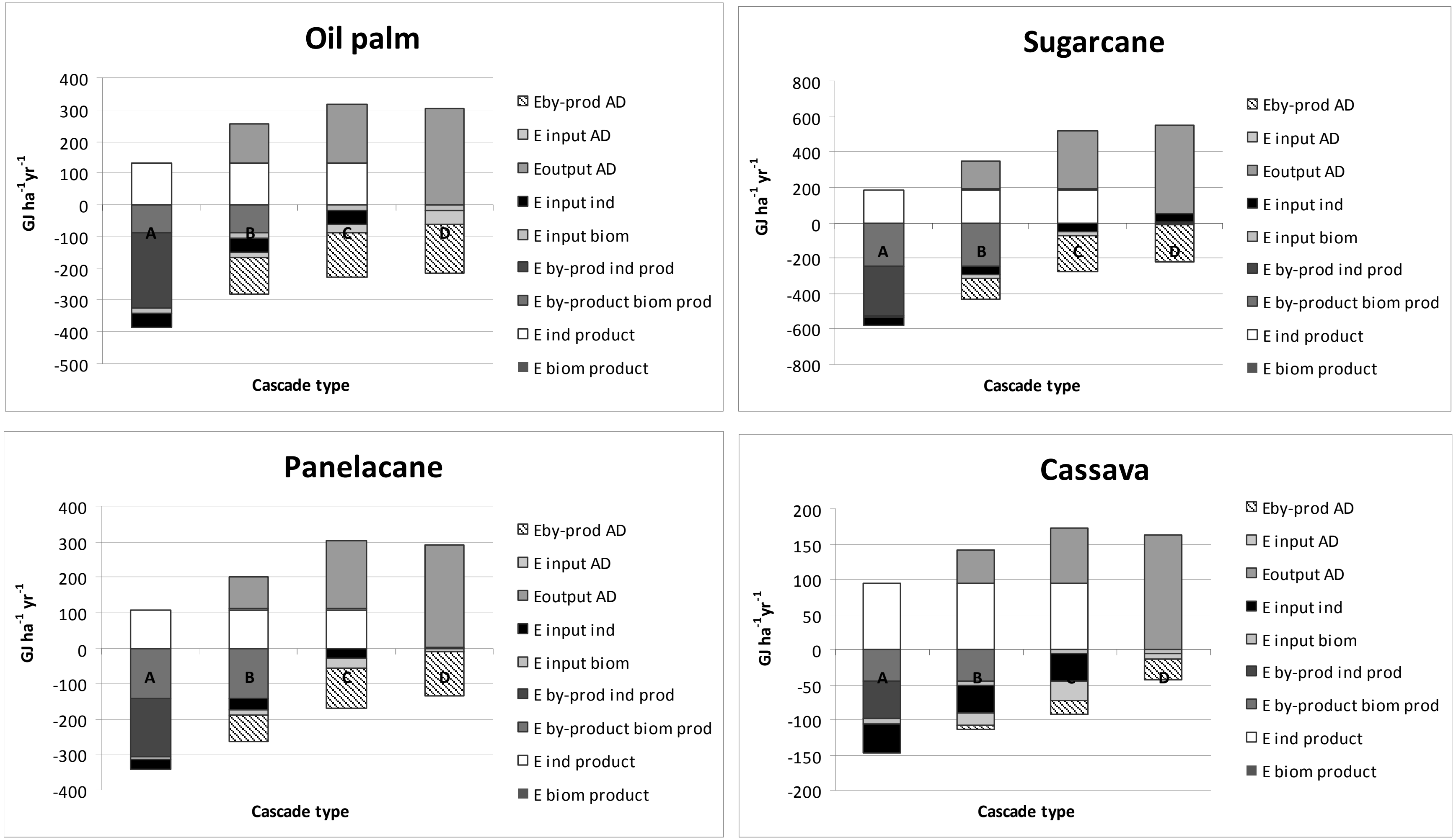

Figure 8.8 Distribution of energy flows among energy inputs, products and by-products for four alternatives cascades based on the current Colombian biofuel commodities with and without anaerobic recovery of the by-products. (Cascade types according to Table 8.13).

Ebiom product: Energy in biomass products exported from the system; *E ind product*: Energy in industrial product exported from the system; *Eby-product biom prod*: Energy in biomass by-products exported from the system; *Eby-prod ind prod*: Energy in industrial product exported from the system; *Einput biom*: Energy input for biomass production; *Einput ind*: Energy input for industrial production; *Eoutput AD*: Energy output AD unit; *E input AD*: Energy input AD unit; *Eby-prod AD*: Energy from the residues remaining in the digestate.

The $E_{balance}$ of the cascades was calculated by excluding the non-utilized energy content of the by-products in order to better foresee the contribution of anaerobic digestion for energy recovery. Energy balances for cascades A not benefiting from AD, are in this case 72, 128, 75, 45 GJ ha yr^{-1} for oil palm, sugarcane, panelacane and cassava, respectively. The extra net energy outcome delivered by AD as calculated for the other cascades has been converted into biofuel equivalents and equivalent land savings as shown in Table 8.15. In the same table, the positive contribution of AD for the recovery of nutrients and water is also exemplified.

Table 8.15 The added value of AD to biofuel cascades in Colombia. (Definition of the cascades as in table 8.13)

Oil palm

	Extra Net Energy Output from AD		Equivalent extra biofuel			Land savings	N in digestate	Water in digestate
	[GJ ha^{-1} yr^{-1}]	Relative to cascade A	[l ha^{-1} yr^{-1}]	[GJ yr^{-1}]	[l yr^{-1}]	[ha]	[ton yr^{-1}]	[ton yr^{-1}]
B	105	1.5	2,933	19,552,332	545,502,363	270,461	3,169	3,073,466
C	158	2.2	4,395	29,294,828	817,314,171	405,225	25,450	3,995,941
D	170	2.3	4,730	31,530,408	879,685,969	436,149	25,450	2,703,523

Sugarcane

	Extra Net Energy Output from AD		Equivalent extra biofuel			Land savings	N in digestate	Water in digestate
	[GJ ha^{-1} yr^{-1}]	Relative to cascade A	[l ha^{-1} yr^{-1}]	[GJ yr^{-1}]	[l yr^{-1}]	[ha]	[ton yr^{-1}]	[ton yr^{-1}]
B	144	1.1	7,725,830	7,725,830	215,547,606	106,869	10,978	8,727,698
C	290	2.3	11,574,750	11,574,750	322,930,976	160,110	13,449	10,658,004
D	296	2.3	14,069	18,030,669	858,076,162	143,028	13,449	1,868,038

Panelacane

	Extra Net Energy Output from AD		Equivalent extra biofuel			Land savings	N in digestate	Water in digestate
	[GJ ha^{-1} yr^{-1}]	Relative to cascade A	[l ha^{-1} yr^{-1}]	[GJ yr^{-1}]	[l yr^{-1}]	[ha]	[ton yr^{-1}]	[ton yr^{-1}]
B	84	1.1	4,008	4,537,893	215,957,506	60,256	5,388	4,452,969
C	170	2.3	8,069	9,134,755	434,721,310	121,294	6,665	5,450,887
D	172	2.3	8,200	9,283,641	441,806,746	123,271	6,665	965,727

Cassava

	Extra Net Energy Output from AD		Equivalent extra biofuel			Land savings	N in digestate	Water in digestate
	[GJ ha^{-1} yr^{-1}]	Relative to cascade A	[l ha^{-1} yr^{-1}]	[GJ yr^{-1}]	[l yr^{-1}]	[ha]	[ton yr^{-1}]	[ton yr^{-1}]
B	44	1.0	2,099	4,856,064	231,099,183	108,921	6,564	6,075,733
C	71	1.6	3,370	7,796,169	371,018,245	174,867	17,599	7,302,152
D	89	2.0	4,227	9,778,987	465,380,187	219,341	17,599	3,072,634

From table 8.15 it can be observed that, extra net energy outputs for the different crops fluctuate between 44 and 144 GJ ha^{-1} yr^{-1} when only industrial by-products are recovered, i.e. cascade B, whereas when all by-products are added value using AD benefits can increase to 71-290 GJ ha^{-1} yr^{-1}. When the full digestion of the crop is considered 89-296 GJ ha^{-1} yr^{-1} extra net energy outputs result as compared with current biofuel systems being promoted. In terms of land all these savings would mean that for all crops a minimum saving of one hectare per hectare land invested could be saved which is the case when only industrial by-products are added value. In other words, half of the land demanded would be needed to provide the same energy output. Savings from the other systems are even greater, when AD is used to add value to the whole crop around two times more energy is produced as compared to bioethanol or biodiesel systems, meaning only 30-35% of the area used to produce the biofuels is needed to deliver the same energy output.

The added value of AD to biomass chains is also important in terms of nutrient recovery. In the case of cassava, 25-30% total N, 45-55% total P and 55-60% total K is removed in the root harvest (Howeler 2001) and therefore are expected to be found back in the by-products of bioethanol processing, i.e. vinasse, bagasse and peels. The case of sugarcane portrays a different scenario. In this case only a minor portion of the nitrogen remain in the aerial biomass, i.e. 10% of the fertilizer applied, the rest being found back in the vinasse and bagasse with the majority of it in the bagasse, i.e. 80%. In contrast, phosphorus is mainly found in the vinasse, which can supply 60% of the fertilizer demand whereas bagasse contains only 8% of the phosphorus (Kee Kwong et al. 1987; van Haandel 2005). Anaerobic digestion is specially suited over other technological alternatives like combustion; composting or animal feed production to recover this value. If aerial biomass is exported from the system for animal feed production for example, these nutrients need to be compensated by the use of additional artificial fertilizer, which implies extra costs that need to be compensated by the extra income from the animal feed sales. If residues are composted only a fraction of the nitrogen is recovered in the final product, i.e. 35%. Similarly if by-products are left in the field for decomposition nutrients are only partially incorporated in the soil for the next cropping season. When combustion is performed Nitrogen is lost whereas Phosphorus and Potassium can be partially recovered in the ashes depending on the temperature used of the operation. As depicted in table 8.15 the advantage of anaerobic digestion to recover nutrients from industrial effluents is especially evident in the case of sugarcane and panelacane, whereas in the case of oil palm and cassava, the flows from the digestion of aerial biomass are especially important.

The recovery of water via anaerobic digestion represents not only an advantage but a need given the organic load in the effluents from biofuel production and their high water consumption. The digestion of the whole crop represents very important water savings in this case since digestion can be performed at high solid content in contrast with ethanol and biodiesel industries requiring high amounts of water. For the studied systems advantages in terms of water savings from current biofuel producing systems to full anaerobic digestion biomass conversion fluctuate between 1,292 and 8,789 kton yr^{-1} for oil palm and sugarcane, respectively, i.e. cascade D as compared to cascade C.

Beyond the presented estimations, when analyzing the use of residues for anaerobic digestion, the theoretical values need to be confronted with the reality regarding the existing uses for by-products. Palm kernel cake and oil palm leaves, are rich in nutrients and have been proven to be feeds of high quality. The same is valid for leaves of the cassava plant. Other by-products as oil palm fibres and sugarcane bagasse can be combusted providing significant energy savings in the industrial processes which tend to be intensive in use of thermal energy. On the other hand residues such as sugarcane trash, vinasse and palm fruit bunches remain interesting energy sources as their current management cause environmental problems. Figure 8.9 shows a comparison of the nutrient and energy content of the different flows as compared to soy bean meal and corn. Although the actual value of the by-products for animal feed or combustion will also depend on other factors such as digestibility and water content, the figure allow categorization of the flows. As can be observed the nitrogen content of the flows seems low as compared to that of soybean meal. In terms of energy, palm kernel cake, palm fiber, sugarcane bagasse and glycerine show interesting attributes.

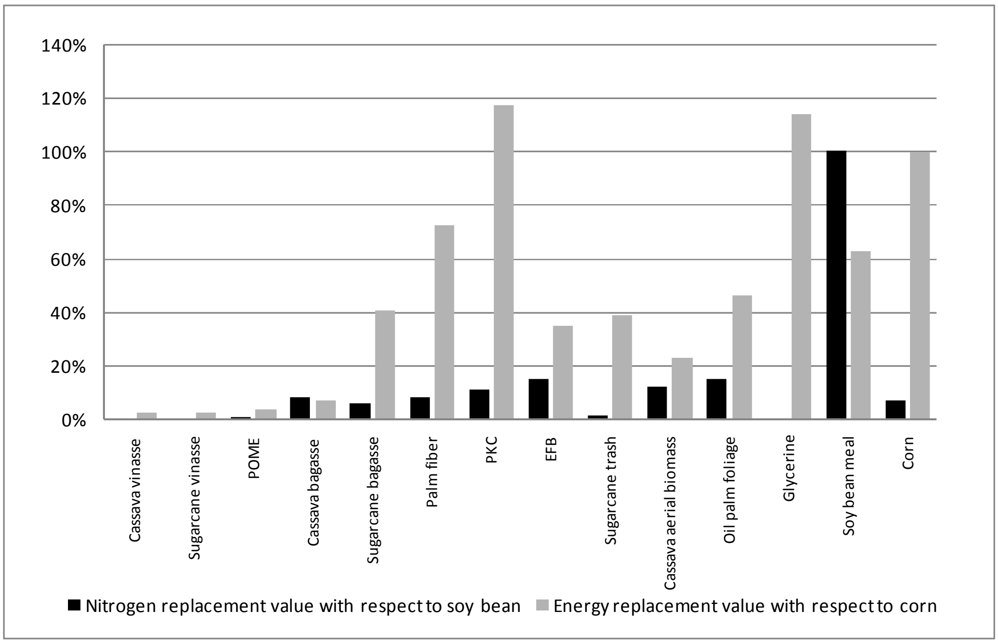

Figure 8.9 Nitrogen and energy content of the different by-products analyzed relative to soy bean and corn, respectively (Abbreviations as in Table 8.14).

The actual use of by-products by the different agroindustries is expected to be high. In the case of oil palm according to MAVDT (1998), 70-80% of the residues including the leaves are already receiving a use. In the sugarcane industry in Colombia bagasse is as well receiving a use for electricity generation. Because of the previous, this analysis has been complemented by calculating the net energy outputs when AD is used to digest only the residual wastewaters and 30% of the (semi) solid by-products including aerial biomass. As can be observed in Table 8.16 even under these circumstances, AD is able to provide important land savings, i.e. 70-170% of the land expected to be used in 2010 for biofuel production.

Table 8.16 The added value of AD to biofuel cascades when partial reuse of residues is performed

	Extra Net Energy Output from AD		Equivalent extra biofuel			Land savings	N in digestate	Water savings
	[GJ ha^{-1} yr^{-1}]	Relative to cascade A	[l ha^{-1} yr^{-1}]	[GJ yr^{-1}]	[l yr^{-1}]	[ha]	[ton yr^{-1}]	[ton yr^{-1}]
Oil palm	51	0.7	1,414	9,425,584	262,970,076	130,381	6,571	1,180,999
Sugarcane	122	1.0	5,786	7,415,242	352,889,973	42,756	5,572	9,306,790
Panelacane	71	0.9	3,371	3,816,046	181,604,900	50,671	2,754	4,752,344
Cassava	36	0.8	1,712	3,960,199	188,465,156	88,827	7,550	5,295,258

The final choice regarding the best use of residues will ultimately depend in the economical gains that can be obtained. In order to have a better perspective on the value of AD in the economic context of Colombia, Table 8.17 shows an indication on the price of different products that AD could potentially substitute. As can be observed, natural gas has the lowest price among the compared energy carriers, i.e. only 25% of the price of electricity. Prices of biodiesel and bioethanol as fixed by governmental resolutions are higher than those of natural gas. Therefore if AD is to play a role in the vehicular market, adjustments in legislation providing incentives for its consumption should be made accordingly.

With respect to the value of nitrogen, our data show that animal feed is enormously favored over N fertilizer. Similarly, the monetary value of water is also minimum.

Table 8.17 Prices of substitute products from AD (October 2008)

	Unit	Price
Natural gas	[Col$ GJ^{-1}]	20,129
Gasoline	[Col$ GJ^{-1}]	63,243
Diesel	[Col$ GJ^{-1}]	43,957
Electricity	[Col$ GJ^{-1}]	81,947
Bioethanol #	[Col$ GJ^{-1}]	64,467
Biodiesel##	[Col$ GJ^{-1}]	61,392
Nfertilizer*	[Col$ KgN^{-1}]	2,043
Water	[Col$ ton^{-1}]	3,000
Animal feed **	[Col$ KgN^{-1}]	8,069,538
Land rental***	[Col$ ha^{-1} yr^{-1}]	315,000

RESOLUCIÓN MME 18 0222, 27/02/06. ## RESOLUCIÓN MME 182160. 28/12/07
*For urea (46-0-0) ** Calculated base don the price of nutritional blocks from cassava, considering 18,156 Col$ per unit and 0.0023 Kg N from vinasse per unit (Arriaga Sierra 2008)
***Land rental price in the Atlantic region (Arriaga Sierra 2008)

Finally, the added value of AD was calculated in brut economic terms considering that methane is used for electricity production at 35% efficiency, whereas digestate is valued for its N and water content. As can be observed in Figure 8.10 the low contribution of N fertilizer replacement and water replacement to total economic benefits is evident. Still substantial savings are obtained ranging from 130,000 to 965,000 million Col$ per year, equivalent to 1.5

and 9 million per ha per year, respectively. The highest economic benefits per year are obtained in the case of oil palm, followed by sugarcane.

From the presented analysis it is clear that anaerobic digestion of by-products from Colombian biofuel industry can provide with substantial land savings as well as significant advantages in terms of water and nutrient recovery. It has also been shown that AD of the full crop can provide with similar net energy output as compared to systems producing biofuels and digesting residues. Current biofuel systems seem however inefficient from the perspective of energy use if considering by-products are exported from the system. The ultimate desirability of implementing AD systems to add value to by-products depends on the alternative uses they are actually receiving and the market trends. Since in Colombia the infrastructure for delivering natural gas exists for both vehicular and the domestic/industrial market, the feasibility of promoting biogas as energy alternative will depend upon its economic competitiveness with other energy carriers within those markets. Further, the incentives given for the extra benefits provided by the technology, i.e. nutrient provision and water savings can be of crucial importance if considering their important amounts. The feasibility of AD technology will also depend upon environmental legislation providing adequate valuation of the avoidance of negative externalities from by-products of the biofuel industry such as water pollution and GHG emissions.

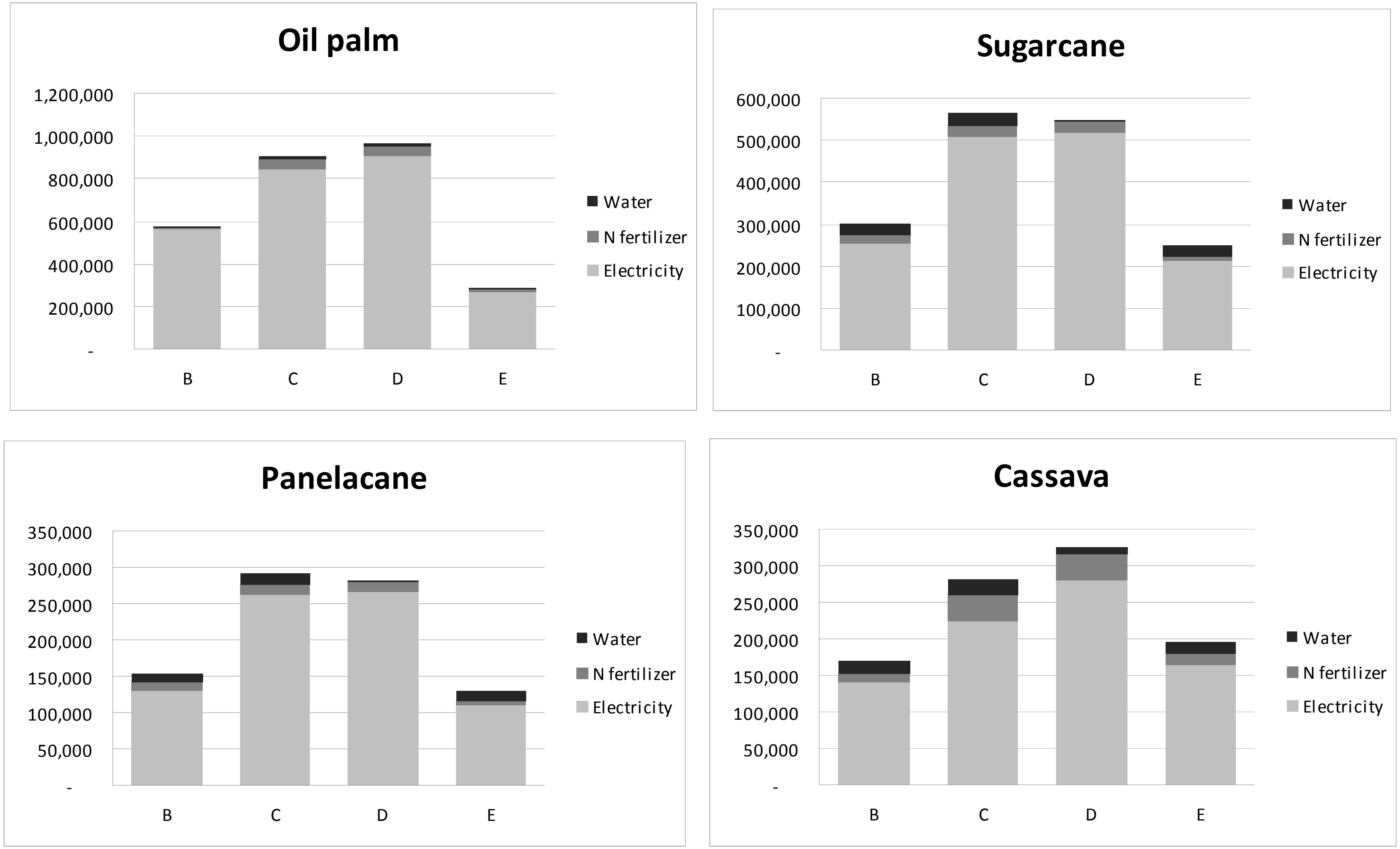

Figure 8.10 Distribution of economic benefits from AD in million Colombian pesos per year (Methane produced is used for electricity production at 35% efficiency; Cascade types according to Table 8.13.

Chapter 9

Summary and General Discussion

1 INTRODUCTION

The overall objective of this thesis has been to assess the potential contribution of anaerobic digestion (AD) to the sustainability of biomass chains. Research questions underlying this thesis are invoked by the increased interest in bioenergy as an alternative to fossil fuels coupled with augmented concerns regarding competing claims for land and other resources. Whereas numerous opportunities for adding value to biomass cascades by recovering useful energy and enhancing possibilities for closing nutrient, water and carbon cycles are foreseen from anaerobic digestion, so far its protagonism has been limited.

The lack of methodology to assess the possible contribution of anaerobic digestion (AD) in biomass cascades as well as the existence of knowledge gaps regarding technological potential were main challenges undertaken as part of this research.

The main objective of this thesis has been *to assess the contribution of anaerobic digestion to the sustainability of biomass chains, by gaining insight in the technological potential of anaerobic digestion to recover energy and valuable by-products from energy crops and agroresidues, and evaluating biomass cascades involving AD technology for their feasibility and desirability*.

From the main objective, five speficic subobjectives derive, namely:

(i) *to develop simple methods for screening plant material suitable for anaerobic digestion*

(ii) *to gain insight in the trade-offs in terms of energy and digestate output during the (co)digestion of crop and residues.*

(iii) *to develop a sustainability framework for the design and evaluation of the contribution of anaerobic digestion to biomass cascades*

(iv) *to apply the environmental dimension of this framework to the evaluation of the role of AD in alternative biomass cascades;*

(v) *to analyze the contribution of AD in the case of Colombia considering current biofuel legislation.*

Following the main findings of this research are described and grouped into relevance categories, i.e. scientific achievements, methodological impacts and societal consequences.

2 SCIENTIFIC ACHIEVEMENT

2.1 Influence of test conditions in BMP assessment of plant material

In this study the impact of different test conditions in the BMP assessment of plant material using the Oxitop ® set-up was prioritized in order to provide guidelines for higher test accuracy and simplification (Chapter 3). The use of NaOH pellets for CO_2 capture and the impact of the combined use of different pretreatment/storage methods for plant samples were studied. In addition, factors affecting the stability of the test such as inoculum type, inoculum concentration and the use of buffering systems were addressed. In the presence of the NaOH pellets, a concomitant accumulation of Volatile Fatty Acids (VFA) and increase in pH occurred resulting in a lower CH_4 recovery. The CO_2 absorption capacity of the pellets at all the tested concentrations negatively impacted the carbonate system in the liquid phase. Drying and grinding plant material influenced the BMP assessment resulting in an BMP increase of 44, 25 and 43% for mustard, endive and green beans, respectively, with regard to the fresh 1 cm samples. Similar findings were reported by Sharma et al (1988). A relationship was found between the increase in BMP with comminution and the proportion of lignin surface in relation to the total fiber surface. Test stability in a BMP test has been shown to be directly related to pH conditions in the assessment. Different inocula show different capacities for the conversion of intermediates to methane and tolerance to toxicity. The previous mainly influencing the conversion rates and test duration but likely also the BMP assessment in relation to pH/VFA toxicity as found in this study. Further, our results have shown a clear inhibitory effect of phosphate buffered bottles with molarities of 30 and 50 mM. Effects were found in both conversion rates and BMPs of plant material, accompanied by acetic acid accumulation. Caution is raised in not exceeding a 20mM concentration as it might affect the BMP assessment of plant material as shown by the observed effect in the control bottle. Our results are in agreement with previous findings of Conrad et al (2000) and Paulo et al (2005), who studied the inhibition of (acetoclastic) methanogenesis by phosphate buffer in anaerobic environments using non-plant samples. The resulting guidelines for proper test performance are provided in 3.1 and 3.2 of this Chapter.

2.2 Resource quality for anaerobic digestion

The developed OxiTop® set-up was employed for screening plant material and developing predicting models for the estimation of the anaerobic biodegradability of plant material with the aim of better defining the resource more suited for anaerobic digestion (Chapter 4). The anaerobic biodegradability of the 15 European plant samples assessed was found to fluctuate between 34 and 70%.

The individual fiber fractions as determined by the van Soest method, i.e. NDF: Neutral Detergent Fibre; ADF: Acid Detergent Fibre; ADL: Acid Detergent Lignin, and the fractions of crude protein and starch were assessed in the 15 plant samples. Empirical and theoretical linear models were developed to get further insight in how substrate composition relates to anaerobic biodegradability. A major contribution of this research has been empirically proving the relation between anaerobic biodegradability to the amount of cellulose plus lignin as analytically assessed by the van Soest method, i.e. ADF value. The possibility of excluding the hemicellulose content in equations for biodegradability estimation has been suggested in this study as the developed models omitting this variable showed a higher predictive value. The latter can be attributed to the higher hemicellulose anaerobic conversion and the fact that it needs to be degraded previously to cellulose. Our findings are in agreement with those recently reported by Buffiere et al (2006) using 6 food wastes suggesting ADF as a good biodegradability estimator, and go beyond into proposing a predictive equation. Moreover our findings contest those of Chandler (1980) proposing lignin as a sole predictor of anaerobic biodegradability whereas they are in agreement with previous reports suggesting the poor value of lignin as a sole estimator of BMP(Chynoweth et al. 1993; Tong et al. 1990). The role of lignin as part of a lignocellulosic complex and especially in relation to the accessibility of cellulose is therefore stressed over solely its intrinsic refractory character. The predictive model was compared to four conceptual models. The later models were found to be statistically sound if judging from the R^2 and F_{test} value. Apart from being theoretically meaningful, the ADF-based empirical model requires the least effort compared to the conceptual models as individual fractions of cellulose, hemicellulose and lignin do not need to be assessed, which enhances the accuracy of the model's estimation.

The ADF model was used to predict the biodegradability of 114 European crop and crop residues samples using a database developed by Stenberg et al (2004). Average biodegradability found was 53%, whereas a four fold difference was found between minimum and maximum values. The database allows distinguishing among biodegradability of different plant parts. The average biodegradability of green leaves, mature straw, pods, stems and whole plants was 63%, 39%, 71%, 44% and 53%, respectively. The previous show how crop residues like straws and stems have in general low anaerobic potential per unit solids. Nonetheless, interestingly, the pods of barley and maize along with the green leaves of oilseed-rape, sugar beet, carrot and hemp were found to be the most promising substrates showing between 70% and 79% anaerobic biodegradability. Hence, a choice for residues instead of plants competing with food is still possible without compromising methane yield per unit solids. From our results and those predicted from the database, several legumes, grasses and residual green leaves of different European crops are identified as having a good potential considering their intrinsic anaerobic biodegrability. Beyond study of equations predicting biodegradability, in Appendix 4.2 of Chapter 4, the results of the study were also meaningful to explore possibilities to predict hydrolysis rates. In this case it was found that the total fiber content provides a reasonably good correlation (R^2=73%) with the first-order hydrolysis constant (k_h).

Also in relation to the resource quality of crops and residues with anaerobic potential, in Chapter 5 of this thesis, the influence of maize-manure ratios on the methane production and the digestate characteristics was studied. The emphasis of the study was the change in nutrient availability, heavy metal content and the methane production potential of the digestate at digestion times exceeding 20 days, and codigestion ratios higher than 30% maize silage. In addition, the availability of nutrients in the liquid and solid part of the digestate was evaluated in order to study their respective application potential. As in the case of experiments performed at shorter digestion times and lower crop content in the mixture, anaerobic digestion favored nutrient availability (Lehtomaki et al. 2007). After 61 days 20-26% increase in NH_4^+ and 0-36% increase in PO_4^{3-} was found. Inorganic nutrients were found to be mainly present in the liquid portion of the digestate, i.e. 80-92% NH_4^+ and 65-74% PO_4^{3-}.

Increase in manure content in the mixture showed a positive effect in the methane production rate and the total amount of nutrients in the digestate. Digestion time and increased proportion of maize silage in the mixture positively influenced the availability of PO_4^{3-}. A linear relation between increase in crop content in the mixture and PO_4^{3-} availability in digestate is observed in all treatments up to 50% maize silage content. No relation was found between the maize: manure ratio and the NH_4^+ behavior in relation to initial concentrations.

2.3 Factors affecting the role of AD within biomass cascades

Beyond the influence of resource quality in the anaerobic digestion potential of crops and residues, the benefits of AD within a cascade are influenced by the specific features of its insertion within a context. The previous pose different restrictions and opportunities regarding boundary conditions, i.e. temperature and transport distances, resource availability, the type and amount of energy demanded and the potential reuse of the nutrients and water.

The influence of the previous factors in the net AD energy recovered by an AD unit from different substrates was exemplified in Chapter 6. Our findings supporting previous studies suggesting that the energy performance of biogas systems is highly dependent on systems conditions especially type of substrate, biogas reuse and digestate reuse (Berglund 2006; Borjesson and Berglund 2006).

The input characteristics as defining the brut energy output of the AD unit, will define the contribution of the different operations to the total energy input. In this respect, heat loses become the most important loses when high value substrate such as energy maize is employed, whereas in the case of a low energy substrate such as manure, the indirect energy of the infrastructure facilities as assumed for an standard European CSTR unit, become the most important energy input.

Similar efficiencies are achieved in the production of thermal, electric and mechanical work in AD units, however in the case of electricity production the heat reuse is a crucial consideration. Energy losses from not reusing the heat produced in a maize digestion unit can be as important as the sum of all other energy inputs provided evaporation is excluded, i.e. 18.2 GJ d^{-1}. The possibility for digestate reuse and disposal is found to be the most influential factor affecting the energy performance of an AD unit in terms of expected ranges of variability (Chapters 6 and 7). Separation of liquid and solid fractions combined with the application of liquid digestate and combustion of the solid effluent showed to be an energy profitable option. Transportation showed not to be a crucial factor if distances are around 10 km, however at around 100 km it would constitute 38-54% of the energy inputs in the case of low energy value residues (Chapters 6). In line with the previous in the analysis of the added value of AD to bioethanol cascades from cassava the transport component differing among centralized or decentralized systems showed no to have major implications in the energy outcomes (Chapter 7). In the same chapter it was also shown that the separate digestion of liquid and solid flows lead to better net energy outcome from the AD unit, i.e. 86% vs. 67% for the centralized system. Per ton subtrate and considering a different ra

2.4 The added value of AD to Colombian biofuel cascades

In Chapters 7 and 8 of this thesis, emphasis was placed on quantifying possible outcomes from AD for alternative biofuel cascades in Colombia. Following the main results in terms of energy, Greenhouse gas (GHG) balance, nutrients and water are summarized.

Energy and GHG balance: Quantitative energy outcomes in the systems studied in Chapter 7 made evident that without the energy recovery provided by AD, the production of bioethanol from cassava in Colombia is not sustainable from an energy and GHG perspective. The results showed to be largely dependent on variables like cassava drying, type of fuel used and the separation of flows in the AD system. The decentralized cassava systems (DS) showed a much better energy and GHG performance as compared to their counter part, the choice for artificial drying being crucial in this respect. The use of solar drying is recommended as it shows not to significantly affect the land area used by the systems whereas it has an important impact in the energy balance, i.e. the net energy losses in the centralized system (CS) will become only 27% of original ones when solar drying is implemented. Under same conditions of solar drying, AD scenarios in both centralized and decentralized systems will be the only ones delivering a positive energy outcome, 3.4 and 4.8 times more energy than demanded. Such positive outcome will also influence the GHG emissions, the centralized system would produce only 2.2 kg CO_{2eq} l_{EtOH}^{-1} vs. 6.8 kg CO_{2eq} l_{EtOH}^{-1} assessed under artificial drying, whereas the CS+AD will generate net GHG emissions savings, i.e.-1.7 kg CO_{2eq} l_{EtOH}^{-1}.

In Chapter 8, AD also showed to substantially contribute to the energy efficiency of studied cascades. The benefits in this case fluctuated depending on the by-products that were added value via AD. Adding value only to wastewaters and 30% of solid by-products including aerial biomass implied that 0.7 to 1 times more energy was produced as compared to the systems without AD. If other residues are added value up to 2.3 more energy can be produced.

Nutrients: When analyzing the role of AD in cassava cascades as compared with alternative systems adding value to residues via composting and animal feed, total nutrient recirculation achieved was higher using AD. For the centralized system, the system with AD allowed to recirculate 42% of the nutrients (including N, P, K), versus 37% of the system using compost. In the case of the decentralized system, contribution of AD was much higher due to the fact that the animal feed scenario implies the export of the nutrients outside the system boundaries.

In Chapter 8 total Nitrogen recirculation was analyzed for the alternative cascades. Ranges were fluctuating in between 3,169 and 25,450 ton N yr^{-1}, depending on the cascade. An interesting feature is to observe the highly important contribution of AD to recirculate nutrients present in aerial biomass, especially evident in the case of oil palm and cassava (See Table 8.15).

Water: In relation to water use, the digestion of by-products can potentially generate a substantial impact in biofuel production systems, realizing that they are intensive water consuming industrial processes. When liquid flows are digested separately the cassava case study showed that 70% of the total water output could be recirculated (Chapter 7). The previous without considering the proportion of the total water input left in the digestate, i.e. 12-14%. The differences between using AD to add value to by-products instead of compost or animal feed are especially evident in the cassava case study. Overall significant differences in net water use result in the different systems, the CS being a highly water demanding system 505,502 ton yr^{-1} in contrast with a water saving system in the CS+AD, i.e.-19,193 ton yr^{-1}. In both DS systems similar water consumption results equivalent to 10% of that in the CS, i.e. 53,756-55,784 ton yr^{-1}, given that the water evaporated in the animal feed process is assumed to be treated and reused as well.

The importance of AD for water savings is even more interesting than its role for water treatment. Whereas water consumption in biodiesel and specially bioethanol production are very high, AD does not require substantial water inputs. According to our estimation, 27-31 liter water per liter ethanol is used in the cassava production systems without accounting the water needed for steam production. Of these, 21-23 liter are provided for the ethanol production itself , i.e. water for washing tubers and pulping, whereas the rest is incorporated in the cassava biomass. In Chapter 8 it is shown than when using anaerobic digestion to produce bioenergy, total water savings fluctuate between 1.3 and $8.8x10^3$ tons per year respectively for oil palm and sugarcane biofuel production in 2010.

3 METHODOLOGICAL IMPACTS

3.1 Simplified experimental methods for the assessment of biodegradability of plant material

In this thesis the use of batch experiments for assessing biodegradability, hydrolysis rates and digestate composition has been proven to be suitable provided that a good adapted inoculum is guaranteed. In Chapter 3 and 4 the development and use of a simplified Oxitop® protocol for the screening of plant material is shown. In chapter 5, multiflask batch experiments are described and shown to deliver similar results to continuous experiments when predicting nutrient mineralization at short retention times. Further, as part of the author’s research work in the CROPGEN Project a publication was produced showing the possibility of assessing hydrolysis rates using batch experiments instead of continuous reactors provided that a good quality inoculum is guaranteed (Pabon-Pereira et al. 2008).

3.1.1 Recommendations for screening plant material based on its anaerobic biodegradability using an Oxitop® Protocol

The OxiTop® system is a pressure monitoring device originally developed for Biological Oxygen Demand (BOD) measurements. The system comprises the measuring heads and a controller, and uses an infrared interface for data transfer. Advantages of the system are the possibility of carrying out many measurements in parallel and the minimization of human interference in the test, as pressure data is collected automatically by the controller at time intervals defined by the user. Despite the listed advantages, the OxiTop® system has as major limitation the pressure limit of the measuring head, i.e. 0.30 atm. Such limitation causes restrictions on the amount of sample that can be used in the experiment, which in turn pose challenges for achieving sufficient representativeness in samples from non-homogeneous material such as crops and agro-residues. In addition, the produced overpressure consists of both CH_4 and CO_2, requiring gas analysis of the head space for assessing the Chemical Oxygen Demand (COD) balance in the test vials. Within this research an OxiTop® protocol has been developed striving to overcome its limitations and provide a simple and reliable test for screening purposes. In Chapter 3 guidelines and recommendations are given for the preparation, follow-up and calculations related to the application of the OxiTop® system for anaerobic testing. Following main features are summarized:

(i) The use of NaOH pellets to avoid biogas composition monitoring and double headspace volume is not advisable since their presence severely influences the stability of the BMP test.
(ii) Due to the non-homogenous nature of plant samples, it is proposed that drying and grinding should be favoured if maximum conversion, replicability and comparability is desired. Such a procedure can be easily made part of a protocol. Not to underestimate are also the additional practical advantages like the fact that dried grinded samples can be stored for a longer period of time in a reduced space and can be used as well for COD, calorimetry and fiber analysis determination. To avoid the non-enzymatic browning effect, freeze drying should be favoured.
(iii) A balanced culture that includes a very active methanogenic population, combined with a low S/I ratio of about 0.4 provides maximum BMP results and minimizes test duration, i.e. 3-6 days for 80% COD conversion.
(iv) Carbonate buffer offers as an advantage the possibility of increasing the molarities without noticeable toxicity effects, therefore allowing higher substrate concentrations. In this case it is advised to use N_2/CO_2 mixture gas for flushing bottles to avoid the increase in pH. The maximum allowable phosphate buffer concentration might be set at 20mM as higher concentrations may negatively affect the BMP assessment of plant material considering its observed effect in the blank bottle. When deciding on the buffer molarity to employ, a small range of pH fluctuation is to be allowed in the test, considering possible toxicity interference which is expected to change according to the microbial community. In the applied set-up using digested primary sludge a 5 mM phosphate buffer apparently sufficed since only 0.15 mM VFA accumulated, and pH was stabilized at 7.2 ±0.1.
(v) Evidence of the influence of the blank bottle in the results of the BMP test has been found (Chapters 3 and 5). Per definition, the absence of substrate makes the blank bottle already different in kinetic and toxicity behaviour. Such difference may already impact the corrected biogas production curves. The selection of the appropriate inoculum and S/I ratios and the addition of nutrients as they significantly differ from the test bottle.

In Chapter 4, the developed OxiTop® protocol was applied showing its usefulness for screening plant material. Reproducibility of the test was excellent, average difference in biogas production among duplicates being 3% and fluctuating between 1 and 5%. Further, as final methane production varied in a narrow range i.e. 61-71%, depending on the expected composition of the biodegradable plant material methane sampling could be avoided for screening purposes.

3.2 Overall comparison of approaches for anaerobic biodegradability estimation: A balance between accuracy and complexity.

In Chapters 3 and 4 of this thesis an effort was done to simplify the test methods for biomass quality assessment for anaerobic digestion. Experimental methods were developed as well as predictive equations. So far, a thorough analysis is lacking in which the accuracy achievable in the measurement and/or estimation of the BMP value is placed in perspective, relative to its usefulness for anaerobic reactor design or substrate screening for energy production.

First, the accuracy of the BMP test and of the chemical analyses procedures is to be considered. Biodegradability assays are influenced by different test conditions as reported elsewhere (Angelidaki and Sanders 2004; Muller et al. 2004; Rozzi and Remigi 2004b) and shown in Chapter 3 of this thesis. Given that the biodegradability tests are not standardized, variations in BMP value not related to the intrinsic properties of test material are to be expected. With regard to the chemical analyses procedures, in our research NDF and ADF duplicates showed very low standard deviation, i.e. 1 and 2% in average, respectively. The ADL value was more prone to variation, requiring a higher number of replicates. Overall a 5% average deviation was allowed. Apart from van Soest, other methods for the evaluation of structural components of lignocelluloses material are available, i.e. TAPPI, Nuclear Magnetic Resonance (NMR), Klasson lignin. They are expected to give different results (Fernandes and Lier van 2007; Fukushima and Hatfield 2004; Hatfield and Fukushima 2005; Hatfield et al. 2006). Especially with regard to lignin analysis, the mentioned methods show different results and their accuracy depends largely on the crude protein content and potential soluble lignin of the samples analyzed (Fukushima and Hatfield 2004; Hatfield and Fukushima 2005). Studies conducted in the past for predicting biodegradability have used different methods. Whereas Chandler et al (1980), Tong et al (1990) and Eleazer et al (1997) used the Klason or 72% sulphuric acid method for lignin determination, Moller et al (2004) and Buffiere et al (2006) have used the ADL method as in this study, hence limitations are evident in their comparability. Since methods employed for both BMP testing and chemical analyses procedures depend on the facilities available in different laboratories, when using literature values for substrate screening or energy yield estimations, accuracy is certainly missed.

Regarding the usefulness of the BMP assessment, laboratory measured values are often used to design and estimate the energy output of full scale reactor systems. The reality is, however, that these values are only indicative since when comparing laboratory experiments with pilot and full scale reactors different performance is found attributable to the lower controllability of the full scale systems, the possibly better microbial specializations in time and differences in secretion enzymes and emulsifiers (Schlattman et al. 2004; Speckmaier et al. 2005). It is clear that in this case, the use of the values assessed under laboratory conditions is only indicative.

In Table 9.1 the different approaches valid for the assessment of estimation of the BMP value are compared in their accuracy and complexity.

Table 9.1. Accuracy and complexity of different methods for measuring/estimating BMP

	Approach	Accuracy				Complexity	
		R^2	AIC	RSS	SD (%)	Data input	1/[sample.person^{-1}. day^{-1}]
A1	Literature				Up to 44% (a)	None	-
A2	Average $\hat{y}_i = \bar{y}$	0	-90	0.036	5%	None	-
A3	Total COD $\hat{y}_i = K * COD_i * \overline{B}_o$	8	-84	0.047	6%	EA	0.19
A4	sCOD+pCOD $\hat{y}_i = K * COD_i * ((sCOD_i * \overline{B}_s) + (pCOD_i * \overline{B}_p))$	30	-79	0.020	4%	EA, sCOD	0.21
A5	Empirical model (Eq. 4) $\hat{y}_i = K * \mathrm{COD_i} * (0.87 - (0.97 * ADF_{\mathrm{i}}))$	86	-114	0.006	2%	EA, ADF	0.37
A6	Conceptual model IV (Chapter 4)	75	-101	0.010	3%	EA, NDF, ADL	0.56
A7	BMP test				5-10%	Test, Biogas amount,composition,EA	5

$\hat{y}_i$ is the estimated BMP value for sample i; K is the constant value 0.35 l CH_4 gCOD^{-1}; COD_i is the COD value of sample i in gCOD gVS^{-1}; $\bar{B}_o$, $\bar{B}_p$, $\bar{B}_s$ are the average total, particulate and soluble biodegradability of crop material, respectively; AIC: Akaike Information Criterion; RSS: Residual Sum of Squares; SD Standard deviation; Measurements required; NDF: Neutral Detergent Fiber; ADF: Acid Detergent Fiber; ADL: Acid Detergent Lignin. Note: The calculation on the samples per person per day takes into account the necessary freeze drying, grinding and VS measurements for all the cases in addition to the measurements specified in the column. This is also considered in the case of the BMP test.

Seven approaches are compared in their accuracy and complexity, starting from the estimation requiring the minimum endeavor and moving towards the most detailed one. Approach 1 consists of using already available literature values to estimate the BMP value of a certain crop. In this case the expected variation depends on the different methods employed and possible differences in substrate characteristics, i.e. genetic diversity, harvest time, pretreatments. Approach 2 considers an average BMP value for all crops. In this case the average BMP value assessed in the present study is used (0.29 m^3 CH_4 kgVS^{-1}), which agrees with average BMP values of plant samples reported in literature. Obviously, for these first two approaches no laboratory analyses are needed. Approach 3 departs from the maximum theoretically attainable methane yield as described by the Buswell equation (Symons and Buswell 1933) and multiplies it by an average biodegradable fraction ($\bar{B}_o$). The value of $\bar{B}_o$, i.e. 0.55, has been estimated from the results of this study by the method of minimization of the square sum of the error. Approach 4 considers the COD partitioning of a sample assigning individual values to the degradability of particulate and soluble fractions. The biodegradable fractions of each of the components is defined as the average of those calculated for the individual fractions in this study, that is B_p = 0.94 and B_s =0.46, respectively. Approaches 5 and 6 correspond to the two best-fit models developed in this study based on fiber composition (Chapter 4). Finally, approach 7 is the BMP test which is the most elaborated one.

The accuracy of the models is defined by means of three statistical indicators, the coefficient of determination (R^2), the Akaike Information Criterion (AIC) and the residual sum of squares (RSS). R^2 indicates the proportion of the variability in the dependent variable that is accounted for by the independent variables, giving a value to the strength of the correlation, the AIC is an index which includes a specific term for model complexity, which means that models with a high number of parameters are penalized (Akaike 1974). If two models are compared, model 2 is considered to give a better fit than model 1 if AIC_1-AIC_2>5. The RSS account for the variability not explained by the model and can be used to estimate the standard deviation, making the comparison of all approaches possible (See Table A9.1.1 in Appendix 9.1 of this publication).

The complexity of the approaches compared is defined by first considering the required input demanded by the specific approach, and then calculating the simplicity in samples per person per day, according to the previously defined input. A complexity indicator is then given by the inverse of such value.

As can be observed in Table 9.1, the use of the distinctive biodegradability properties of the soluble and particulate COD for biodegradability prediction does not improve the accuracy of the estimates. Approaches A5 and A6 gave the best estimates of measured values as indicated by their R^2 value. Further, and according to the AIC criteria, they are also the only models that justify the use a higher number of variables compared to the use of an average value (A2).

When introducing complexity in the analysis, it is clear that the effort required for the BMP test is substantially higher than that required for any of the other approaches. Further, it can also be observed that the use of the empirical model requires a third of the effort of the conceptual model as only the ADF fraction, representing lignin plus cellulose, needs to be assessed avoiding the need of separately assessing the lignin amount. Considering both accuracy and simplicity the ADF model (A5) is preferred for material screening. The limitations of the model regarding variables not accounted for like particle size or inhibition due to toxic components present for example in agroindustrial waste, make the BMP test still suitable for substrate screening purposes.

3.3 Sustainability assessment framework for the evaluation of the role of AD within biomass chains

In Chapter 2 of this thesis a framework has been proposed for the design and evaluation of the role of anaerobic digestion in biomass cascades. Innovative aspects of the framework are the development of a typology of cascades and of a sustainability framework useful both for evaluation and design of alternative biomass cascades. In the typology of cascades, the role of AD in the cascade is proposed to be classified as multifunctional, protagonist or contributive, depending on the used scheme of the original biomass. The implications of such typology are then better defined and discussed by applying the dimensions and principles of the cascade chain theory. In addition, a sustainability framework is then built upon the multidimensional character of the sustainable development concept, proposing environmental, social and economic objectives, criteria and indicators for addressing the contribution of AD to sustainable biomass use. The environmental dimension of the framework is further elaborated by proposing an energy model for its operationalization.

Different aspects of the framework developed are applied in chapters 5, 6, 7 and 8 of this thesis. Our results corroborate how conclusions about sustainability of bioenergy production are not desirable as they hide the implications of the different assumptions made. The case study on the role of AD to add value to bioethanol production from cassava in Colombia analyzed in Chapter 7 clearly exemplifies the previous. Therefore the evaluation of bioenergy systems performed at a generic level as in Chapter 8 is only regarded as indicative as it hides important assumptions and changes in system configuration impacting the output of the systems. Similar conclusions at the inner AD unit are exemplified in Chapter 6, stressing again the importance of choices in systems design for concluding on the role of AD in biomass cascades.

The focus in the application of the sustainability methodology in this thesis was on the net outcome at system level instead of that per unit product. This choice was deliberately made as it is acknowledged that systems as a whole are the ones defining the resource use efficiency of biomass. It is also at a system level that the complexity of the interactions at environmental, social and economic level are better perceived and that possibilities for optimization of the cascade are better perceived as complementarities and trade-offs are made evident. Calculating outcomes per unit product is suitable for comparison purposes with other studies as performed in Chapter 7 but not for stating if a product is or not sustainable per se as choices in assumptions, system boundaries and variable chosen for allocating are determinant and tend to remain hidden.

Another important methodological choice of this thesis was performed in chapter 7 were the definition of the systems was deliberately chosen to reflect reality. Such choices enrich the analysis but the sensitivity analysis is then of crucial importance to be able to distinguish among the implications of different variables thereby better defining possibilities for optimization of the systems. Additional consideration is that in this thesis *“the added value of AD”* is defined as the difference between an existing system without AD and a proposed one incorporating AD, the careful definition of the departing system majorly influences the net outcome.

Regarding measuring units, in this thesis energy, water, nutrients and land were given priority for quantifying the environmental sustainability implications of biomass systems. In chapters 5, 6 and 8 of this thesis, flows of nutrients and water were converted to their energy equivalence based on the energy required to produce fertilizers and drinking water, respectively. In Chapter 6 it was shown that in the case of manure the energy equivalence of nutrients can constitute up to 50% of the brut energy output of the flow. This choice allows producing single energy measurements simplifying comparisons at system level. However it is noticed that when accounted within an overall energy balance underestimation of their value results, i.e. the value of clean water and phosphorus are hardly visible in the energy balances despite their importance in terms of mass and resource scarcity. Exemplifying the previous in chapter 5 the energy savings from the introduction of organic fertilization to replace artificial fertilizers in maize digestion systems was found not to be of major importance, i.e. only 1% and 3% increase in the net energy balance. A better approach for comparison purposes is allowed when such flows remain in their own units as was the case in Chapter 7 and 8 of this thesis.

4 CONSEQUENCES FOR SOCIETY

4.1 The choice of resources for anaerobic digestion

In Chapter 2 of this thesis a typology of cascades based on the role of AD was presented. Three possible roles the technology can play for adding value to biomass were suggested, i.e. multipurpose, protagonist and contributive perspectives. In this thesis research emphasis was placed in the *protagonist* or *contributive* role of the technology, in the first case AD is used to add value to whole crops, whereas in the second case AD is inserted within a biomass cascade in order to add value to by-products.

Although energy crops can potentially deliver higher brut energy benefits per unit area, in Chapter 4 it was shown that among crop residues those having a good biodegradability can be found as well. The choice for crops or residues goes beyond resource quality and depends on the context defining availability, transport distances and current alternative uses of land and by-products. Hereafter, some considerations related to the choice for crops or residues for anaerobic digestion are presented as far as can be concluded from the results of this thesis.

4.1.1 Choosing crops for anaerobic digestion: The BMP value in context

In this study the importance of the BMP value has been stressed for the selection of biomass material suitable for anaerobic digestion. In view of the maximization of the energy output under competing claims for land and resources the BMP value needs to be placed in context when AD is to serve a *protagonist* role in biomass cascades.

The brut energy yield of a particular crop can be expressed per unit input material [m^3CH_4 ton^{-1}], per unit reactor volume [m^3CH_4 m^{-3}] or per unit area [m^3CH_4 ha^{-1}], the last one being of relevance regarding competitive land use. In Eq 9.1, the brut maximum energy output of a system per unit land or energy yield, Ey [m^3 CH_4 ha^{-1}], is defined as a function of the agricultural yield, Y_{crop} [kg fresh matter ha^{-1}], the volatile solids content of the substrate, VS [kg VS kg^{-1}fresh matter], and the BMP value [m^3 CH_4 $kgVS^{-1}$].

$$Ey = Y_{crop} \times VS \times BMP \qquad (9.1)$$

Understanding the variation among the independent variables in Equation 9.1 is crucial to get insight into the need of an accurate BMP value for crop screening purposes, when energy crops are considered for renewable energy production.

The overall expected variation in Ey according to reported literature values compiled elsewhere (Lehtomaki 2006; Pabon-Pereira and van Lier 2007), is in the range 500-12,390 m^3 CH_4 ha^{-1}, meaning a 25 fold possible difference (See Table 9.2).

Table 9.2 Variation in biomass yield, volatile solids content, biological methane potential and energy yield of different lignocellulosic biomass as reported in literature

Variable	Unit	Overall EU crops	Maize	Triticale	This study
Y_{crop}	Kg ha^{-1}	2180-41130 [a] # 25000-110000	17200-31400[c] * 42100 [c]###	30000 approx	-
VS	kgVS kg^{-1}	0.07-0.84 [e]	0.17-0.51 [c]	0.17-0.64 [e] 0.27-0.41[g]**	0.10-0.68
BMP	m^3 CH_4 $kgVS^{-1}$	0.17-0.55 [b,c,e]##	0.27-0.37 [c] Up to 0.51[f] 0.33-0.4 [g]	0.21-0.28 [c] 0.41-0.44 [g] Up to 0.55 [e]	0.18-0.37
Ey	m^3 CH_4 ha^{-1}	500-12390 [b,c,e]	5300-12390 [c]	1800-3600 [c]	-

(a)(Venturi and Venturi 2003);(b)(Lehtomaki 2006);(c)(Amon et al. 2007a; Amon et al. 2007b); (d)(El Bassam 1998); (e)(Pabon-Pereira and van Lier 2007); (f)(Heiermann et al. 2002); (g)(Plöchl and Heiermann 2006); *Data in KgVS Ha^{-1}; ** Data in gTS g^{-1}; # Upper value refers to average value for conventional crops, below value includes lignocellulosic biomass such as Miscanthus, fiber sorghum, Giant reed; ##Values as low as 0.014 had been reported for eucalyptus and bamboo but these values are not considered to be representative(Chynoweth et al. 1993); ### Average maize yield in EU15.

It is clear that the variation range of the crop yield is much bigger (19 to 50 times) than that of the VS (12 times) and BMP value (3.2 times). If looking at a single crop specie such as maize, *Ey* variation can be up to 3 times, in this case the VS content is the parameter showing major variability (3 times), followed by the yield (1.8 times) and BMP value (1.4 times) (Amon et al. 2007a; Amon et al. 2007b). In the case of triticale, the reported *Ey* value presents a lower range of variation (2 times), but a similar pattern is evident in which *VS* is the variable showing the biggest range of variation (2.4 times) followed by *BMP* (1.1 time). Apparently, both VS content and biomass yield play a more important role in the selection of crop varieties and harvest times than the assessed BMP value. An indication in this direction was already found in the study by Amon et al (2007b) who reported that when harvesting seven different maize varieties at the harvest time with the highest biomass yield, no significant differences were found in the specific methane yield. In that study the time of harvesting was found to be the most crucial parameter determining the energy yield rather than the maize variety because of its influence on the overall biomass yield.

Since the brut energy yield from anaerobic digestion of crops is mostly related to the crop yield and not to the intrinsic anaerobic biodegradability of the sample as explained in section 2.2.2, the implication is that the design of sustainable crop rotations should depart from the point of view of agronomic considerations.

4.1.2 The value of residues for energy generation using anaerobic digestion

In this thesis it has been shown how society can benefit from the better use of residues when they are valorised via anaerobic digestion. The value of residues in the net energy outcome of biomass cascades was approached in Chapter 5, 6, 7 and 8.

In Chapter 5 the impact of the use of manure as codigestion material and of the reuse of digestate was investigated by roughly quantifying the energy balance and the Net Energy Value (NEV) of alternative AD systems using maize silage and/or manure for biogas production for the case of the Netherlands. When codigesting maize and manure, a 19% higher net energy output per ton maize as compared to the system supplied with maize only is found.

This is the result of the combined effect of the nutrient and energy import of manure into the system. The savings provided by using residues can be translated into land terms, i.e. 245±4 ton manure can replace a hectare of energy maize.

In Chapter 6 net energy generated per ton vinasse is found to be similar to the energy generated per ton manure but only 5-20% of the energy generated by energy crops. Clearly, advantages of digesting these highly polluting voluminous residues are underestimated when measured only in energy terms.

In Chapter 7 bioethanol production from cassava in Colombia was selected as case study to gain insight in how environmental outcomes of a biofuel producing system can be affected by implementing AD as an option for adding value to by-products. Indeed, the energy balance, GHG balance and water balances fluctuated in a wide ranged in relation to the use given to by-products, i.e.-1,809 to 637 TJ yr^{-1}, -0.3-5.3 Kg CO_{2eq} l_{EtOH}^{-1}, -19,193-505,502 ton yr^{-1}, respectively.

The energy content in residues from cassava bioethanol production constitutes 52% of the total energy content of the cassava plant. Thereby, in the CS where composting is used only 48% of the energy in cassava is recovered as useful energy output, i.e. ethanol, whereas in the CS+AD a total energy efficiency of 92% is found, i.e. 41% of the energy is recovered in the form of electricity and heat from the biogas produced. In the DS also 48% of the energy is recovered as usable energy, i.e. ethanol. The energy contained in the leaves and stalks, peels, vinasse and bagasse is not recovered as direct energy but in an indirect form as part of animal feed, for an extra 40% of the total energy input. Similarly in the DS+AD in total 89% of the energy in cassava is recovered as usable energy. The two systems with AD provided with significant savings in the energy input for the biofuel productive activity, i.e. only 26% and 7% of the direct energy required for the ethanol conversion step were required in the AD supported centralized and decentralized systems, respectively.

In Chapter 8 of this thesis great differences are found in the net energy output of the Colombian cascades studied. The contribution of by-products appears crucial constituting 41-68% of the sum of all energy flows.

It was shown that cascades not benefiting from the use of residues can potentially be delivering a negative net energy gain when including the lost energy content in by-products in the energy balance. Energy in by-products including field residues constitute 51%-71% of the total energy content in the crop. Industrial by-products constitute a lower share of the crop energy as compared to residues from crop production except in the case of oil palm. The energy content in aerial biomass appears especially relevant because the net energy output of sugarcane, panelacane and oil palm become positive only when this flow is included.

When the energy loss in by-products is omitted from the energy balance under optimal industrial conditions we calculated energy gains of 72, 128, 75, 45 GJ $ha^{-1}yr^{-1}$ for oil palm, sugarcane, panelacane and cassava, respectively, when AD does not make part of the cascade. Depending on which by-products are valorised via AD, their energy contribution to the different biofuel systems fluctuates between 51-158, 122-290, 71-170, and 36-71 GJ $ha^{-1}yr^{-1}$, for oil palm, sugarcane, panelacane and cassava, respectively.

4.2 Implications of this research for Colombia exemplifying the larger bioenergy debate

In this thesis the added value of anaerobic digestion was set in perspective by analyzing the particularities of Colombian biofuel policy and the possibilities for anaerobic digestion within this scenario. In items 2.4 and 4.1.2 of this Chapter, the calculated gains in terms of energy, nutrients, water and land have already been presented. Our findings show how the introduction of anaerobic digestion could potentially contribute to more sustainable use of resources, in Colombia and elsewhere in the world.

Furthermore a major contribution of this thesis has been the compilation and analysis of otherwise scattered and incomplete information about biofuels in Colombia and especially about bioethanol production from cassava. The use of this information for analyzing the role of AD, so far underestimated within the biofuel policy in the country, is also a major contribution that can enrich the debate and generate awareness on the value of biomass and the role that anaerobic digestion can play to increase resource use efficiency within this context.

4.2.1 Consequences of the introduction of AD in land use for biofuel production in Colombia

As shown in Table 8.12, it is projected that in year 2020 the area dedicated to biofuels will be 6.5 times more, i.e. 0.7 and 5.8 for bioethanol and biodiesel, respectively, than the original agricultural land dedicated to the same crops in 2003 which was used only for conventional food production. Considering the previous, savings in land use by harvesting additional energy from the same biomass via anaerobic digestion are of major interest.

When only industrial by-products are valorised via AD, energy gains are at least doubled meaning one hectare per hectare land invested could be saved or half of the land demanded would be needed to provide the same energy output. When the full digestion of the crop is considered 89-296 GJ ha^{-1} yr^{-1} extra net energy outputs result as compared with current biofuel systems being promoted, meaning only 30-35% of the area used to produce the biofuels would be needed to deliver the same energy output. Similar advantages of AD can be expected in any country.

The savings in land use could become especially important in the case of oil palm, for which increase in area is already taking place and is expected, to grow almost four times in the next ten years. In contrast, in the short to medium term the production of biofuels from sugarcane will not require an expansion of the area planted. The latter is a result of the fact that the sector conceives the production of biofuels as a business strategy to diversify economic risk. The production of biofuels will be done at the expense of the production of sugar. In this order of ideas, the net creation of employment at farm level would be near to zero. On the other hand, however, less direct effect on prices of sugar at national level are expected as the result of the shift in export market towards biofuel production. As well, little additional environmental risks associated with the generation of new plantation are expected to occur. Rural employment derived from the sugar based industry will be further ameliorated due to increased mechanization at both farm and industrial levels.

Competition in the use of residues currently used for animal feed could take place considering current uses especially in the case of cassava and oil palm. Current prices of feed as compared to Nitrogen fertilizer favour the sales of products for animal feed. Prices of methane as compared to prices of animal feed will determine its economic feasibility. Since the price of natural gas is much lower than other energy carriers, the incentives given for methane production would define the real risks of competition.

4.2.2 Opportunities and constraints for implementing anaerobic digestion in Colombia

Beyond complementarities for biomass cascades, anaerobic digestion can offer interesting opportunities for sustainable development in Colombia under different scenarios. Implications of scales, other energy carriers' availability and prices, set the ground for defining feasibility and desirability of specific endeavors.

(i) The use of Natural Vehicular Gas in Colombia has had a positive acceptance and is an open niche for upgraded biogas. Additionally, the fact that there is an existing legislation enforcing the use of biofuels for vehicular use, makes this option more promisible. Nonetheless, nowadays natural gas in Colombia has the lowest price among the compared energy carriers including the prices already fixed for biodiesel and bioethanol. Although the use of biogas as a vehicular fuel could be considered alternative to currently enforced biofuels, it could also be seen as a complementary fuel. Nowadays, vehicules using natural gas as fuel are in their majority flexifuel cars, meaning that they are able to run on liquid fuel as well. In any case, if biogas is to play a role in the vehicular market, adjustments in legislation providing incentives for its consumption should be made accordingly.

(ii) Biogas also has a natural market in the wide expanded gas grid in Colombia, which has been receiving major incentives in recent years. The consumption of natural gas is expected to more than double by year 2020 as compared to 2010. Increase in the demand is expected to come primary from the thermal and industrial sectors, whereas residential consumption already widespread will soon stabilize. The integration of biogas technology in this setting is feasible only if coming from large scale installations due to current technological limitation in biogas upgrading. The direct use of biogas for injection to the grid or as vehicular fuel as previously introduced should be the most supported markets over electricity, because of the higher efficiencies achieved, i.e lower losses from the transformation to other energy carriers.

(iii) The use of biogas in the industrial sector can be especially attractive in the case of big industries peripherically located and with limited access to electricity. Such a possibility was exemplified in chapter 7 of the thesis by the centralized system for bioethanol production from cassava. In this case, the expected location of the site hinders the access to the electricity grid inducing the use of diesel for electricity production. As shown, the alternative use of biogas produces important savings in term of energy and GHG emissions. Industries are also a natural market for the heat co-supplied by the CHP units that transform methane into electricity. In agroindustrial cluster the promotion of AD can provide important additional saving in the form of water and nutrients resulting from the use of the digestate. Further, the use of biogas from industrial by-products onsite avoids transport costs and losses.

(iv) In isolated areas of the country currently not connected to the grid, AD could be used to add value to domestic residues and animal waste for the generation of biogas. Territories lacking energy access usually also lack access to public services as potable water and sanitation. In addition, these areas receive bad quality energy service characterized by its low frequency, low quality and reliability, high levels of technical losses and high service costs. Interesting is also to explore the possibility of using locally produced crops for energy generation as an alternative income generation for farmers. In these areas agriculture is mainly practiced under subsistence scheme with low possibilities for integration into the (inter)national market. Thereby non-food application of agricultural products could be seen as important incentives. In that, AD represents an opportunity to add value to residues and widen possibilities for farmers in areas where dispersion, deficient transport infrastructure and differences in yields could be seen as weaknesses for macro biofuel projects as in the case of panelacane and cassava.

(v) The potential of AD for innovative biomass cascading setups is also to be realized. The case of a grass biorefinery taking advantage of underutilized and highly degraded pastureland in Colombia is yet to be explored. Complementarities with existing animal production in these areas could potentially provide even better synergies as AD could be flexibly used for the codigestion of grass, manure and biorefinery residues.

4.2.3 Reflections on current legislation related to biofuel production in Colombia

In view of the important socioeconomical consequences of bioenergy projects, as proposed in Chapter 2 of this thesis, legislation providing incentives for these developments should depart from setting clear and workable sustainability criteria. Primary social objectives are that living conditions of the concerned population are improved and the existing social structure is recognized and enhanced.

Although current biofuel legislation recognizes the importance of the social component, to materialize those objectives remains a challenge to be undertaken. The strategy on biofuels portrays a very clear hierarchy of roles and control over strategic resources. The social contributions of the strategy are very localized. The need for “economy of scale” as a driver for competitiveness further restricts small to medium size farmers. Additionally, the fact that just few main stakeholders possess a dominant role in the production of biofuels creates an unproper power structure for the distribution of benefits. When producers are so dependent on very few traders and biofuel producers there is a risk of monopoly and squeezing of benefits.

Indeed, the private – public alliance that so far has triggered the rapid implementation of the biofuel program can also potentially endanger the sharing of the benefits in that it monopolizes access to decision making power and resources. This also leads the discussion to a rather paradoxical situation. The relevant role of the private sector can improve investment and technology transfer which in turn can increase energy yields per unit of land. This in itself can limit environmental risks related with biodiversity losses due to cropland expansion. Also a reduced impact on commodity prices can be the result, in that there is less competition for biomass resources. On the other hand, however, as it has been introduced, such circumstances can hinder proper benefit sharing and rural employment.

Colombian biofuel policy presents positive characteristics similar to those presented by Bos et al (2008). Examples of those positive features of Colombian policy are firstly the setting of a blending obligation creating a specific market demand for the new products, issue specifically addressed by first national biofuel policy. Secondly, the choice for technologically feasible non-food products, i.e bioethanol and biodiesel, can also be seen as a succes factor. Thirdly, the availability of suitable infrastructure which is the case of Colombia means taking advantage of the liquid fuel infrastructure and the installed capacity of consolidated industries in the country as sugarcane and the oil palm industry. Additionally the Colombian government promoting biofuel to provide alternatives to the agricultural sector is comparable to the agrification era in The Netherlands, as presented by Bos et al (2008).

Although the environmentally sound idea behind biofuels has been widely promoted in Colombia, large scale biofuel production can be conceived as a risk and a challenge considering existing criticisms not fully tackled by the government and the promoters. Additionally, the biodiesel policy stimulating production beyond the blending target could potentially increase the vulnerability of the sector if international markets are aimed for.Another challenge of the legislation is to foster investment in research and development in more specialized bio-based products beyond the bulk production of biofuels.

In this research the added value of AD has been stressed beyond the energy domain into the possibility for reclaiming nutrients and water. Legislation recognizing this value is however lacking and an important challenge to be undertaken not only in view of the promotion of AD but also in view of substantial water use of biofuel industries promoted now. The case of water exemplified the situation. Water availability in Colombia is substantial, i.e. 60,000 m^3 per person per year. The resource, however, is undervalued resource (Dinero 2008). Water used in agriculture represents 54% of the national consumption. Yet, usage rates are so low that for agriculture its use is practically free. Within this subsector, major consumption corresponds to pastures (84%), whereas perennial crops use only 9.3% of water. On the other hand, it must be realized that industrial water use such as in the biofuel industry irrevocably results in pollution of sureface waters if wastewaters are not adequately dealt with. Uncontrolled discharge into the environment is a negative impact reaching beyond the system boundaries of the agro production field. Regarding nutrients, in Colombia 46 millions tons of fertilizers are used per year. Worldwide, phosphorous is perceived as a scarce resource and 80% is used in agriculture. Biofuel policy fostering agricultural development should incorporate these constraints. AD offers the possibility to tackle this issue, efficiently recycling the mineralized nutrients back to the field.

4.2.4 Global perspectives on the bioenergy debate

In recent years, the legal enforcement of bioenergy production of liquid fuels has been witnessed in different regions of the world (Chapter 1). The previous has taken place in the form of fixed targets for the contribution of biofuels to the overall automotive energy

consumption, or as compulsory blending regulations of gasoline and diesel with fixed proportions of bioethanol and biodiesel, respectively.
Whereas bioethanol and biodiesel are attractive energy carriers due to their liquid character, their perceived environmental and socio-economic advantages are being more and more questioned. Main criticism is directed towards their limited energy gains, the need of fossil fuels for their production and the required land for biomass cultivation which in turn generates undesirable competition with food and other uses of land.
This thesis has been approached as an effort to give scientific input to the bioenergy debate by shifting the focus from the use of land for single product output towards the maximization of the outputs of a biomass system. It does so by focussing in the added value of a specific technology, anaerobic digestion.
The thesis has shown how AD is able to convert both energy crops and residual biomass into energy using a minimum amount of energy inputs plus allowing for nutrient and water recirculation. Our numerical findings for the Colombian situation in terms of net benefits from biofuel cascades as shown in Table 8.15 are indicative of the potential of AD to recover energy from by-products and full crops, i.e. 1-2.3 times land savings had been calculated to be attainable. As such, this potential is also expected to be available in other settings.
However as net outputs have been shown to be highly sensitive to industrial technological design and biomass yields, real figures are expected to vary. The actual evaluation of the gains in resource efficiency of a cascade by AD should be performed on a case by case basis going beyond theoretical estimations into the contextualization of the system. In this way sustainable resource use can be seen as the result of the integration of the whole biomass chain instead of that of a single product performance.
Still the question remains whether the contribution of anaerobic digestion is significant enough to keep hope for bioenergy as an option fitting with the vision of sustainable development. In the introduction of this thesis the trends towards the triplication of energy use and the 50% increase in global population by 2050 with concomitant increase towards more energy intensive consumption patterns has been presented. Such trends are expected to generate different levels of disturbance in different regions of the world as their vulnerability changes regarding available resources and demands. Hence cautious and specific rather than over optimistic and generalized approaches are still prefered.
The actual contribution of a bioenergy system to the overall goal of sustainable development goes beyond the limits of the cascade itself towards the way perceived needs are actually satisfied. In this sense is crucial that decisions are made on the minimum criteria that maximize human and nature well being, whereas flexibility is allowed in the way priorities are set for specific settings according to their own needs and resources. The previous in acceptance that resources are limited and endless needs will only take society towards the opposite direction of the sustainable development vision.
At a macro level legislation should provide with the means to guarantee that flexibility is in place and provide with the incentives for the recovery of resources instead than for its wasteful use. Keeping the flexibility in biomass systems is crucial to adapt to changes in land use coming from diet requirement changes and population growth. In addition, expected and

desirable technological improvements are also to be considered within the scope of flexibility, as the production of energy via biomass is still limited by the inefficient capture of solar radiation of plant material.

As a whole it is suggested that the bioenergy debate should go beyond the issue of energy into that of resource use efficiency and competing claims within specific socio-economic contexts. In this sense the focus is shifted from a single product or single indicator measuring a specific output, into the performance of a whole system in its specificity to satisfy first local, then regional and then global needs.

5 RECOMMENDATIONS FOR FUTURE RESEARCH

5.1 Technological research

In Chapter 3 of this thesis comminution was proposed for the developed OxiTop®protocol. Comminution increases the suitable sites for enzymatic attack and is expected to exert a higher influence in samples containing more biodegradable particulate material than in those with higher amounts of non-biodegradable material, i.e. lignin, and/or insignificant amounts of particulate in relation to soluble matter. A rough first approximation of the relationship between fibre composition and particle size was observed when plotting our results and those of Sharma et al (1988), suggesting a relationship between ADF and increase in biodegradability in relation to comminution. More research is desirable to further confirm this hypothesis, such research should be oriented towards the development of models correlating both biomass composition and particle size with biodegradability using a higher range of variation in sample composition and applying the same test conditions. Such research would allow defining real bioavailability of substrates permitting better extrapolation of BMP results to full scale applications.

The influence of the blank bottle in the assessment has been shown as important factor affecting BMP assessment in chapters 3 and 5 of this thesis. This is an important aspect of the BMP test which deserves further study.

5.2 Sustainability studies

Complexity is an inherent quality of biomass systems and sustainability studies, as multiple process units and types of flows need to be accounted. Sustainability operationalization departs from the positive presumption that complexity can be tackled by simplification for which choices need to be made regarding indicators and flows to consider in the analysis. In this study environmental criteria and indicators were chosen having the cascading concept and especially the added value of AD to resource use efficiency, as guiding criteria. The choice for resource use efficiency as guiding the analysis implied that insufficient attention was given to pollution issues which remain to be studied. Similarly resource use efficiency should be set into perspective in comparison with resource availability or scarcity. This issue can be of special importance to foster the adequate use of scarce materials such as phosphorus or undervalued resources such as clean water.

In this research, quantitative results and material flow analysis as a methodology gained importance over social and economic considerations. However, in Chapter 8 of this thesis an effort was made on addressing the variability in socioeconomic conditions that can shape the way in which a technology like anaerobic digestion can potentially play or not an important role. Such approach allows better predictions for pathways towards sustainable use of resources.

It is desirable to undertake detailed studies to better conclude on the feasibility and desirability of specific biofuel projects in Colombia. In Chapter 8 data used were not specific and as shown in Chapter 7, specific features of system design can substantially impact conclusions on sustainability aspects of biomass use for energy.

The sustainable use of crops and crop residues for AD remains a challenge to be undertaken as part of integrated studies that approach the technological features in combination with the specific agricultural advantages and constraints of specific crops.

APPENDIX 9.1

Table A9.1.1. Statistical indicators applied for the comparison of different approaches for the estimation of BMP

Indicator	Formula
RSS	$RSS = \sum \hat{e}^2$
SD	$S = \sqrt{\frac{1}{n-p} RSS}$
AIC	$AIC = n \cdot \ln\left(\frac{RSS}{n}\right) + 2p + \left(\frac{2p(p+1)}{n-p-1}\right)$

S: Estimated standard deviation; n: number of experiments;
p: number of parameters; RSS: Residual Sum of Squares

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Appendixes

Samenvatting

1 INTRODUCTIE

De algemene doelstelling van dit proefschrift is het vaststellen van de potentiele bijdrage van anaerobe gistingsprocessen (AG) in een duurzame biomassaketen door:

(i) het inzichtelijk maken van de technologische potentie van AG om energie op te wekken en waardevolle bijproducten te produceren uit energiegewassen en restproducten van de landbouw, en

(ii) het evalueren van de haalbaarheid en wenselijkheid van biomassacascades met gebruik van AG als conversietechnologie voor restproducten, alsmede het vaststellen van de toegevoegde waarde van AG.

De onderzoeksvragen die aan dit proefschrift ten grondslag liggen komen voort uit de toenemende interesse in bio-energie als een alternatief voor fossiele brandstoffen en de toenemende zorg met betrekking tot concurrerende claims op land en andere bronnen, zoals water en nutriënten. Ondanks de vele mogelijkheden die worden toegeschreven aan de biomassacascades voor het opwekken van energie en de mogelijkerwijs te verbeteren water- en koolstofkringlopen door AG, is er nog weinig specifiek onderzoek naar dit onderwerp gedaan.
Het ontbreken van een methodologie om de potentiële bijdrage van AG in biomassa cascades te schatten en de hiaten in kennis over de technologische mogelijkheden waren de grootste uitdagingen die zijn opgenomen in deze studie.

2 SAMENVATTING

Dit proefschrift is een combinatie van experimenteel onderzoek en systeemanalyse. Het experimentele deel richt zich op twee doelen:

(i) het ontwikkelen van eenvoudige methoden om plantmateriaal te beoordelen op geschiktheid voor AG en

(ii) het verkrijgen van inzicht in de energieopbrengst en overige gistingsproducten gedurende de (co)vergisting van gewassen en gewasresiduen.

Deze aspecten worden besproken in hoofdstuk 3, 4 en 5 van dit proefschrift.

Als onderdeel van het experimenteel onderzoek in **Hoofdstuk 3** is een Oxitop® protocol verfijnd om, uitgaande van de potentiele energie-inhoud van het plantmateriaal, een betere beoordeling te kunnen geven van de geschiktheid van bepaalde planten voor AG. Factoren gerelateerd aan de proefopzet die de testresultaten beïnvloeden omvatten het gebruik van i) NaOH pellets voor CO_2 adsorptie, ii) voorbehandeling van het substraat, iii) het inoculum en iv) de toegepaste pH buffer. Het gebruik van NaOH pellets en de voorbehandeling van het substraat beïnvloedde de resultaten het sterkst. Met het ontwikkelde Oxitop® protocol is in **Hoofdstuk 4** de relatie onderzocht tussen de hoeveelheid en samenstelling van de in de plant aanwezige ligno-cellulose vezels en het biochemische methaan-potentieel (BMP), alsmede de eerste-orde hydrolyseconstante (k_h). De hoeveelheid ligno-cellulose vezels gemeten als Acid

Detergent Fibre (ADF) en de Neutral Detergent Fibre (NDF), zoals geanalyseerd volgens de "van Soest" methode, blijken geschikte parameters te zijn om planten te karakteriseren op hun BMP en k_h. Het ontwikkelde model wordt in dit proefschrift verder gebruikt om de biodegradeerbaarheid te voorspellen van 114 Europese plantmonsters. Deze resultaten zijn vervolgens gebruikt om geschikte gewassen en gewasresten te identificeren voor AG. Het ADF model is relatief eenvoudig, heeft een hoge voorspellende waarde en verdient daarom de voorkeur voor het testen van plantaardig materiaal voor AG. Echter, een BMP test blijft noodzakelijk aangezien het ADF model niet corrigeert voor deeltjesgrootte en potentiële inhibitie. Naast het louter bio-chemisch methaanpotentieel van een bepaald gewas dienen agrarische parameters, zoals duurzame gewasrotatie, een onderdeel te zijn van de evaluatie. De netto methaanopbrengst van een agrarisch veld is immers meer afhankelijk van de gewasdichtheid en specifieke opbrengst dan van de BMP van een gewas.

De ladingsgewijs bedreven experimenten beschreven in **Hoofdstuk 5** gaan nader in op de kwaliteit van het digestaat gedurende co-vergisting van maïs en mest. De verkregen resultaten laten een toename zien van respectievelijk 20-26% en 0-36% van het opgeloste NH_4^+ en PO_4^{3-}, na twee maanden gisting. De grootste fractie gemineraliseerde nutriënten is aanwezig in het vloeibare deel van het digestaat namelijk 80-92% NH_4^+ en 65-74% PO_4^{3-}. Een toename van het mestgehalte in de substraatmix laat een positief effect zien in de methaanproductie. Een langere gistingtijd en een verhoging van het maïsgehalte in de mix leiden tot een verhoogde concentratie PO_4^{3-} in het vloeibare digestaat.

In het tweede deel van dit proefschrift ligt de focus op het verkennen van de toegevoegde waarde van AG binnen verschillende biomassacascades, met het oog op duurzaamheid en de daarbij behorende criteria. De onderzoeksdoelen voor dit deel van het project zijn:

(i) het ontwikkelen van een raamwerk voor het ontwerpen en evalueren van de bijdrage van AG in biomassacascades in termen van duurzaamheid;

(ii) het vaststellen van de te behalen milieuwinst om aan de hand van het ontwikkelde raamwerk de potentiële bijdrage van AG te evalueren binnen de alternatieve biomassacascades, and

(iii) het analyseren van de potentiële rol van AG in Colombia binnen de huidige biobrandstof wetgeving.

In **Hoofdstuk 2** van dit proefschrift wordt de rol van AG binnen biomassacascades beschreven aan de hand van een cascadeketen theorie. Het ontwikkelde duurzaamheidsraamwerk, aan de hand waarvan de rol van AG wordt geëvalueerd, omvat de drie duurzaamheiddomeinen Mens, Milieu and Welvaart. De meetbare "milieuparameters" binnen het ontwikkelde raamwerk op basis waarvan de potentiële bijdrage van AG wordt geëvalueerd zijn teruggebracht tot de parameters energie en land. In **Hoofdstuk 6** is een gevoeligheidanalyse van de energiebalans van een AG installatie uitgevoerd dat vervolgens is toegevoegd aan het in hoofdstuk 2 beschreven model. De gevoeligheidsanalyse laat zien dat bij het gebruik van hoogwaardige energiegewassen zoals maïs, waarbij productie van elektriciteit wordt nagestreefd, de warmteverliezen, die ontstaan bij de omzetting van biogas naar elektriciteit, het rendement van de AG installatie bepalen. Echter, indien laagwaardige substraten zoals mest worden gebruikt, bepaalt de indirecte toevoer van energie die is gekoppeld aan de benodigde infrastructuur, het algehele rendement. Voorbeelden zijn energie voor transport en verwerking van afvalstromen. In de hoofdstukken 7 en 8 wordt het duurzaamheidsraamwerk toegepast voor de Colombiaanse situatie. De resultaten in **Hoofdstuk 7** laten zien dat de productie van bio-ethanol uit cassave vanuit een energie en broeikasgasemissie perspectief alleen duurzaam is indien AG een deel van het proces is. Hierbij worden met behulp van AG de organische reststromen verwerkt tot een additionele energiebron (methaan). De exacte uitkomst van de evaluatie is sterk afhankelijk van diverse variabelen zoals de noodzaak om substraten te drogen, de gebruikte brandstof voor het fermentatie- en destillatieproces, het type AG systeem en de toepassingsmogelijkheden voor het geproduceerde biogas en digestaat. Uit **Hoofdstuk 8** blijkt dat de bijdrage van energiestromen gerelateerd aan gevaloriseerde bijproducten cruciaal is in de evaluatie van andere Colombiaanse biobrandstofcascades. Deze stromen omvatten 41-68% van alle energiestromen binnen zo'n cascade. Voor palmolie, suikerriet, panela-suikerriet en cassave de geschatte energiebijdrage van deze bijproducten aan de verschillende biobrandstofcascades varieert tussen respectievelijk 51-158, 122-290, 71-170, and 36-71 GJ $ha^{-1}jaar^{-1}$. In de bestudeerde ketens levert AG een aantoonbare positieve bijdrage aan het terugwinnen van gemineraliseerde meststoffen en herbruikbaar water. De te verwachten revenuen ten aanzien van energie, meststoffen en herbruikbaar water zijn vervolgens gebruikt om een inschatting te geven van de potentieel haalbare economische voordelen en voordelen gerelateerd aan noodzakelijk landgebruik onder de geldende Colombiaanse omstandigheden.

3 EINDOVERWEGING

Zoals vermeld in de inleiding van dit proefschrift zal de komende decennia het energieverbruik verdrievoudigen. Naar alle verwachting, zal dit leiden tot regionale verstoringen op diverse niveaus, een en ander afhankelijk van de hoeveelheid regionaal aanwezige grondstoffen en het locale verbruik. Óf en op welke wijze AG systemen een positieve bijdrage zullen hebben op de regionale energievoorziening is nog onduidelijk. Het proefschrift maakt echter duidelijk dat AG een toegevoegde waarde geeft aan bestaande en de nog te ontwikkelen bio-energie systemen, passend in een duurzame energievoorziening.

De resultaten uit dit proefschrift geven aan dat AG systemen in staat zijn om zowel energiegewassen als agrarische reststoffen om te zetten in duurzame energie met een minimaal energieverbruik. Daarbij geven de voorgestelde AG systemen de mogelijkheid om lokaal het gezuiverde water, het vergistte digestaat, als meststoffen te hergebruiken. Van de andere kant blijkt dat het gekozen technologische concept en de agrarische biomassa opbrengst in grote mate de netto energieproductie bepalen. Praktijkdata zullen dan ook sterk van elkaar verschillen. In hoeverre de AG systemen daadwerkelijk zullen bijdragen aan een hoger rendement in het efficiënt gebruik van de bio-grondstoffen zal dan ook van geval tot geval bestudeerd moeten worden, waarbij de systeemafhankelijk parameters een belangrijk onderdeel van de evaluatie zullen zijn.

Het al of niet duurzaam gebruik van organische grondstoffen is daarom afhankelijk van de mate waarin een geïntegreerde aanpak binnen de biomassaketen is toegepast en kan niet worden afgemeten aan het productierendement van één enkel eindproduct, t.w. opbrengst aan energiedrager. Het verdient aanbeveling om met enige voorzichtigheid en zeer specifiek energie uit biomassa te promoten en geen overoptimistische en algemene benaderingen toe te passen.

Research impressions

1. OxiTop ® set-up for assessing anaerobic biodegradability of plant material
2. Hermes Arriaga Sierra MSc student from Wageningen conducting his research on cassava bioethanol production under the framework of this thesis and in collaboration with the International Center for Tropical Agriculture-CIAT in Palmira, Colombia
3. Titration stages during macro COD determination of plant material
4. Full scale anaerobic Continously Stirred Tank Reactor (CSTR) in Northern Ireland
5. Lab Scale CSTRs used for maize silage digestion experiments at the Environmental Technology subdepartment Wageningen University
6. Johannes Erchinger, German farmer, shares with us maize silage from his farm to run our experiments
7. Fresh plant samples ready to be added to the OxiTop ® set-up
8. Microscopic picture depicting grass fibre anaerobic decomposition
9. Claudia Pabón monitoring biogas production from energy crops using the OxiTop ® set-up
10. Collecting grass with Katja Grolle for testing our batch set-up
11. Staff from Petrotesting collects cassava plants in Llanos Orientales, Colombia (Picture by Hermes Arriaga Sierra)
12. Batch set-up used for muti-flask batch experiments. The valve on top allows for automatic pressure release
13. Full scale anaerobic CSTR digesting grass, maize silage and cow manure in Leer, Germany
14. Getting fresh sludge for our experiments from a full scale anaerobic CSTR reactor
15. Set-up employed for van Soest determination of biomass fibre components


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Acknowledgements

Getting started and actually finishing a PhD thesis is a task that involves the conspiracy of many factors. As in any other case it all starts by making a wish. In my case, when I finished my MSc studies I had this eagerness to keep on learning and experiencing what Wageningen had to offer. My desire was broad. It involved gaining laboratory experience, learning more about appropriate rural technologies, going deeper into the sustainability implications of technological choices and contributing with my work to the reality of my country, Colombia. And so it happened that by that time the EU had just granted for the CROPGEN Project and the Environmental Technology sub-department of Wageningen University (ETE) had received the offer to take over the task of one of the partner institutes that originally formulated it. Jules and Grietje approached me with the opportunity, which in principle was only for carrying the two year tasks of the project related to anaerobic test standardization for crop material. By the same time I met Maja, and the idea of getting the Sustainable Development and Food Security (SD&FS) group involved into an integrated research focusing in anaerobic digestion came into being. It all happened very quickly and I took some months to think it over from Colombia where I finally made the decision to do the PhD, starting my research on October 1st, 2004. In this way all the elements came together: the technology I most wanted to learn about, the rural approach, the holistic sustainability approach and Colombia.

As in any other journey, people are who make the difference along the path. In my case the journey is marked by the presence of two exemplary women researchers: Grietje Zeeman and Maja Slingerland. Not only have they been my mentors but also my source of inspiration all the way as scientists that have focused their career on socially relevant, practical research: Science in Action. *Dear Grietje, from my beginning in ETE your commitment with the decentralized sanitation concept has inspired me. Thank you for offering me the possibility of learning about anaerobic digestion despite my limited technological background. Your always critical insights, open attitude and social focus have marked the time I have enjoyed working with you. Now we will continue working together, Great! Dear Maja, you have been the most important figure in my PhD journey. Not only you supported me academically and provided the financial means for me to finish my PhD under equitable working conditions, but you were always the human figure behind the scene. You were there when I needed to get Enrique in the Netherlands, when I lost perspective about the future and when my personal life was complicated. Thanks for keeping me in track and setting boundaries to my overflowing enthusiasm. Our inspiring out-of-the-box discussions were always refreshing. I have no words to express my gratitude and admiration to you.*

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Walking the PhD path is a journey of perseverance and patience. Although the first is certainly my quality the second sometimes lacked. In many occasions my urge to do “something useful” made me deeply question my choice for a “scientific title”. Fortunately friends and family were always there to cheer me up and keep me in track. They made joyful what at moments seemed a too long lonely journey.

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About the author

Claudia Patricia Pabón Pereira was born on 20th October 1976 in Bucaramanga, Colombia. She finished secondary school in La Quinta del Puente School, Bucaramanga, Colombia, graduating with honors as class valedictorian in 1993. That same year, she was recognized with the Andrés Bello award for achieving 3rd place at national level, in Colombia's college admissions test. In 1999, she completed the Industrial Engineering degree at Javeriana University in Bogota, Colombia. During her studies she combined her academic studies with fine arts and violin lessons, and joined several student groups including the University Chaplaincy, the interuniversity action group "Gobernar a Colombia", and the Industrial Engineering Faculty group "Objetivo Calidad". In 1999, she was representative of Javeriana University at the "First Colloquium of Cultural Exchange" in Montreal, Canada. By the end of her studies Claudia was selected to attend the Program for Excellence in Professional Education (PEP), a one-year leadership and personal development program offered to Colombia's most outstanding undergraduate students.

In 2000 Claudia joined the newly created Metropolitan Corporation for Planning and Development of Bucaramanga-CORPLAN. As the organization's Urban Strategic Plan Coordinator, Claudia was responsible for the design and implementation of a participatory methodology, the purpose of which was the inception of a long-term strategic plan for Bucaramanga´s Metropolitan Area.

In September 2002 she started Master Studies in Environmental Sciences in Wageningen University with the support of a scholarship of the Japan-IADB Fellowship Program from the Interamerican Development Bank. In 2004, she obtained her MSc diploma with Cum Laude distinction. Her MSc thesis was conducted in collaboration with the Environmental Technology sub-department-ETE and the Environmental Policy Group. The thesis elaborated the design of a sustainability methodology for assessing alternative scenarios leading to closing material cycles in a highland community in Peruvian Andes.

At the end of her Master Studies she was invited to join the ETE to carry out research in anaerobic digestion of energy crops as part of the EU Project CROPGEN. With the aid of the Sustainable Development and Food Security Group, her research was extended and given a holistic perspective leading to the completion of this PhD thesis. Part of this research was done in collaboration with the International Center for Tropical Agriculture-CIAT in Cali, Colombia as a means to contextualize it to her country's reality. In 2008 she received the Storm van de Chijs recognition, awarded by Wageningen University to outstanding female PhD researchers.

Starting July 2009, Claudia will work strengthening the Master Programme in Urban Environmental Management of Wageningen University. This appointment will allow her to combine her academic background and her urban planning experience. Through this professional endeavor, Claudia is partly fulfilling her deepest desire of contributing to the development of human settlements that coexist in harmony with nature.

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List of Publications

Scientific journals

Pabon-Pereira, C.P. Kujawa-Roeleveld, K. Mol, A.P. Zeeman, G. Characterization and optimization of small scale farming systems for material recovery and sustainable management. The case of Sunchochumo Community in Peruvian Andes. Water Environment Management Series 2005. Volume 10. Pg 90-103.

Pabon-Pereira, C.P. Castanares, G. and van Lier, J. B. Optimizing an OxiTop® protocol for screening plant material suitable for anaerobic digestion. Submitted.

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ITSP1 (Insert from additional pdf file)

ITSP2 (Insert from additional pdf file)

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Cover painting by Claudia Pabón. Cover design by Tiago Vilela.

The cover painting depicts the conversion of biomass into biogas. It is also an allegory of the impermanent character of reality calling for the courage and inspiration to recreate it always into new dreams. May we keep on dreaming and materializing the harmonious world we want to live in.