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Biogas from lignocellulosic biomass

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PREFACE

This project has been financed by The Swedish Gas Center (SGC). SGC coordinates the technological development within the field of gas technology and promotes a widespread and efficient usage of gas and is financed by the Swedish Energy Agency and different stakeholders.

The project has been conducted by Grontmij AB and the University of Borås. A reference group (listed below) has been linked to the project with representatives from different stakeholders, associations and companies:

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SUMMARY

Grontmij AB has cooperated with the University of Borås to evaluate the technological and economical possibilities for biogas production from substrates containing lignocellulose, such as forest residues, straw and paper.

The state of knowledge regarding biogas production from cellulosic biomass has been summarized. The research in the field has been described, especially focusing on pretreatment methods and their results on increased gas yields. An investigation concerning commercially available pretreatment methods and the cost of these technologies has been performed. An economic evaluation of biogas production from lignocellulosic materials has provided answers to questions regarding the profitability of these processes. Pretreatment with steam explosion was economically evaluated for three feedstocks – wood, straw and paper – and a combination of steam explosion and addition of NaOH for paper. The presented costs pertain to costs for the pretreatment step as it, in this study, was assumed that the pretreatment would be added to an existing plant and the lignocellulosic substrates would be part of a co-digestion process.

The results of the investigation indicate that it is difficult to provide a positive net result when comparing the cost of pretreatment versus the gas yield (value) for two of the feedstocks – forest residues and straw. This is mainly due to the high cost of the raw material. For forest residues the steam pretreatment cost exceeded the gas yield by over 50 %, mainly due to the high cost of the raw material. For straw, the production cost was similar to the value of the gas. Paper showed the best economic result. The gas yield (value) for paper exceeded the pretreatment cost by 15 %, which makes it interesting to study paper further.

SAMMANFATTNING

Grontmij AB har tillsammans med Högskolan i Borås arbetat för att utvärdera möjligheterna till biogasproduktion från substrat såsom trä, halm och papper innehållande lignocellulosa. Utvärderingen har gjorts med avseende på tekniska och ekonomiska möjligheter.

Kunskapsläget beträffande biogasproduktion från cellulosahaltiga substrat har sammanfattats. Forskningen inom området har beskrivits och speciellt fokus har legat på förbehandlingstekniker och den ökning i gasproduktion som nyttjandet av teknikerna kan innebära. En undersökning har genomförts beträffande kommersiellt tillgängliga tekniker och kostnaderna för dessa. En efterföljande ekonomisk analys av biogasproduktion från lignocellulosahaltiga substrat har kunnat svara på frågor som rör lönsamhet av dessa tekniker. I den ekonomiska utvärderingen har alla substrat – trä, halm och papper – förbehandlats med ångexplosion och för papper kombinerades ångbehandling med tillsats av NaOH. De kostnader som presenteras avser kostnader för förbehandlingssteget då denna studie antog att förbehandlingsmetoden skulle kopplas till en befintlig anläggning och att de cellulosarika substraten skulle samrötas med andra substrat i en samrötningsanläggning.

Resultaten indikerar att det är svårt att tillhandahålla ett positivt nettoresultat när förbehandlingskostnaderna jämförs med värdet av den producerade gasen för två av substraten – GROT och halm. Detta beror i huvudsak på de höga kostnaderna för råmaterialet. När det gäller GROT var förbehandlingskostnaderna 50 % högre än intäkterna från gasen, i huvudsak beroende på kostnaderna för GROT. För halm visade det sig att förbehandlingskostnaderna var ungefär lika som värdet av den producerade gasen. Papper påvisade det bästa ekonomiska resultatet då värdet av den producerade gasen var mer än 15 % högre än förbehandlingskostnaderna. Detta medför att det är intressant att undersöka papper mer ingående i framtiden.

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1 INTRODUCTION

At present, one of the most important prerequisites for sustainable development is the production of appropriate fuels from biomass, which can be utilized as an alternative to fossil fuels. Biogas produced from waste materials is a promising renewable energy source, which is already used in the production of heat and electricity as well as for car fuel in many different countries. The biogas process can be applied on virtually all biological material, but fractions with low degradability will limit the amount of biogas produced and thus lower the efficiency of the process. The most abundant raw material that exists is lignocellulosic biomass, such as hardwood, softwood, grasses and industrial, as well as, agricultural residues. Accumulation of lignocellulosic wastes in large quantities can lead to, or contribute to, many environmental problems. On the other hand, the conversion of these materials into renewable fuels presents great potential in gradually decreasing the use of nonrenewable fossil resources (oil, coal, and natural gas)[1]. Due to their chemical composition, including high sugar content, lignocellulosic waste can be converted to number of value added products, such as ethanol, biogas, lignin as well as organic acids and enzymes[2].

Lignocellulosic biomass mainly contains cellulose, hemicelluloses and lignin and has the potential to be used as raw material for biogas production. However, the compact crystalline structure, the fact that lignin physically shields the cellulose and hemicelluloses parts, makes these materials more resistant to anaerobic digestion[3,4]. A suitable pretreatment method is, therefore, needed to increase the biodegradability or digestibility of lignocellulosic materials. By breaking down the structure, removing the lignin and reducing the crystallinity, a pretreatment process will enhance the solubilization of the material resulting in improved methane production during the subsequent anaerobic digestion process.

1.1 ORGANIZATION AND COMPETENCE

The project has been conducted by the University of Borås and Grontmij AB.

Grontmij has been project manager and the project was headed by Peter Berglund Odhner. Other people involved in the project were: Ilona Sárvári Horváth, University of Borås; Maryam Mohseni Kabir, University of Borås; Anna Schabbauer, Grontmij; Martin Råberg, Grontmij and Mikael Jönsson, Grontmij. Ilona is a researcher within the field of pretreatment methods for lignocellulose rich materials. Anna has previously been involved in anaerobic digestion projects at Svensk Biogas in Linköping. Additional staff from the University of Borås and Grontmij has been involved as the need arose.

The research group at the University of Borås has many years of experience in raw material processing and hydrolysis of lignocellulose rich materials in connection with bio-ethanol production. This knowledge is now being used in the field of biogas. Grontmij is currently working on development projects concerning biogas production. The company provides operational support to biogas processes and upgrading facilities as well as has practical knowledge of commercial production of biogas.

2 AIM AND METHOD

The aim of this study was to make a compilation of the research for effective pretreatment methods of lignocellulosic biomass for biogas production, focusing on wood, straw and paper. A broad literature study, consulting over 100 written articles on the subject, was conducted in order to gain an understanding of the research which had recently been carried out, and moreover what future research will be focusing on. Based on the results found in literature and information via business contacts, regarding suppliers and equipment, the commercial availability of the pretreatment method was evaluated. A model was constructed to serve as the basis of the process design by which a technical economical evaluation was carried out.

This model was constructed using the program "Engineering Equation Solver", developed by two professors, Dr. William Beckman and Dr. Sanford Klein, both from the University of Wisconsin, teaching mechanical engineering thermodynamics. The program itself contains an extensive library of mathematical and thermophysical property functions making it possible for the person carrying out the modeling to focus on the issue they wish to illustrate rather than gathering raw data and working out equations. The knowledge lies in knowing how to utilize the built in data.[5]

Using the model to carry out a technical economical evaluations for the substrates and pretreatment methods in question, made it possible to make conclusions as to the possibilities for biogas production from these kinds of feedstock. In addition, the model was utilized to make interpretations about probable challenges.

It was necessary to set restrictions for the technical and economic variables and evaluations in the report as it is not possible to encompass all factors and partial processes that occur in a full scale plant. The restrictions were set with regard to:

- Substrates considered
    - Wood
    - Straw
    - Paper
- Pretreatment methods evaluated economically
    - Steam explosion
    - Steam explosion with addition of a diluted chemical
- Energy flows utilized

    - Input and output of energy (kWh) from the process
    - Discussion concerning output of energy
- Plant layout and design
    - Delivered feedstock to the plant (freight included)
    - Processes (automatic system)
    - No estimates concerning byproducts in the process

2.1 FOUR COMPONENTS

The project had four (4) components:

1. Compilation of the state of knowledge. What research has been done? What has the research shown? What pressure, temperature, mechanical treatment or chemicals are needed for effective pretreatment of lignocellulosic biomass? How high is the biogas yield in relation to a reasonable degree of degradation for each pretreatment method compared with that of the untreated materials, respectively?

2. Investigations on existing suppliers who can deliver the type of equipment needed. Cost estimates are made for potential pretreatment methods in which providers cannot yet provide investment costs.

3. Economic evaluation for assessment of the economic viability of biogas from lignocellulosic biomass. Under what conditions is it economically correct to digest cellulosic biomass? How does biogas production by digestion measure up in relation to combustion or thermal gasification of cellulosic biomass for example?

4. Description of challenges for lignocellulose based biogas production and the questions that remain before the technology can be commercialized.

The proposed study explored the existing knowledge regarding pretreatment methods for substrates containing lignocellulose. This study aimed to raise the state of knowledge in which the potential for biogas production from cellulosic biomass was investigated. There are many different substrates and variations of substrates within the three main groups specified. For example, when considering straw, rice straw, wheat straw and corn straw are possibilities. Regarding woods chips, Japanese cedar chips, Eucalyptus and spruce chips can be considered. When considering paper, newsprint, office paper and paper tube residuals are possible options.

When setting conditions for the economic evaluations in this report, it was important to use substrates that were readily available in Sweden. Therefore, calculations and conclusions were based on substrates which could easily be obtained in Sweden.

2.2 TENDERS AND PREVIOUS EXPERIENCE

The technical and economic data concerning pretreatment of lignocellulosic biomass was gathered through tenders and contacts with different entrepreneurs and suppliers. Information from literature and previous experience from similar processes was also used in the economic evaluation.

2.3 CALCULATION AND ECONOMIC CONDITIONS

The economic evaluation focused on the cost of pre-treatment for the current feedstock versus the output of biogas or methane gas. The value of the gas has been estimated in the calculations. The economic evaluations were based on certain conditions more thoroughly described in the section titled “Process and technical data”.

3 BIOGAS PRODUCTION FROM LIGNOCELLULOSIC BIOMASS

3.1 SCIENTIFIC RESEARCH

When preparing this literature review the focus was put on summarizing the results published in different scientific studies aiming to investigate the possibility of utilizing three different lignocellulosic substrates i.e. wood, straw and paper for biogas production.

Because of the low digestibility of these materials an appropriate pretreatment is needed prior to anaerobic digestion in order to enhance the methane yield. Scientific databases, such as ScienceDirect, Wiley online library, Springerlink and Pubmed central were used applying relevant key words, such as pretreatment, methane, biogas, lignocellulose, waste, biodegradation to find the related latest data published during the last decade, mostly between 2003-2011.

Several studies were found which investigated the effects of different pretreatment methods on the structure and further on the anaerobic digestibility of these materials. The results of the investigations showed that by using a pretreatment method, the (enzymatic) hydrolysis of cellulose and hemicelluloses could be noticeably accelerated providing greater yields during the following anaerobic digestion[6].

3.2 THE NEED OF PRETREATMENT

One of the most significant current discussions regarding global issues today is related to climate conditions, which are polluted by human activities, natural events and the use of various contaminants such as fossil fuels, diesel and gasoline. Currently, one of the most important prerequisites for sustainable development is the production of appropriate fuels from biomass, which can be utilized as an alternative to the current use of fossil fuels. Biofuel can definitely be a proper substitute for conventional fuels.

Lignocellulosic biomass exists as the most abundant raw materials such as hardwood, softwood, grasses, as well as household, industrial and agricultural residues. However, their low digestibility is one of the major problems when considering utilizing these materials for renewable fuel production. Pretreatment is therefore an important step prior to the bioconversion of lignocellulosic biomass into value added products. These materials contain mainly cellulose, hemicelluloses and lignin making up a compact structure, where lignin physically shields the utilizable cellulose and hemicelluloses part from the degrading enzymes. Thus, it is crucial to change this compact structure in order to make cellulose and hemicelluloses more accessible to the enzymes breakdown and to convert them into fermentable sugars[7] . There are several pretreatment methods that have been studied, including physical, chemical and biological pretreatments, which have been studied. These methods increase the solubilization of the substrate by removing the lignin through breaking down its structure and reducing celluloses' crystallinity. In this way, the biodegradability, or digestibility of lignocellulosic materials, will be effectively enhanced[8].

In biogas production from lignocellulosic biomass, microorganisms are able to utilize a wide range of organic compounds (such as pentoses, hexoses, fatty acids, proteins and lipids); therefore, the main goal of a treatment for biogas production is to increase accessibility to the holocellulose content of the lignocellulosic material[9]. An effective treatment should increase the porosity of the substrate making the carbohydrates more accessible to the enzymes. At the same time, it is important that the different fractions are preserved without degrading or loosing organic matter as well as limiting the formation of inhibitors. In addition, the treatment should be economically feasible.

Unfortunately, a method suitable to treat all types of lignocellulosic raw materials for production of all different types of biofuels has not yet been identified[10].

Within the following chapters different pretreatment methods on three different lignocellulosic materials – wood, straw and paper – have been reviewed.

3.3 PRETREATMENT METHODS

Several pretreatment techniques have been studied intensively prior to both biogas and ethanol production from lignocellulosic substrates with respect to facilitating the biological degradation. Each of the treatment methods has its advantages and drawbacks[11].

These pretreatment methods can be divided into mechanical, thermal, chemical as well as, biological treatments or a combination of these techniques as it is shown in Table 1.

Table 1. A summary of techniques investigated for enhancing biogas production from lignocellulosic materials.

Technique	Subdivision
Mechanical	Milling
Thermal	Steam explosion Thermal hydrolysis
Chemical	Acid hydrolysis Alkaline pretreatment Ionic liquids pretreatment Oxidative pretreatment
Biological	Fungi
Co-digestion	Two or more substrates

Co-digestion is yet another method used to enhance biogas production. This method entails planning loading of the digester so that an advantageous blend of different substrates serve as organic load. This ultimately means e.g. that substrates with low nitrogen content but high carbon content can be mixed with a substrate that contains a high amount of nitrogen but a low amount of carbon in order to obtain a balanced C/N ratio. In this way, the microbiological processes in the digester balance themselves at very little cost to the plant operator.

3.3.1 MECHANICAL PRETREATMENT

During mechanical treatment milling is applied to cut the lignocellulosic biomass into smaller pieces which can effectively work on reducing the crystallinity and the degree of polymerization resulting in increasing available surface area for the attachment of degrading enzymes[12].

The milling process can be performed on wet or dried basis based on the mill type. Colloid mill and fibrillator can only work properly for wet materials, such as wet paper and paper pulps while roller mill, extruder and hammer mill are usually used for dry materials. Furthermore, mill ball can work on either dry or wet materials[13].

3.3.2 THERMAL PRETREATMENT

Thermal treatment refers to pretreatment methods performed at higher temperatures. The hemicelluloses part is the first to solubilize at temperatures above 150-180°C followed shortly thereafter by the lignin part[14]. During the break down of hemicelluloses acids will also be formed, which then will act as catalysts in the further break down and hydrolysis accelerating the solubilization of hemicellulose’s oligomers[15,16].

However, the risk of formation of inhibitory products, such as phenolic and heterocyclic compounds, furfural and HMF, especially in acidic conditions is elevated in heat pretreatment[17,18]. These inhibitory or toxic products have an adverse effect on the microorganisms during the subsequent bioconversion processes[19]. Therefore, pretreatment at temperatures of 250°C and above should be avoided due to production of unwanted products and pyrolysis reactions[20].

Steam explosion

The steam explosion process is performed at high temperatures (i.e. up to 240°C) and pressure (i.e. up to 33.4 bar) and lasts for a few minutes. The pressure is released and biomass cools down quickly thereafter. The main purpose of this treatment is to get 80-100 % of the hemicellulose fraction solubilized making the cellulose fraction accessible to enzymatic hydrolysis[21]. In addition, depolymerization of minor parts of cellulose and lignin can also be achieved.

The governing factors for the effectiveness of the treatment are the temperature and the retention time. The retention time determines the degree of hemicellulose's hydrolysis, and can thus, greatly enhance the fermentation process that follows. On the other hand, long duration of pretreatment leads to the formation of inhibitory products which negatively affect the subsequent biological degradation process. Determining the appropriate retention time for the steam explosion treatment needs to consider the moisture content of the biomass; the higher the moisture content, the longer the time period needed for the steam pretreatment[22]. The temperature controls the steam pressure inside the reactor. Higher temperatures generate higher pressures leading to an increased difference between atmospheric pressure and the pressure in the reactor. The pressure difference results in the evaporation of the moisture content in the biomass and causes the explosion[23].

The treatment conditions used are often described by using the severity factor (log R0)[24]:

$\log R0 = \log (t. e^{(T-100)/14.75)})$

Where,

t= resident time (min)

T=Reaction temperature in degrees Celsius

In order to optimize treatment conditions for lignocellulosic materials, it is important to be able to relate the net product yield to the pretreatment severity[25].

3.3.3 CHEMICAL PRETREATMENT

Acid hydrolysis

Acid hydrolysis is categorized into two groups depending on the acid concentration; dilute acid pretreatment or high concentration acid pretreatment. According to the literature reviewed, dilute acid treatment is among one of the most effective methods for lignocellulosic biomass[26,27]. Dilute acid treatment typically carried out, either at high temperatures ($T > 160°C$) and continuous flow with low solids loading and short retention times (e.g. 5 min), or low temperatures ($T \leq 160°C$) and batch process with high solids loading at longer retention times (e.g. 30-90 min)[28,29].

There is a variety of acids reported in literature that have been applied to a wide range of feedstocks, including softwood, hardwood, herbaceous crops, agricultural residues, wastepaper, and municipal solid waste. Among the acids, (i.e. dilute sulfuric acid, dilute nitric acid, dilute hydrochloric acid, dilute phosphoric acid, and peracetic acid) dilute sulfuric acid has been broadly applied due to its low cost and high effectiveness.

When dilute acid is added to the biomass and the mixture is kept at 160-220°C for a few minutes, this treatment offers good performance in the breakdown of hemicelluloses recovering monomeric sugars and soluble oligomers from the cell wall into the hydrolyzate. Consequently, the removal of the hemicellulose fraction increases the porosity of the material enhancing the digestibility[30]. However, lignin is not significantly removed in this process. Therefore, this method is more suited for biomass with low lignin content[31].

Several studies showed that in order to achieve maximum hemicellulose recovery, particular attention should be paid to the applied treatment time, since there is only a relatively short time interval in which the hemicellulose degradation can occur to a considerable extent while the sugar decomposition is still small. Furthermore, it was found that conditions which gave maximum hemicelluloses removal and recovery in the hydrolyzate did not always result in the highest enzymatic digestibility[32].

The drawback of this method is the risks of further degradation of hemicelluloses to furfural and hydroxymethyl furfural, which then have an inhibitory effect on the subsequent microbial processes.

Concentrated acid pretreatments are mainly performed at low temperatures using concentrated H_2SO_4 and HCl (30-72 %)[33,34]. These are powerful agents for cellulose hydrolysis and give high sugar yields (almost 100 % of the theoretical hexose yield). However, highly concentrated acid causes corrosion. Thus, the material used to construct the reactor must be highly resistant to corrosion. In addition, the acid has to be recovered and the acid containing steam produced must be neutralized. Due to its high cost this pretreatment method is not economically feasible for commercial use[35].

Alkaline pretreatment

Alkaline pretreatment is one of the major chemical pretreatment techniques used. This pretreatment refers to application of various bases, including sodium hydroxide[36,37,38], potassium hydroxide[39], calcium hydroxide (lime)[40,41,42], aqueous ammonia[43,44] and ammonium hydroxide. Alkaline pretreatment mainly results in delignification, together with solubilization of a remarkable amount of hemicelluloses. It is successful in removing acetyl and the various uronic acid substitutions on hemicelluloses which otherwise may decrease the accessibility of enzymes to hemicellulose and cellulose surfaces[45,46].

The efficiency of alkaline treatment extensively depends on the properties of the lignocellulosic material treated and on the treatment conditions. Generally, alkaline pretreatment is more successful on the substrates with low lignin content such as hardwoods and agricultural residues than hardwoods with higher lignin content[47]. Alkaline pretreatment is based on saponification of intermolecular ester bonds cross linking lignin and hemicelluloses resulting in a decreased degree of polymerization (DP) and crystallinity, the disruption of the lignin structure and the separation of linkages present between hemicelluloses and lignin[48],[49].

Among the different alkaline solutions investigated for the treatment of lignocelluloses, aqueous ammonia and lime (calcium hydroxide) pretreatments are considered to be the most effective and inexpensive methods.

Pretreatment with NaOH also shows great enhancement in the subsequent enzymatic saccharification phase by decreasing crystallinity and increasing the degree of polymerization. However, significant drawbacks of this method are the high cost and the need of recovery, which make it difficult to apply in large scale implementations[50].

Ionic liquids (ILs) pretreatment

Dissolution of cellulose is one of the targets of ionic liquids (ILs) pretreatment. It has currently gained wide attention with regards to these kinds of treatments within the research community since the chemicals used are considered to be efficient and environmentally sound novel cellulose solvents[51].

The attraction of this method refers to its ability to dissolve huge amounts of cellulose under mild conditions and to the possibility of recovering almost 100 % of the used ILs to their initial purity[52].

The separation mechanism using ILs involves the hydrogen and oxygen atoms of cellulose hydroxyl groups acting in the formation of electron donor – electron acceptor (EDA) complexes which interact with the ILs[53]. The interaction between cellulose-OH and ILs finally results in the dissolution of cellulose. The solubilized cellulose can then be recovered by precipitation using anti-solvents such as ethanol, methanol, water or acetone. Within this pretreatment process, the crystallinity of cellulose significantly decreases along with noticeable changes in the macro and micro structure of cellulose[54].

ILs as treatment agents have several advantages such as biodegradability, broad selection of anion and cation combinations, low toxicity, low viscosity, low hydrophobicity enhanced electrochemical stability, thermal stability, high reaction rates, low volatility with potentially minimal environmental impact, and non-flammable property[55].

The most commonly used ILs reagents include N-methylmorpholine -N-oxide monohydrate (NMMO), 1-allyl-3- methylimidazolium chloride (AMIMCl), 1-n-butyl-3- methylimidazolium chloride (BMIMCl), 3-methyl-N-bytylpyridinium chloride (MBPCl) and benzyldimethyl (tetradecyl) ammonium chloride (BDTACl)[56,57,58,59].

Oxidative pretreatment

An oxidative pretreatment is carried out by the addition of an oxidating agent, such as hydrogen peroxide, ozone, oxygen or air. The main purpose of this pretreatment is delignification. The oxidizing chemicals are highly reactive with the aromatic ring of lignin residues, and, consequently, the lignin polymer will be converted to carboxylic acids[60]. However, the formed acids can cause inhibition in the fermentation processes that follows, which means that these inhibitors have to be neutralized or removed before the substrate enters to the digester. Aside from delignification, the oxidative treatment also affects the hemicellulose fraction. Unluckily, due to the non-selectivity of the oxidant, further degradation of hemicelluloses have been observed, which implies that a substantial part of the hemicellulose fraction can no longer be utilized in the further conversion to biogas[61].

Wet oxidation

The wet oxidation method has been widely used as an alternative to steam explosion. Wet oxidation is a form of hydrothermal treatment, where oxygen or air is used for the oxidation of dissolved or suspended components in water at temperatures above 120°C (e.g. 148-200°C) for a period of 30 min[62,63]. In industrial applications, wet air oxidation processes have been used to handle waste with high organic matter by oxidation of soluble or suspended matter, with oxygen in the aqueous phase at high temperatures (150-350ºC) and pressure (5-20 MPa)[64]. The most important factors in wet oxidation are the oxygen pressure, the reaction time and the temperature.

As a result of wet oxidation, cellulose is partly degraded, hemicelluloses are being hydrolyzed and lignin is subjected to oxidation and cleavage. All these alterations lead to an increase in the accessibility of the substrate to enzymatic hydrolysis[65]. Wet oxidation has been proven a promising method for pretreatment of lignocelluloses because it ruptures the crystalline structure of cellulose[66] and has been a successful alternative for the treatment of wheat straw and hardwood[67].

3.3.4 BIOLOGICAL TREATMENT

A significant drawback with mechanical, thermal and chemical pretreatment techniques is the requirement of high energy input for an improved biomass conversion. Moreover, these methods are generally carried out using expensive instruments and chemicals. In contrast, utilizing microorganisms to enhance the biodegradability of organic matter and consequently methane production, offers advantages such as low-capital cost and low energy demand. In addition, these methods are environmentally sound[68]. On the other hand, biological treatment methods require long resident times because the rate of the biological hydrolysis is usually very low[69,70].

Lignin is known as a major factor to determine the extent of biomass degradation in anaerobic conditions[71], and biological pretreatment methods have been considered as effective and cheap methods of delignification.

Generally, improvement in methane production by fungi is explained by the disruption of cell wall structure. Additionally, lignin degradation also increases the surface area of the cellulose to develop its susceptibility to microbes and enzymes[72]. Microorganisms, such as brown, white and soft rot-fungi, are engaged to degrade hemicelluloses and lignin, but due to its high resistance only a very small amount of cellulose will be degraded[73].

Among the large amounts of fungi which work to degrade lignocellulosic materials, a white rot fungus, *Ceriporiopsis subvermispora*, is identified as the superior biopulping fungus that can degrade lignin without intensively breaking the cellulose[74]. Other examples for fungi, used for the biological treatment are *Phanerochaete chrysosporium*, *Trametes versicolor*, *Trametes hirsuta* and *Bjerkandera adusta*[75].

3.4 BIOGAS PRODUCTION FROM WOOD

Since the gas yield of untreated wood samples have been found to be almost zero, several pretreatment methods have been investigated aiming to improve the biogas production from different wood samples. The results found in the literature are summarized in the Appendix and some of them are discussed below.

Nakamura et al.[76] studied the effect of steam explosion on wood chips (Eucalyptus globules) at a pressure of 25 atm and a steaming time of 3 min prior to biogas production. The methane yield obtained was 0.194 m^3/kg TS after the steam explosion treatment, compared to just 0.014 m^3/kg TS from the untreated samples. The amount of methane produced depended on a decrease in Klason lignin (high molecular weight lignin). Furthermore, it has been observed that 80% of the holocellulose was converted into methane. Similar results were achieved by Take, et al.[77] when steam explosion treatment was applied on wood, Japanese cedar chips, prior to biogas production. The treatment conditions were 4.51 MPa (258°C) for 5 min. The pretreated sample yielded 0.180 m^3/kg TS methane, while the methane yield for untreated wood samples was almost zero.

In another study, anaerobic digestion of Japanese cedar wood was carried out after pretreatment with two different strains of white root fungi, *Ceriporiopsis subvermispora*, *i.e.* CBS 347.63 and ATCC 90467[78]. The strains were cultivated on wood chips with and without the addition of wheat bran for 4-8 weeks. The results showed that methane production during the subsequent digestion phase increased with increased cultivation time of the fungi on the treated material. The maximum methane yield of 0.083 m^3/kg raw material was obtained by the treatment with *C. subvermispora* ATCC 90467 in the presence of wheat bran for 8 weeks. This corresponds to 35 % of the theoretical yield based on the holocellulose content in the decayed wood[79].

Mirahmadi, et al.[80] have performed alkaline pretreatment using 7 % wet weight NaOH on milled spruce (softwood) and birch (hardwood) samples at different temperatures between -15 and 100°C. Anaerobic batch digestion assay was then performed at thermophilic conditions (55°C) for 30 days. Treatment of birch at 100°C led to a methane yield of 0.46 m^3/kg VS, compared to 0.25 m^3/kg VS for the untreated birch samples. On the other hand, the best results for spruce were obtained when the samples were treated with NaOH at 5°C resulting in a 74 % improvement in the methane production. Furthermore, it was concluded that the use of alkaline treatment was more successful for hardwood than for softwood. There was, however, almost no destruction of lignin observed.

Teghammar, et al.[81] studied the effect of NMMO pretreatment on spruce (softwood), triticle straw and rice straw to enhance the biogas production. Pretreatments were carried out at 130°C for 1-15 hours followed by anaerobic batch digestions of treated and untreated samples for six weeks. The digestion of untreated spruce chips (10 mm) and milled (< 1 mm) spruce, rice straw and triticale straw resulted in methane yields of 0.011, 0.066, 0.022 and 0.030 Nm^3/kg raw material respectively. The NMMO-pretreatment significantly improved the methane yields; the improvements were 400-1,200 %. Methane productions of 0.125, 0.245, 0.157 and 0.203 Nm^3 CH_4/kg raw materials were obtained for the pretreated chips and milled spruce, rice straw and triticale straw samples respectively.

3.5 BIOGAS PRODUCTION FROM STRAW

Based on the results found in the literature and summarized in the Appendix, it is difficult to conclude which pretreatment method that works best with straw.

One important aspect is that mechanical treatment, like milling is of vital significance for the production of biogas. Straw from different kinds of cereals seem to affect the gas yield as well.

Generally, non-treated (chopped) straw generates about 0.180-0.200 m^3 CH_4/kg VS. Milled straw generates even higher yields.

In a study of Sharma et al.[82] the effect of particle size was investigated for wheat straw and rice straw through anaerobic batch digestions. Among five particle sizes (0.088, 0.40, 1.0, 6.0 and 30.0 mm), the maximum biogas yield was produced from raw materials with a particle size of 0.088 and 0.40 mm, both resulting in an almost equal quantity of gas production. It was, therefore, concluded that grinding below 0.40 mm would be uneconomical. Size reduction of wheat and rice straw produced 0.249 m^3 CH_4 /kg VS and 0.365 m^3/kg VS, respectively, while using larger particle size (30.0 mm) yielded 0.162 and 0.241 m^3 CH_4 /kg VS from wheat straw and rice straw respectively[83].

Dererie, et al.[84] applied 96 %-lime ($Ca(OH)_2$) containing 3 % $CaCO_3$ on chopped oat straw with particle size of 5-15 mm at 55ºC for 24 hours. The treated samples were then subjected to anaerobic batch digestion for 35 days resulting in a methane yield of 0.287 m^3/kg VS. Other pretreatment methods, such as steam explosion alone and steam explosion with acid were also applied on the same substrate resulting in lower methane yields.

In another study, wheat straw was exposed to steam explosion pretreatment at 180°C and 15 min[85]. The result showed that the pretreatment enhanced the methane yield by 20 %, i.e. 0.331 Nm^3/kg VS methane was produced from the treated samples, while the untreated (milled) straw gave 0.275 Nm^3/kg VS methane. Further, it was found that a longer resident time and higher temperature did not considerably increase the methane yield. The optimum temperature for steam explosion pretreatment was concluded to be between 160 and 200°C[86].

Zhang et al.[87] carried out experiments on conversion of rice straw into biogas using a high-rate anaerobic digestion system, anaerobic-phased solids digester system (APS-digester system). They investigated the effect of different pretreatments, i.e. mechanical, thermal and chemical using ammonia. The highest biogas yield was achieved when combining grinding to 10 mm particle size, heating at 110ºC and using 2 % ammonia. The biogas yield of untreated whole rice straw was 0.38 m^3/kg VS which increased to 0.47 m^3/kg VS by applying this combination of the treatment methods.

Zhong et al.[88] compared the results of biogas production from corn straw which was subjected to 8 % NaOH, 5 % ammonia and 4 % urea pretreatments at an ambient temperature of (15±2°C) for 20 days prior to anaerobic digestion. All pretreatment methods led to significant degradation of hemicellulose, cellulose and lignin. Among the alkaline methods applied, corn straw treated with NaOH resulted in a gas yield of 0.472 m^3/kg VS, which was 207 % higher than that of the untreated sample.

3.6 BIOGAS PRODUCTION FROM PAPER

According to the literature data found and presented in the Appendix, the yield of gas from paper also varies depending on the type of paper (pulp and paper sludge, paper tube residual, etc.), methods and inoculum used. In general, the methane yield was determined to be between 0.1 and 0.2 m^3/kg VS for the untreated paper samples.

Newsprint has been exposed to acetic-nitric acid reagent prior to anaerobic digestion[89]. It was observed that pretreatment with only acetic acid could not effectively dissolve lignin even when highly concentrated acid (80 %) and elevated temperature (in a boiling water bath) were used. On the other hand, it was found that treatment with 35 % acetic acid together with 2 % nitric acid increased the lignin removal from newsprint residues by about 80 %. This treatment increased the methane production to 0.270 m^3/kg VS, while 0.100 m^3/kg VS methane was obtained from untreated newsprint during the subsequent anaerobic digestion tests[90].

Alkaline pretreatment has also been applied on newsprint in a study by Clarkson et al.[91]. The result showed that pretreatment with 10 % NaOH considerably enhanced the biodegradability of newsprint resulting in 0.120 m^3/kg COD methane production compared to only 0.08 m^3/kg COD for the untreated samples.

In another study, pulp and paper sludge (PPS) was treated with different concentrations of NaOH prior to anaerobic digestion[92]. The best result was achieved when 8 g NaOH /100 g TS sludge was applied, resulting in 0.32 m^3 CH_4/kg VS, amounting to an increase of 184 % compared to the control sample.

Fox et al.[93] used wet oxidation to enhance methane production from newspaper waste. Wet oxidation was carried out at 170, 190, and 210ºC, with a retention time of 1 h. The highest lignin removal efficiency was achieved at 190ºC in which approximately 65 % was removed. The following batch anaerobic digestion tests also showed that the highest methane yield of newspaper could be achieved after this treatment, 59 % of the initial total COD could be converted to methane. The anaerobic cellulose removal varied from 74 % to 88 %.

Teghammar et al.[94] investigated paper tube residuals as substrate for biogas production. Steam explosion treatment with the addition of sodium hydroxide and/or hydrogen peroxide has been applied to improve the biogas production. The best result was obtained after steam explosion at 220°C for 10 min and with the addition of both 2 % NaOH and 2 % H_2O_2. Treatment under these conditions resulted in an increase in methane production by 107 % i.e. 0.493 Nm^3/kg VS methane was produced from the treated samples[95].

3.7 CO-DIGESTION

Beside pretreatment prior to anaerobic digestion, co-digestion was also investigated for the utilization of lignocellulosic materials. Recently, it has been realized that co-digestion can be an interesting option for improving yields of anaerobic digestion[96]. Co-digestion is the simultaneous digestion of a homogenous mixture of two or more substrates. The use of co-substrates can improve the biogas yield due to the positive synergisms established in the digestion process, providing a better nutritional balance and suitable moisture content required in the digester feed[97].

Animal manure usually contains high ammonia concentrations, which can cause inhibition in the digestion process. On the other hand, lignocellulosic materials are difficult to digest as they contain a significant fraction of lignin. However, co-digestion of manure and plant materials has been shown to be a successful way to utilize these materials in an anaerobic digestion process; together the materials complement each other and the risk of the inhibition decreases. The manure fraction provides a wide range of nutrients while the high carbon content of the plant materials results in a balanced carbon/ nitrogen ratio of the feedstock being loaded in the digester[98].

Lehtomaki et al.[99] studied anaerobic co-digestion of grass silage, sugar beets and oat straw together with manure in semi-continuously fed continuously stirred tank reactors (CSTRs). The results showed that mixing manure with crops corresponding to up to 40 % of the VS in the feedstock was beneficial, resulting in methane yields of 0.268, 0.229 and 0.213 m^3/kg VS for co-digestion of manure with grass, sugar beet tops and straw, respectively. The methane yield obtained from manure alone was 0.155 m^3/kg VS.

In another study, Lehtomaeki[100] used continuously fed and stirred reactor for co-digestion of cow manure and straw. Digestion of cow manure and straw counting up to 30 % of VS added resulted in 0.213 m^3/kg VS methane in 20 days at 35ºC. Increasing the straw concentration to 40 % of VS added resulted in a reduced methane yield of only 0.157 m^3/kg VS under similar conditions. In comparison, the methane production from the reference reactor (cow manure only) was 0.151 m^3/kg VS.

Demirbas[101] studied anaerobic co-digestion of straw and manure mixed in different ratios. The experiments were run for 28 days at mesophilic conditions (35°C) in bath reactors. Methane production of only manure was considerably high i.e. 0.234 m^3 CH_4/kg VS, whereas, co-digestion of manure and straw with a mixing ratio of 1:1 (VS) resulted in only 0.182 m^3 CH_4/kg VS.

Mueller et al.[102] investigated the effects of biological treatment on a mixture of straw and manure. Batch digestion assays were carried out with loading of 40 g/l solids in mesophilic digesters. The results showed that the biogas yield was improved from 0.293 m^3/kg (untreated straw/manure) to 0.318 and 0.343 m^3/kg for the pretreated straw/manure using *Pleurotus sp. "florida"* for the pretreatment for 60 and 90 days, respectively.

3.8 CONCLUSIONS

The literature review showed that the production of biogas or methane gas from durable feedstock such as wood, straw and paper can increase significantly with different pretreatment methods. According to this review steam explosion at high temperature (< 200°C) for a short period of time (5-10 min) is the best option for pretreatment of current feedstocks with regard to the improved gas yield (Figure 1). In the case of wood and straw the steam explosion treatment resulted in methane yields of around 0.2 m^3/kg VS and 0.3 m^3/kg VS, respectively (Figure 1). On the other hand, after the chemical treatment of straw using 8 % NaOH (and without steam explosion) the methane yield obtained was less only around 0.2 m^3/kg VS (Figure 1). Furthermore, the steam explosion treatment of paper was only effective when additional chemicals (NaOH, or both NaOH and H_2O_2) were added to the slurry during the treatment. Steam explosion with the addition of 2 % NaOH together with 2 % H_2O_2 resulted in around 0.5 m^3/kg VS methane, while the methane production after steam explosion treatment with the addition of 2 % NaOH alone was around 0.4 m^3/kg VS. The most significant improvements in gas yield and which methods were used to obtain them are specified below (Figure 1).

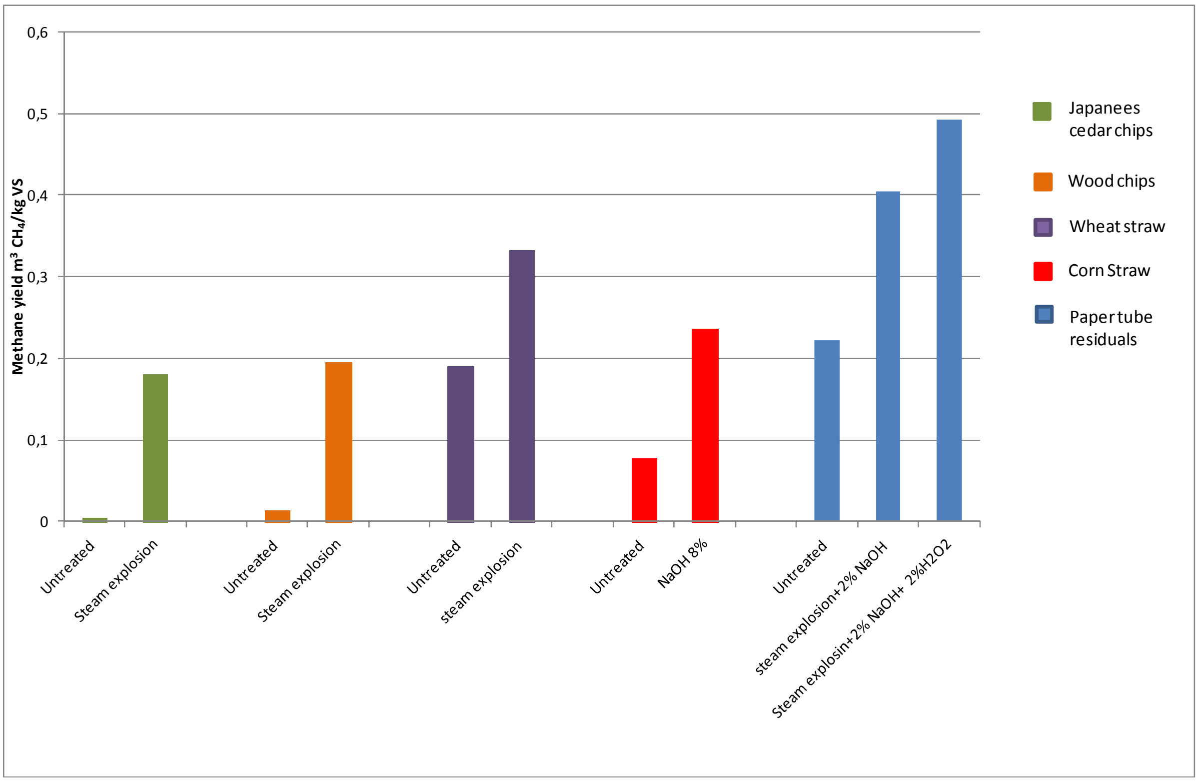


Figure 1. The most significant increases in methane yield and the methods used to obtain them for wood, straw and paper samples, as compared to the methane yield obtained from the untreated materials, respectively.

For wood chips and Japanese chips the methane yields found in the literature and presented in the Appendix are given as m^3/kg TS. However, when presenting these yields on the figure they were modified to m^3/kg VS assuming that the VS content is 88 % of the TS content.

In the technical economic evaluation that follows, the steam explosion pretreatment was investigated and methane yields of 0.2, 0.3 and 0.4 m^3/kg VS was used for pretreated wood, straw and paper feedstock, respectively, in the calculations.

4 SUPPLIERS OF EQUIPMENT

The literature review made it possible to narrow down the choices of substrates and pretreatment methods to proceed with and consider further in the economic evaluation that followed. Choices were based on increase in methane yield when comparing untreated and pretreated wood, straw and paper. It was established that steam explosion was the most effective method for lignocellulosic substrates and in the case of paper, addition of NaOH was needed in order to obtain an acceptable methane yield. In order to make the transition from lab scale reactors and published research articles to full scale plants, it was necessary to contact equipment suppliers who could provide functional and reliable technical solutions for steam explosion with the additions of chemicals as a pretreatment method.

Grontmij has, in cooperation with the University of Borås, conducted a survey of relevant suppliers to comprehend technical and economic data for steam explosion techniques in some cases with the addition of chemicals to answer the main question:

- Does the cost of steam explosion as a pretreatment method correspond to the maximum gas yield output after the treatment for the current feedstock?

Although there are not many equipment suppliers in Sweden, thermal hydrolysis is a technique which has been utilized abroad in various applications for liquid substrates. Thermal hydrolysis is used to accelerate the hydrolysis step of anaerobic digestion. By increasing the temperature and pressure it is possible to achieve changes in the structure of the substrate making it more biologically accessible to the organisms involved in the subsequent fermentation step. This results in a more complete fermentation, which usually coincides with an increase in gas yield.

A brief discussion of relevant suppliers for thermal hydrolysis equipment and, as a development of thermal hydrolysis steam explosion is described below.

4.1 CAMBI – THP PROCESS

The Norwegian company Cambi is a major supplier of technology for enhanced anaerobic digestion of municipal and industrial sludge. Cambi’s Thermal Hydrolysis Process (THP) has been used worldwide since 1995.

THP has been implemented in existing and “green field” projects designed to reduce disposed sludge quantities and the cost of building and operating digesters. Cambi THP is a high pressure steam pretreatment system for anaerobic digestion of municipal and industrial sludge and biowaste. Initially, the sludge is pumped into the pulper and preheated to 97°C. In the reactor the temperature increases to 165°C at 6 bar. Steam at 11 bar is then introduced in the reactor. The sludge material is flashed and in this process the cell walls implode or explode (see Figure 2 for an illustration of Cambi's THP-process).

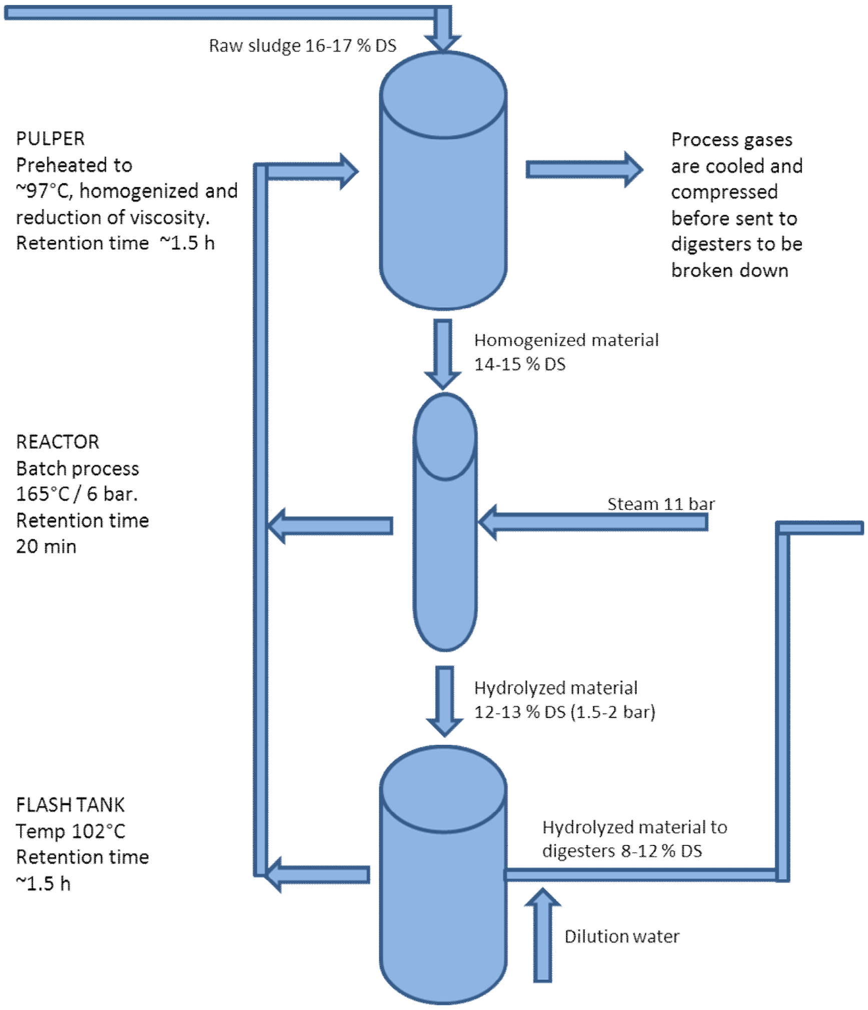


Figure 2. Cambi's THP-process which leads to rupture off cells making the biomass more readily available to microorganisms in the anaerobic digestion process (sketch modified after www.cambi.no[103]).

According to contacts with Cambi, they cannot provide solutions for steam explosion pretreatment of solid matter such as wood or paper. Mainly their process works with sewage sludge from wastewater treatment plants. Another problem is that their process does not work at the required pressure and temperature mentioned in the literature review. Cambi promised, however, that they could provide assistance regarding parts of the designed process we proposed in this report. Unfortunately, Cambi has not responded to our requests[104].

4.2 BIOREFINEX

Another company that works with steam and steam explosion is a Canadian company called Biorefinex (also called Biosphere). Their patented BioRefinex process, performed in a so called "thermal hydrolysis reactor", uses high pressure and saturated steam to degrade all organic material and destroy all pathogens while retaining the valuable nutrients present in the material. The hydrolyzed output is then fractionated using a series of centrifuges to maximize value and to produce consistent streams of organic fertilizer and nutrient feedstock for biogas production.

As shown in Figure 3, the biorefinery generates six different products in the categories renewable nutrients and renewable energy. In addition, the facility can also provide the overall biorefinery service of receiving and processing materials that would otherwise be considered waste and sent to landfills, in exchange for tipping fees.

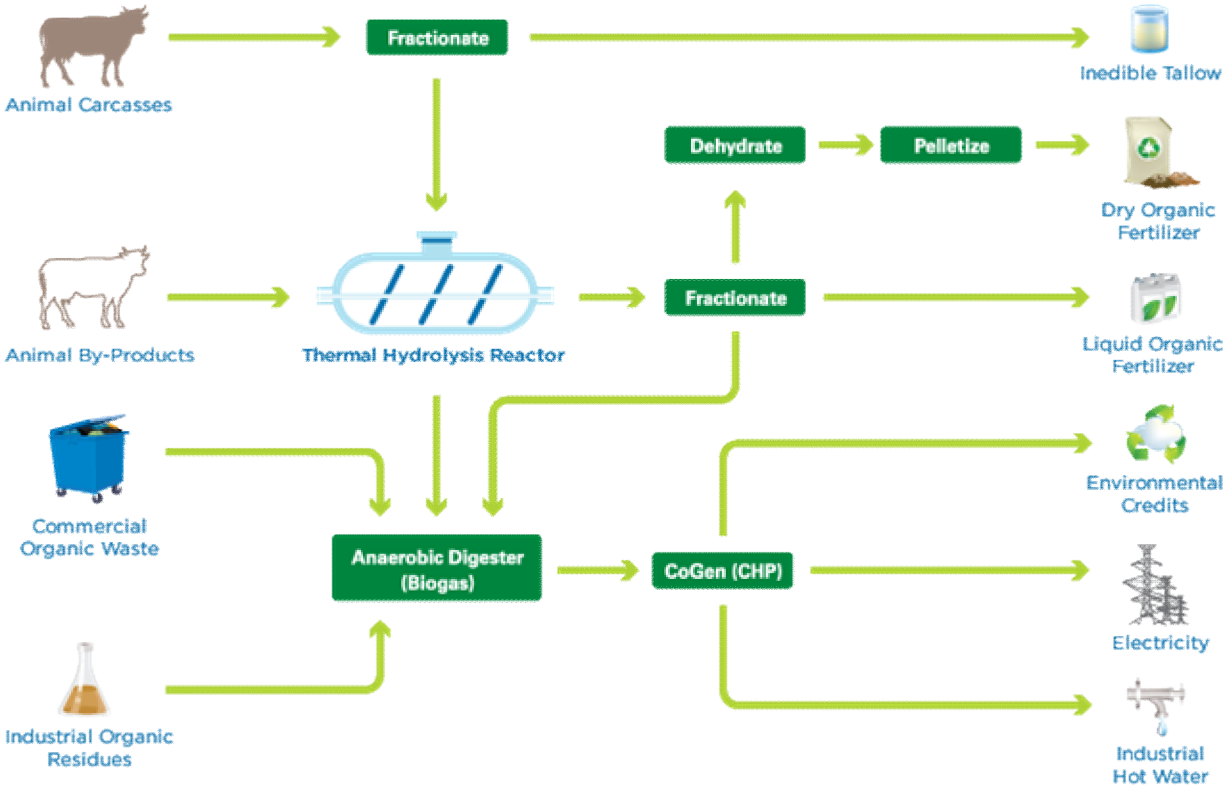


Figure 3. Outline of the system developed by Biorefinex. The biorefinery generates six different wholesale commodity products under the Renewable Nutrients and Renewable Energy categories. These include: dry pelletized organic fertilizer; liquid organic fertilizer; inedible tallow; electricity; industrial hot water; and carbon offsets (www.biorefinex.com[105]).

Biorefinex has been contacted by Grontmij and replied that they cannot provide the service we are looking for in this project, but were helpful regarding process configuration and layout[106]. The company provided data about the reactor tank (size and material) and flows of energy.

4.3 THE PAPER INDUSTRY AND OTHER COMPANIES

4.3.1 THE PAPER INDUSTRY

In Sweden there are several companies that work with part of the process. The forest and paper industry deals with steam, pressure and steam processes in some of their procedures and can offer technical solutions for components in the process or for technical design.

The pulp and paper industry utilizes steam explosion in one of its initial steps in order to alter the structure of the fibers in the ingoing material (wood chips or recycled paper). In this process the structure of lignin and hemicellulose are altered and broken up, while the cellulose is maintained and ultimately achieved as a separate fiber. This makes the fibers suitable for papermaking.

Initially, steam is blown into the reactor where the wood chips are stored. This is done in order to remove the air from the cells. Next, a chemical solution is added to the reactor resulting in a condensation of the steam and ultimately impregnation of the cells. The temperature is raised and the pressure in the reactor is > 1 atm, meaning that the solution does not reach its boiling point even when the temperature is over 100°C. The mixture is washed in order to separate the fibers from the chemicals. The pressure in the reactor drops and the mixture begins to boil causing the cells to "explode". In this way it is now possible to utilize the high quality fibers and proceed in the papermaking process[107].

It is important to know the composition of the raw material so that the correct chemicals and mixtures of chemicals can be applied. Obviously, one does not wish to degrade the cellulose in the wood, while lignin, which is the glue that holds the structure together, must be degraded in order to obtain suitable fibers. This is important to consider in the implementation of steam explosion as a pretreatment method for wood products used as a substrate for anaerobic digestion in a biogas plant.

4.3.2 NBE SWEDEN AB

A company called NBE Sweden AB in Sveg is testing a pilot plant to produce ethanol from wood materials. They use steam explosion at high temperatures (over 200ºC) and high pressure (around 25 bar). The reactor tank can operate with pressure up to 36 bar. Via a valve the pressure is released and the feedstock "explodes from within". The process is batch fed and can manage up to 0.5 ton per load, which corresponds to around 10,000 tons per year if the reactor is used efficiently.

After the explosion the feedstock is filtered and the sugar is used to produce ethanol in another process. The company has invested 35 million SEK[108] in the whole process including the ethanol step.

The process is similar to our steam explosion process according to temperature and pressure and their knowledge can be useful in the future for steam pretreatment of the feedstock investigated in this study. The company has been contacted for process data.

4.3.3 RUNDVIK MASONITE

In Rundvik, in the middle part of Sweden a company called Masonite uses steam to produce masonite boards. The raw materials used by Masonite's chip boards come from the forest via sawmills. The timber is transported from the forest to the sawmills.

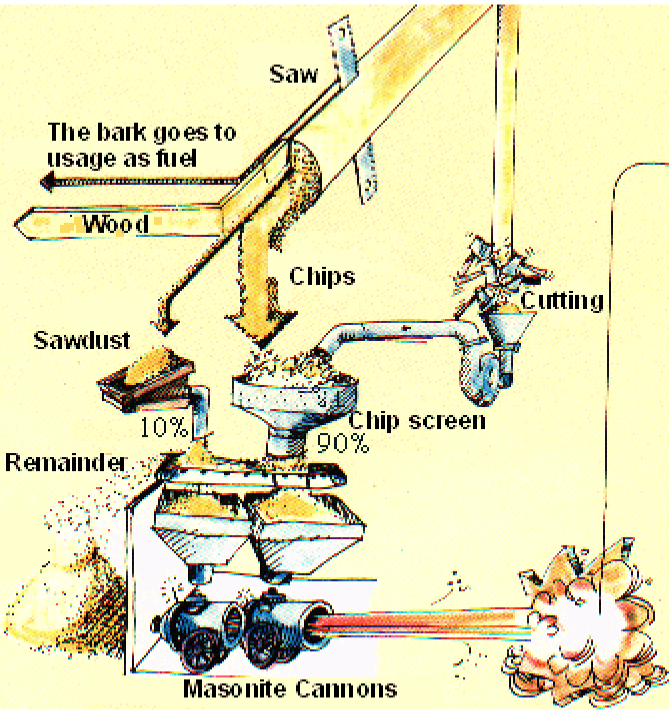


Figure 4. The Masointe process is illustrated in the picture above. The wood chips are minced before the steam explosion process (sketch from www. masonite.se).

When the timber has been barked part is sawn as wood and the rest goes to large chippers, which cut the timber to chips. Chips, sawdust and cutter shavings are delivered to Masonite. The chips and some of the sawdust then go down into the chip cannons where the chips under high pressure and high temperature are comminuted into long fibers. The byproducts are used as fuel for the boilers that feed the cannons and the rest of the manufacturing process with steam[109].

This steam explosion process resembles our intentions and the company has been contacted for process data.

Neither NBE Sweden AB nor Rundvik Masonite are, however, suppliers of equipment for a steam explosion process.

In addition to the Swedish companies mentioned, there are a few companies in Asia, mainly India, that run tests with steam explosion of solid matter such as wood materials.

4.4 CONCLUSIONS

The main supplier of steam explosion equipment is Cambi. Other companies include: Biorefinex from Canada and Xergi from Denmark. All three companies have been contacted by Grontmij.

Unfortunately, there are few companies who can provide complete technical solutions and support that match our requirements. However, robust processes similar to ones that would be required for the anaerobic digestion of lignocellulosic biomass, are present in industrial applications today. Hence, there is a lot of know-how in the field, which could serve the biogas industry well when developing new techniques, process configurations and plant designs.

There are few suppliers who can provide relevant data for biogas applications specifically, meaning that Grontmij had to design the process for steam explosion pretreatment based on earlier experience and through contacts with several different suppliers to receive process and financial data.

Companies that have worked with similar techniques and designs in other industrial applications served as a source of information on technical components for a steam explosion system: Läckeby Water (Purac), CB Package Boilers and YIT Group have knowledge about applications of this type and they were contacted by Grontmij.

5 PROCESS AND TECHNICAL DATA

Today, many of the municipal biogas plants in Sweden are operating under their capacity. At the moment, competition for feedstock is vigorous, which affects the prices of slaughter waste, dairy residues etc. There are, however, large amounts of lignocellulosic feedstock that could be used in the biogas process if it is pretreated in a viable manner.

The average size of a Swedish municipal biogas plant is digestion of less than 100,000 tons of substrate annually. Due to the scale of the many existing biogas plants, the amount of feedstock was limited to 5,000 t/yr organic load. Feedstock amounting to 5,000 t/yr with a dry matter content of 50-95 % mixed with water (to obtain a pumpable slurry) in actuality entails adding much more than 5,000 t/yr for the biogas system to operate adequately. To add more than 5,000 t/yr with a solid feedstock to an existing plant could cause problems with the loading capacity (volume of the digestion tank), vessels, pipe and pumps though it might be possible.

It is, nevertheless, possible to upscale the steam explosion process and thereby potentially reducing the production costs per unit. With a centralized plant for pretreatment of the current feedstock, the production costs might decrease but the transportation costs will most likely increase. A main idea was also to add the steam explosion process to an existing biogas plant and use the process heat (excess energy) within the plant, thereby obtaining other synergies. In conclusion, we are mainly calculating and evaluating a small scale (5,000 t organic load/yr) plant due to the factors mentioned above.

Figure 5 illustrates the principle of steam explosion system for hydrolysis of lignocellulosic feedstock. In the steam generator the water solution is heated to a specific temperature. The steam is lead to a treatment chamber there the feedstock is treated under high pressure and temperature for a certain treatment time. The treated feedstock is then explosively discharged through a pressure vessel into an expansion tank for cool down. During this step water condenses into the hydrolysate. The hydrolysate is then gathered and mixed with other feedstocks before this mixture is subjected for anaerobic digestion

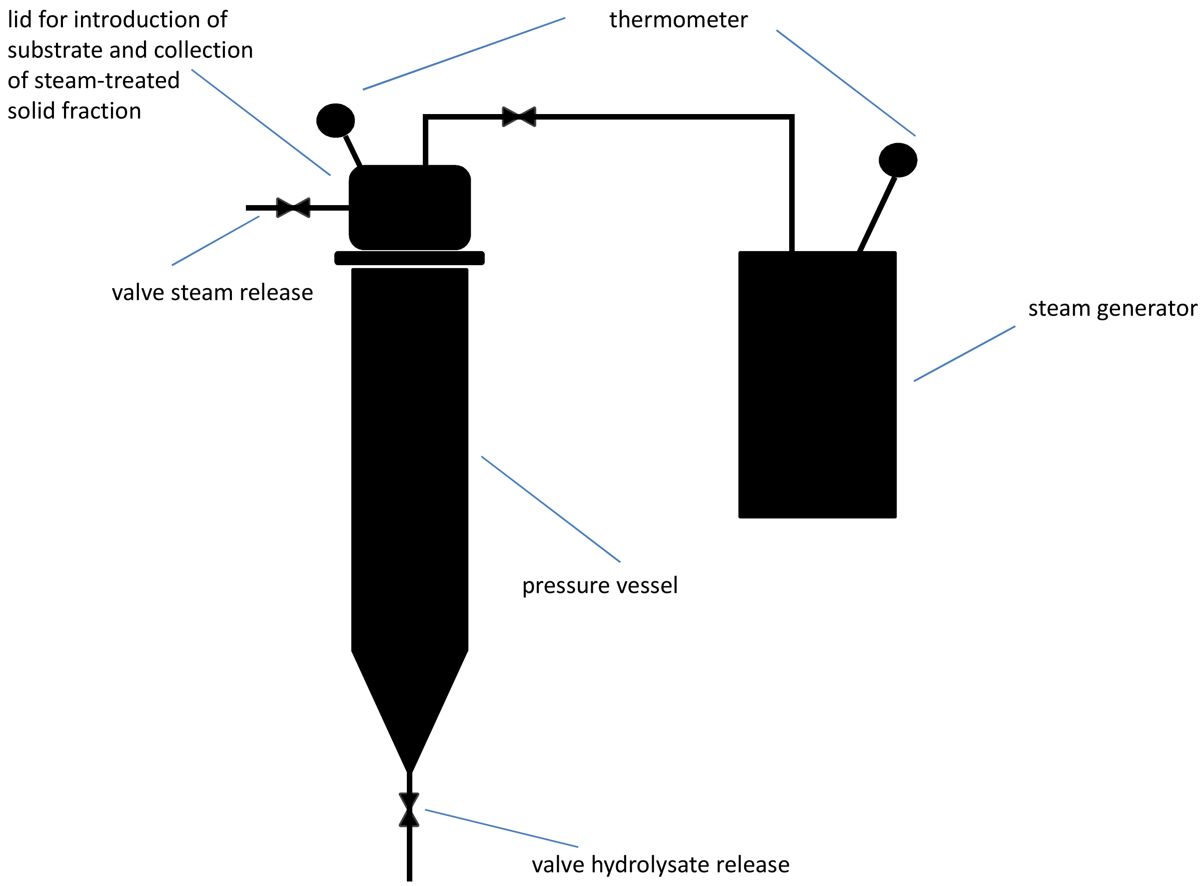


Figure 5. Illustration of the steam explosion principles for hydrolysis of lignocellulosic feedstocks.

This is a manually and simplified model of the steam explosion technique. At a larger scale it is necessary to process the feedstock prior to the steam treatment and mix it with water to a predetermined moisture content. This could vary depending on the feedstock used in the process. Primarily, the process should be mainly automated and loaded manually.

5.1 DESCRIPTION OF THE MODEL

A detailed description of the steam explosion process is provided below. The model shown in Figure 6 was developed by Grontmij and created in the program Engineering Equation Solver (EES). EES was developed as a tool in mechanical engineering thermodynamics at the University of Wisconsin by Dr. Beckman and Dr. Klein. EES gives the numerical solution to a set of algebraic equations and can also be used to:

- solve differential and integral equations
- carry out optimization
- provide uncertainty analyses and linear and non-linear regression.
- generate publication-quality plots
- animation possibilities for process flows

In addition to the solving equations and providing uncertainty analyses, the EES professional version also provides animation possibilities, as listed above. Graphical objects and text placed in a diagram window that have attributes such as location, size, angle and color specified can be controlled with EES variables. Text items can be assigned to string variables that are specified dynamically in an EES program. As the values of these variables change, the displays in the Diagram and child Diagram windows are automatically updated[110].

EES has a large built-in data bank of thermodynamic and transport properties, which is helpful in solving problems in thermodynamics, fluid mechanics, and heat transfer. EES can be used for many engineering applications; it is ideally suited for instruction in mechanical engineering courses and for the practicing engineer faced with the need for solving practical problems.

EES may be used to solve design problems in which the effects of one or more parameters must be determined. EES's parametric table, which is similar to a spreadsheet, provides this capability. The user identifies the independent variables by entering their values in the table cells. EES will calculate the values of the dependent variables in the table. EES also provides plotting capability to display the relationship between any two variables in the table.

EES can also be used to illustrate plant set-ups as there is a built in flow diagram function where it is possible to illustrate the components of the plant, the flows and change the input variable in order to obtain other costs and gas yields for example.

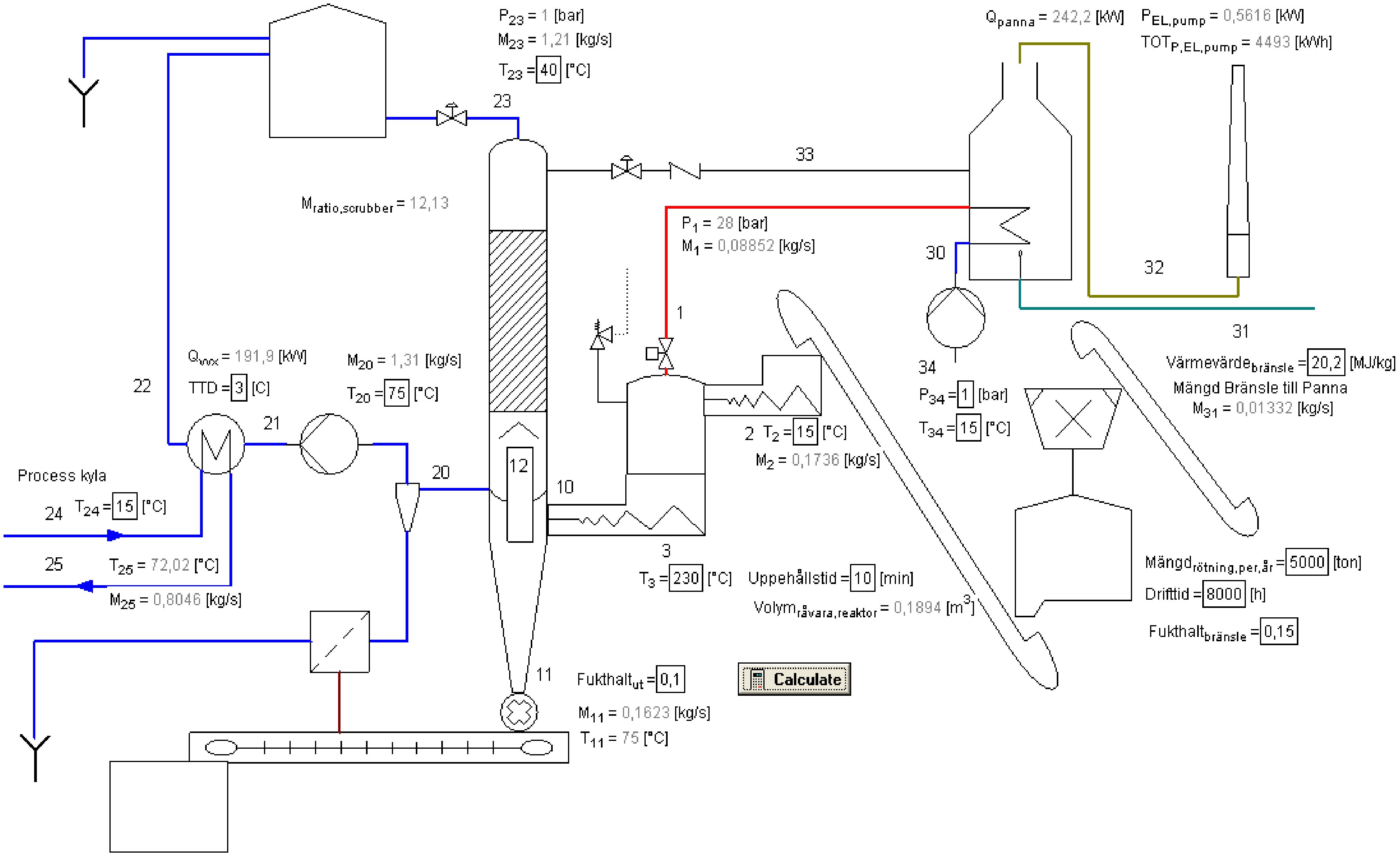
5.1.1 PROCEDURE

The calculations were performed by Mikael Jönsson[111] at Grontmij who has long experience of modeling thermodynamic process systems. The system design was developed by Kjell Manhag[112], Peter Berglund and Mikael Jönsson at Grontmij with assistance from the suppliers mentioned above and previous studies/projects on this topic. Mr. Manhag has more than 35 years of experience with process design of different power plants.

The indata can be varied and the results from the calculations are illustrated in boxes in the flow chart. The use of energy for each step is quoted as kW or MJ/kg feedstock. When altering the input data the model calculates the flow of energy and heat.

5.1.2 DESIGN AND DESCRIPTION OF THE PRETREATMENT PROCESS

The model and process steps are shown in Figure 6. The process cannot be altered, but the input data could be changed.



P_{23} = 1 [bar]
M_{23} = 1,21 [kg/s]
T_{23} = 40 [°C]

Q_{panna} = 242,2 [kW]
$P_{EL,pump}$ = 0,5616 [kW]
$TOT_{P,EL,pump}$ = 4493 [kWh]

$M_{ratio,scrubber}$ = 12,13

P_1 = 28 [bar]
M_1 = 0,08852 [kg/s]

Värmevärde$_{bränsle}$ = 20,2 [MJ/kg]
Mängd Bränsle till Panna
M_{31} = 0,01332 [kg/s]

P_{34} = 1 [bar]
T_{34} = 15 [°C]

Q_{vvx} = 191,9 [kW]
TTD = 3 [C]

M_{20} = 1,31 [kg/s]
T_{20} = 75 [°C]

T_2 = 15 [°C]
M_2 = 0,1736 [kg/s]

T_{24} = 15 [°C]
T_{25} = 72,02 [°C]
M_{25} = 0,8046 [kg/s]

T_3 = 230 [°C]
Uppehållstid = 10 [min]
Volym$_{råvara,reaktor}$ = 0,1894 [m^3]

Mängd$_{rötning,per,år}$ = 5000 [ton]
Drifttid = 8000 [h]
Fukthalt$_{bränsle}$ = 0,15

Fukthalt$_{ut}$ = 0,1
M_{11} = 0,1623 [kg/s]
T_{11} = 75 [°C]

Figure 6. The feedstock is crushed in a knife mill and automatically transported to the pressure vessel. By adding water after the mixing process the feedstock can be pumped to the steam vessel. The steam is produced in the boiler and led to the vessel under high pressure (over 25 bar). In the flash tank the heat or steam enters the water scrubber and the membranes explode. The feedstock is transported to a container and the heat energy (water) is led through some heat exchangers. The temperature of the outflow water is indicated to the left in the figure.

The raw material is transported up via a bucket conveyor and crushed to an appropriate size for steam treatment. The crushed material is transported to a closed tank in which a buffer of raw material is built up. The tank must be sealed to prevent small particles escaping and polluting the environment. The amount of material to be used in the reactor is then transported via a bucket conveyor up to the plug screw (2) feeding the raw material into the reactor.

The reactor is equipped with steam (1) from a steam boiler producing saturated steam at the required temperature. The water to the boiler (30) is pressurized to the correct pressure by a pump.

The saturated steam and the raw material are mixed in the reactor tank and remain there for a predetermined amount of time before the heated raw material is discharged with the feed out plug screw (3). The pressure in the reactor is relatively high and, consequently, the reactor must therefore have a safety valve.

The outlet of the feed out plug screw ejects the material into an expansion silo (11). The treated material falls to the bottom of the expansion silo. The treated raw material is fed to a tank via a conveyor which operates sequentially.

The pressure in the expansion silo will be atmospheric pressure. The consequence is that when the treated raw material comes out of the feed out plug screw there will be a sudden drop in pressure, which causes the water to boil instantaneously. All the water will thus turn into steam, causing the breakdown of the macromolecules of the treated material. The change in volume which the water undergoes when the pressure falls, causes the steam to, at a high speed, rush up and out of the expansion silo through the pipe (12) connecting the expansion silo and the scrubber. The rising steam meets the cold water (23) and condenses in the scrubber. The condensed water runs down into the bottom of the scrubber (10) and is then pumped (21) to the scrubber water circuit. A cyclonic filter captures possible traces of the raw material and returns it to the conveyor belt. The scrubber water moves on to a heat exchanger which recovers the heat contained in the scrubber water.

The recovered heat in the heat exchanger can be used to heat other parts of the digestion process which require heat (24) (25). When the scrubber water has cooled down, the water is led to a water storage tank. The process generates a surplus of water which must be led away from the tank. The surplus water comes from the produced steam and the reduction in moisture content of the treated raw material. The excess water might be used in the biogas process.

Any non-condensable gases are fed into the boiler from the scrubber (33) so that unpleasant odors from the process are minimized.

The hydrolysis process consists of one reactor which could be operated in continuous mode. For the base case capacity, the reactor is a vertical vessel with the volume of 1.0 m^3. The hydrolysates are then explosively flashed out to an expansion tank to cool down at atmospheric pressure.

Since this is in some way a new technique - due to the continuous small scale process and the water scrubber technique for recirculation of heat energy - which has not been tested in practice before, there is a risk that unforeseen problems may arise, necessitating modifications in the process. There are some uncertainties as to how well the proposed process works with regard to handling raw materials, i.e. to what extent must the material be crushed and how much of the raw material will follow the steam flow up into the scrubber. Also the moisture content of the processed output material is uncertain at this point.

The material is not dewatered before being treated with steam. Some experts imply that the feedstock needs to be mixed with water to a dry matter content of 5-10 %. This step is possible to attach to the existing process above. The financial calculation below includes this step.

The steam exploded feedstock is digested in the biogas reactor tank and the steam (water with contaminants) after the flash tank is filtered and the water is re-circulated in the process. Excess water and other particles that might appear in the process may need to be treated in a water treatment plant.

5.1.3 CHEMICALS IN THE PROCESS

The literature review pointed out that addition of chemicals to the steam explosion step had positive effects on gas yield for the current feedstock. There are, however, several problems when considering the needs of diluted acids or bases. The process and the technical components such as pumps, valves and rubber materials are sensitive to low or high pH levels, especially when combined with high temperatures and pressure. Theoretically, it is possible to calculate the cost of added chemicals versus gas yield, but in order to ensure that the process will work technically and from a microbiological point of view, it is, perhaps, necessary to first modify and optimize existing techniques, design and layouts. As mentioned before, there are industrial processes that operate under harsh conditions; a lot can be learned from these applications and some modifications will undoubtedly make the techniques appropriate for biogas production.

Calculations in this report are based on the use of diluted NaOH in combination with steam explosion as this seemed like the best option overall. The reason for this is that concentrated chemicals are expensive and they can cause severe corrosion of materials and equipment. In addition, they are not very pleasant in the working environment.

6 ECONOMIC EVALUATION

There are few scientific studies focusing on commercial evaluations concerning pretreatment of lignocellulosic feedstock such as wood, straw and paper. Most of the studies are just focusing on laboratory scale investigations measuring gas yields for treated vs. untreated materials without regard for cost estimations or energy needs of the pretreatment step. One of the main focuses in this project was, therefore, the economy and cost benefit analysis on a more commercial scale.

Zimbardi et.al.[113] published a paper regarding trials of a continuous steam explosion (SE) plant, with a treatment capacity of about 350 kg/h. The energy and water consumption, equipment costs and manpower needed to run the plant were used as the base case for a techno-economic evaluation of productive plants. The biomass treatment cost was evaluated as a function of the plant scale. Fixed cost breakdown was considered for a plant processing 50,000 t/yr. The steam explosion treatment conditions for straw were 200°C for 3 minutes. The results suggest that the cost of steam explosion varies with the amount of feedstock utilized. The cost of pretreatment for a plant operating at 50,000 t/yr is just over 2 SEK/kg DM straw. For a small plant, less than 10,000 t/yr the costs can amount to 4-5 SEK/kg DM straw. The plant must, however, be much more complex because the aim is to produce sugar, not just pretreated substrate for biogas production, which can affect the costs to a great extent.

In 1999, Schell et al.[114] published a technical and economic analysis of a combination of acid-catalyzed steam explosion and dilute sulfuric acid pretreatments using wheat straw or aspen wood chips to produce sugar. The capital cost and economic analysis of heat and material balances were developed and used to specify equipment sizes.

In that study, the equipment costs were estimated using information from different suppliers such as; Cherncost, Icarus, Guthrie, Stone and Webster Engineering Corp. and Badger Engineers, Inc.

The total capital invested (fixed plus working capital excluding service utilities) was estimated to 4.0 times the costs of purchased equipment. The annual capital charge (depreciation, taxes, insurance and rate of return) was total capital invested times a fixed charge rate of 0.13 or 0.20. Chemical costs were taken from the Chemical Marketing Repcirier. Maintenance was estimated at 4 % of total capital invested and overhead was allocated 60 % of labor plus maintenance.

According to the study, the costs for production of sugar from straw exceeded 7 USD/kg sugar. Based on today’s exchange rate the costs were approximately 50 SEK/kg straw. The study was, however, performed many years ago making it difficult to calculate and evaluate the production costs for a current case.

6.1 COST OF PRETREATMENT WITH STEAM EXPLOSION

The costs described above mainly concern production of sugar from lignocellulosic feedstock. It is less complex to produce more easily degradable feedstock for biogas production. There are, however, few papers or reports that discuss the correlation between steam explosion and biogas production.

The costs of all major equipment such as vessels, pumps, columns and heat exchangers, as well as auxiliary equipment (such as piping, insulation, electrical equipment, instrumentation, etc.) were estimated using tenders and contacts with appropriate suppliers and through previous experience from similar processes.

The fixed capital investment (FCI) of the plant is the total cost of major equipment and auxiliary equipment, cost of buildings directly associated with the process, site development and other costs associated with the plant construction such as contract fees, indirect construction costs, freight, engineering and contingencies. The factors used in determining the FCI are treated in the procedure recommended by Seider et al.[115]. The life expectancy of the plant is assumed to be 15 years after startup and the construction period is set to 1 year.

Annual maintenance and insurance expenditures are considered to be 2 % and 1 % of the FCI, respectively[116]. Yearly manufacturing costs of the plant are calculated as the sum of variable operating expenses (e.g., chemicals, raw materials, utilities and maintenance) and fixed operating expenses including labor wages and plant insurance. The labor wages recommended in literature vary based on the plant's location; however a wage of 500,000 SEK/employee*yr would be enough to cover labor expenses at most locations in Sweden.

Table 2 and Table 3 summarize economic conditions such as interest rate, labor costs, raw materials utilized in the calculations.

Table 2. Economic conditions for the calculations concerning steam explosion technique.

Electrical energy	0.7	SEK/kWh
Operating time	8,409	h/yr
Economic lifetime	15	year
Gas price (methane) sale	0.5	SEK/kWh*
Interest rate	5	%
Unpredictable	10	%
Water cost	10	SEK/m^3
Wood chips**	200	SEK/MWh
Labor	500,000	SEK/yr

* Upgraded gas. In the sensitivity analysis the price is increased by 50 and 100 %.
** For the production of steam in the process.

The cost of buying electrical energy was based on previous studies and the spot market prices from the past years (Nordpool[117]). Operating time was set to approximately 8,000 h/yr which is common for these kinds of processes. The price of methane gas (0.5 SEK/kWh) is similar to the price for natural gas at the moment (October, 2011) and the price has to be competitive.

The interest rate varies due to many factors. According to the values from the past decades, 5 % is a realistic figure.

Unpredictable costs are estimated to 10 % (often set between 10-20 %).

The labor cost is set to 500,000 SEK/employee*yr, but it is probably not necessary with a full time employee because the pretreatment process will be added to an existing biogas plant, which already has operative staff. By adding the pretreatment step described above to an existing plant, the cost of labor for the pretreatment process ought to be reduced due to the fact that the same staff can be utilized in both lines of work (see calculations below).

Table 3. Price and dry matter content for the different raw materials used in the economic calculations.

Feedstock	Organic load, t/yr	Dry matter (DM) content, %	Organic matter (volatile solids), % of DM	Wet weight (WW), t/yr	Price per unit (SEK/t WW)
Wood (forest residues)	5,000	50	95	10,500	540
Straw	5,000	85	95	6,200	800
Paper	5,000	95	95	5,540	500[118]

Farmers often sell straw to animal holders (horse, cattle, etc.). The price in southern Sweden for stored and packed straw is between 600-800 SEK/t wet weight. The price depends on the season and the quality of the straw. The transportation costs vary depending on the distance and can in some cases amount to several hundred SEK per ton. Within 50 km the transportation costs amount to 200-400 SEK/t.

Forest residues (Swedish GROT, which is an abbreviation for rejected tops and branches) can be bought for about 500-600 SEK/t or 200 SEK/MWh. For wood chips (GROT) and paper the price is including transportation within 100 kilometers.

Once the plant FCI and yearly operating costs were determined, a discounted cash flow analysis was employed to evaluate biogas production cost[119].

6.1.1 INVESTMENT

As mentioned above, the economic data was gathered through contacts with different suppliers and through earlier experience from similar engineering fields, such as the paper and bulk industry. There were, nevertheless, difficulties in providing accurate data due to lack of information as a result of our specific demands and the specific scale of the process.

Working capital cost was calculated as the sum of the cost of raw material, chemicals, labor and utilities needed for 30 days production, 30 days of accounts receivable for products, 30 days of accounts payable by the company for feedstock (a negative value) and 7 days of inventory of liquid products[120].

Table 4 summarizes the components and their costs. The calculations are based on an organic load of 5,000 t/yr, which is a small volume compared to other plants mentioned that produce sugar from lignocellulosic feedstock.

Table 4. Direct and indirect fixed costs for steam explosion pretreatment of 5,000 t/yr.

Purchasing	5,000,000	SEK
Installation	2,000,000	SEK
Piping	1,750,000	SEK
Instruments	1,500,000	SEK
Electricity supplying	750,000	SEK
Buildings	875,000	SEK
Place and adaption	750,000	SEK
Total	**12,625,000**	**SEK**
Plant engineering	1,895,000	SEK
Building engineering	175,000	SEK
Total	**2,070,000**	**SEK**
Total plant cost	**14,695,000**	**SEK**

The total investment amounts to approximately 15 million SEK for pretreatment of 5,000 t/yr. The cost of purchasing the plant amounts to about 5 million SEK. This estimate was based on contacts with suppliers and previous experience. Other costs, such as installation and piping, are a percentage of the purchasing value. The percentage used was based on earlier studies, reports and experience from construction of similar plants.

Zimbardi et al.[121] estimated the costs for the production of sugar, by steam explosion and chemical engineering from lignocellulosic feedstock such as wood and straw, to approximately 150 million SEK. The plant in question handled 25,000 t/yr.

According to the calculation, components such as pressure vessels or water scrubbers are only a minor part of the total costs. Installation, piping, instrumentation and plant engineering account for almost half of the investment.

6.1.2 OPERATION AND MAINTENANCE

The capital costs affect the production costs in a major way. Aside from the capital costs, the production cost has to encompass manual labor, maintenance, management, raw material and so forth. Table 5 illustrates the operational and maintenance costs.

Table 5. Operational and maintenance costs (rounded off) for pretreatment of 5,000 ton organic load (forest residues) annually.

Devaluation = I*r/(1-(1+r)^-t)	1,470,000	SEK/yr
Maintenance	294,000	SEK/yr
Insurance	73,000	SEK/yr
Plant management	441,000	SEK/yr
Manpower	125,000	SEK/yr
Supervision	100,000	SEK/yr
Labor equipment	50,000	SEK/yr
Administration	30,000	SEK/yr
Raw material (Grot)	5,670,000	SEK/yr
Total	**8,253,000**	**SEK/yr**

The total costs per year exceed 8 million SEK. The main cost is the raw material. The price for the forest residues was set to 540 SEK/t wet weight. Due to the low dry matter content, the wet weight exceeds 10,000 tons per year.

To produce heat (steam) for the process the calculations were based on wood chips. This expense is included in the calculation (plant management). According to the model, almost 80 % of the heat energy used to produce steam can be reused for other purposes. If this is the case the plant management costs can be substantially reduced.

If 60 % of the excess heat energy is reused, the plant management cost could be reduced by almost 0.2 million SEK/yr. Based on this, the production cost decreases to just over 8 million SEK/yr (Table 6).

Table 6. Operational costs (rounded off) when considering reuse of 60 % of the excess heat produced.

Devaluation = I*r/(1-(1+r)^-t)	1,470,000	SEK/yr
Maintenance	294,000	SEK/yr
Insurance	73,000	SEK/yr
Plant management	241,000	SEK/yr
Manpower	125,000	SEK/yr
Supervision	100,000	SEK/yr
Labor equipment	50,000	SEK/yr
Administration	30,000	SEK/yr
Raw material (GROT)	5,670,000	SEK/yr
Total	**8,053,000**	**SEK/yr**

The price for raw material (forest residues) was set to 540 SEK/t in this calculation. The cost of the raw materials was the main annual cost for pretreatment of the current feedstock with steam explosion. The total production costs for steam explosion as a pretreatment method for forest residues was just over 8 million SEK/yr. This brings the costs to 1,610 SEK/t organic load (forest residues) including the raw material.

The price of the other feedstock differs from forest residues and the price also fluctuates for the current feedstock. Our assumption was that the production cost (steam explosion), excluding the price of the raw material, was similar for the current feedstock.

The capital cost and the raw material represented more than 75 % of the total production costs. Figure 7 illustrates the different parameters in the production costs.

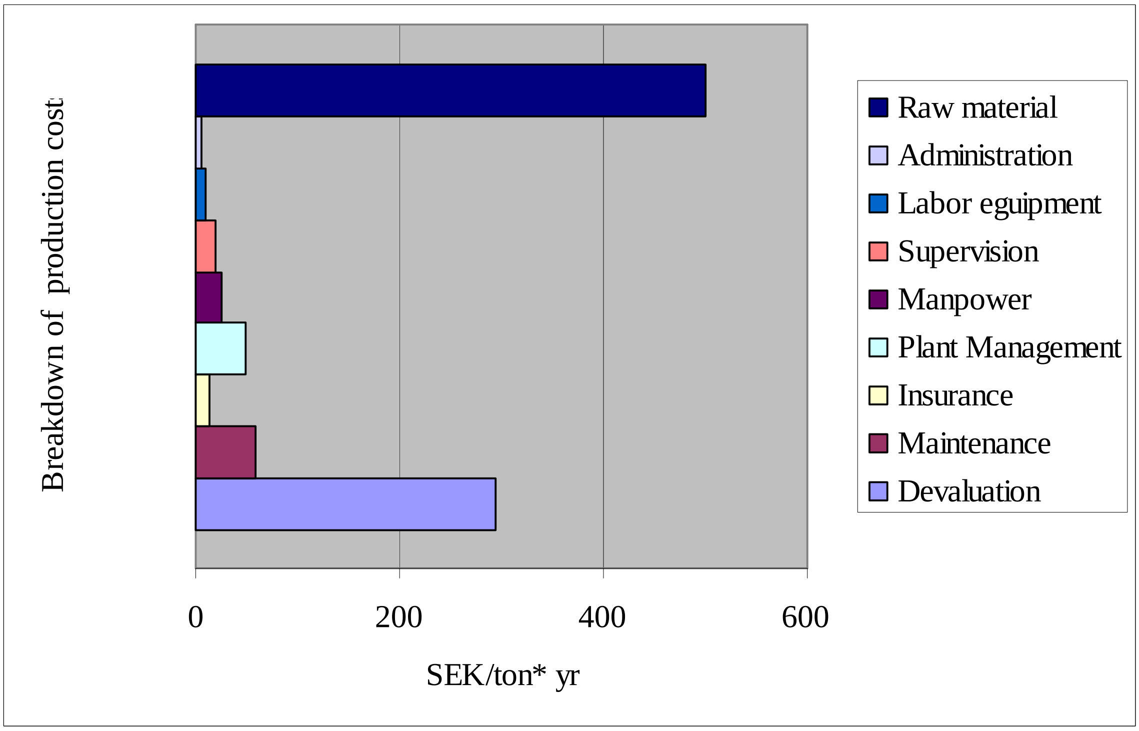


Figure 7. Steam explosion production cost for forest residues divided into production cost units.

6.2 COST OF CHEMICALS

The cost of chemicals, which in certain cases need to be added to the steam explosion treatment to achieve further enhancement in biogas production, was mainly based on the cost of buying the chemical substances used in the process. The feedstock needs to be mixed with the chemicals in a container or similar equipment before entering the steam explosion process. The cost for this was also estimated. The production cost with or without the addition of chemicals was also estimated and discussed the section titled “Economic evaluation” where the results are presented.

Forest residues and straw are not treated with chemicals due to low gas exchange. The only feedstock pretreated with chemicals, as an integrated part of the steam explosion treatment, is paper. When NaOH is added to the system an extensive increase in gas yield can be achieved. The amount and the price (per ton) of paper treated with NaOH is 3,000,000 SEK/yr, based on values obtained in the literature review and an organic load of 5,000 t/yr.

Mixing of feedstock with chemicals requires some kind of container with a mixer, pumps and valves attached to the steam explosion process. This cost is approximately 500,000 SEK for the current volumes including plant engineering. Maintenance and labor costs amount to 100,000 SEK/yr and in total approximately 150,000 SEK/yr excluding the chemical substance.

6.3 GAS YIELD WITH PRETREATMENT AND COST OF PRETREATMENT

Currently, the substrates that are the focus of this report are not usually included as organic load in a biogas production process, which means that the calculations had to be based on the total gas yield as opposed to the increase in gas yield brought on by the pretreatment. Table 7 shows the cost per ton according to wet weight, dry matter and organic matter for the current feedstock

As noted above the average gas yield amounted to 200 Nm^3 CH_4/ton VS (organic content) for wood, 300 Nm^3 CH_4/ton VS for straw and 400 Nm^3 CH_4/ton VS for paper, respectively. With a selling price of 0.50 SEK/kWh upgraded gas the value per ton VS are illustrated in Table 7.

Table 7. The net value of the gas yield produced from pretreated wood, straw and paper with a selling price of 0.50 SEK/kWh upgraded gas.

Feedstock	Gas yield, Nm^3 CH_4/t VS	Gas yield, kWh/t VS*	Net value, SEK/t VS	Total net value, million SEK/yr
Forest residues	200	1,994	997	4.98
Straw	300	2,991	1,496	7.48
Paper	400	3,988	1,994	9.97

* 9,97 kWh/Nm^3 CH_4

The net value per feedstock is used in the calculations below and compared with the cost of pretreatment.

6.3.1 WOOD

Forest residues and wood chips are mainly used as combustion material for the production of heat and electricity. Heat and power plants in Sweden pay approximately 200 SEK/kWh for forest residues. Pretreatment of wood chips, compared to non-pretreated wood, could generate much more gas according to the literature review.

With a selling price of 0.50 SEK/kWh for the methane gas produced and upgraded at the biogas plant the net income will increase to approximately 5 million SEK/yr (200 Nm^3 CH_4/ton VS) by the use of forest residues pretreated with steam explosion. However, the cost of steam explosion, when including raw material, exceeded 8 million SEK/yr.

6.3.2 STRAW

According to the literature review, the gas yield from straw is about 300 ml CH_4/g VS (milled or chopped).

With a methane production of 300 ml CH_4/g VS straw the biogas production will generate an extra income of over 7 million SEK per year, when utilizing 0.50 SEK/kWh as the set price for upgraded gas.

The cost of steam explosion for straw is similar to that for wood. The production cost will amount to 7.3 million SEK/yr. By including the transportation costs of the raw material the costs could exceed the net value of the gas produced from straw. Generally, it is expensive to transport straw due to its low density. Within 100 kilometers the cost is approximately 500 SEK/ton, which corresponds to ca. 2.5 million SEK/yr.

This is the production cost when utilizing the excess energy via the water scrubber. The result will be even more negative without this exploitation.

6.3.3 PAPER

With added chemicals and steam explosion, the gas yield from paper amounts to 400 Nm^3 CH_4/g VS. A combination of chemicals and steam explosion is, however, expensive. For paper, the production cost for steam explosion amounts to over 5 million SEK (including the raw material). Using chemicals (NaOH), the total production costs exceed 8 million SEK/yr. The value of the gas yield amounts to about 10 million SEK/yr. This result indicates that paper could be of great interest for production of biogas pretreated with steam and NaOH.

This is the production cost when utilizing the excess energy via the water scrubber. The result will be even more negative without this exploitation.

6.3.4 RESULTS

Figure 8 illustrates the production costs versus the gas yield in SEK/t VS.

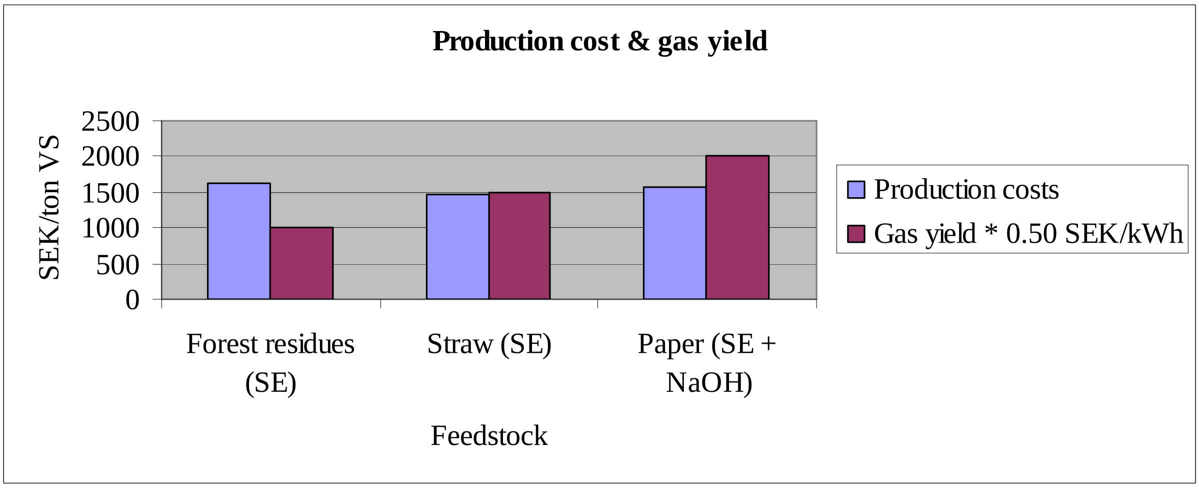


Figure 8. Pretreatment and production cost and gas yield in SEK/ton VS for forest residues, straw and paper. Steam explosion (SE) used for all substrates and for paper SE + the addition of NaOH (0.50 SEK/kWh for the methane gas produced).*

According to the results, straw and paper have a positive net result and might be cost efficient. For paper the gas yield (value) exceeds the production costs by over 20 %. However, if the transportation cost exceeds the value of the increase in gas yield, the result might be negative for both straw and paper. The results indicate that the value of the gas yield does not correspond to the production costs.

The figures are negative when considering forest residues or GROT. In this case, the production cost is 30 % more than the value of the gas produced.

6.3.5 UP-SCALING ANALYSES

The up-scaling analyses regarding production cost was based on previous studies from similar plants. The scaling effect was based on estimates.

By up-scaling the process the capital costs, maintenance, labor and so forth will decrease (per ton), but the transportation costs will increase. The capital costs of the plant do not change linearly with the plant size. Therefore, the effect of capital costs on the production cost is not the same for all capacities and decreases when the plant capacity increases. Labor costs are the second most substantial expense among production cost components, and these costs do not double when considering a plant with double the capacity. The number of plant operators and labor supervisors needed per shift are based on the type and arrangement of the equipment rather than capacity of the plant. Therefore, the effect of labor costs is more significant at lower capacities.

There are two main costs associated with biomass transportation: a fixed cost based on the required loading/unloading time, and a variable cost linearly related to the collecting distance[122]. Wide ranges of transportation cost estimates have been reported in literature for corn Stover and wood chips[123,124]. Based on these estimates and a collecting radius of 15–50 miles (24-80 km), an average transportation cost of 10 USD/ton is considered.

The production cost is based on straw due to its positive results in the economic evaluation.

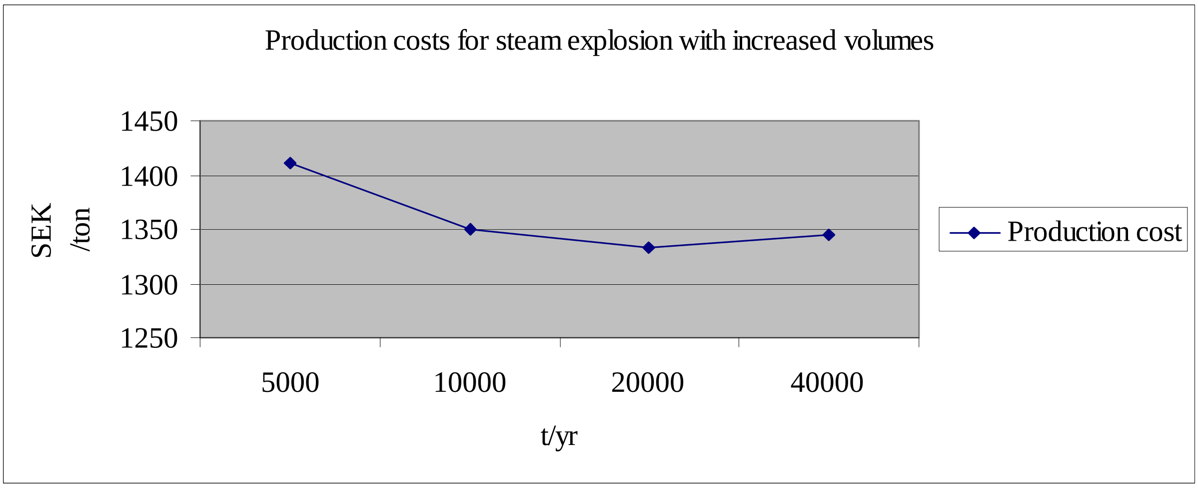


Figure 9. The production costs declines rapidly as the plant size increases, but costs increase again when transportation distances increase.

The production cost decreases with volume to a certain extent, but the transportation costs increase. Production costs increase when transportation costs exceed the positive effects brought on by operating with large volumes. According to this calculation, the production cost of steam explosion increases with the distance from 20,000 to 40,000 t/yr (Figure 9).

By producing 20,000 t/yr, the production cost declines from 1,430 SEK/t to approximately 1,340 SEK/t for straw. Due to higher transportation costs and loss of synergies (use of excess energy from the process) the total costs may be the same for the small scale and large scale plant.

6.3.6 SENSITIVITY ANALYSIS

In order to investigate the effect of the selling price for the methane gas (upgraded fuel), a sensitivity analysis was carried out to study the effect of price on profitability of the process. For this purpose, the price was set to 0.50, 0.75 and 1.00 SEK/kWh gas and the results were investigated and compared. According to this analysis, the price of sold gas (methane) needs to be just shy of 0.50 SEK/kWh for straw, around 0.45 SEK/kWh for paper and over 1.00 SEK/kWh for forest residues to receive a positive net result (Figure 10).

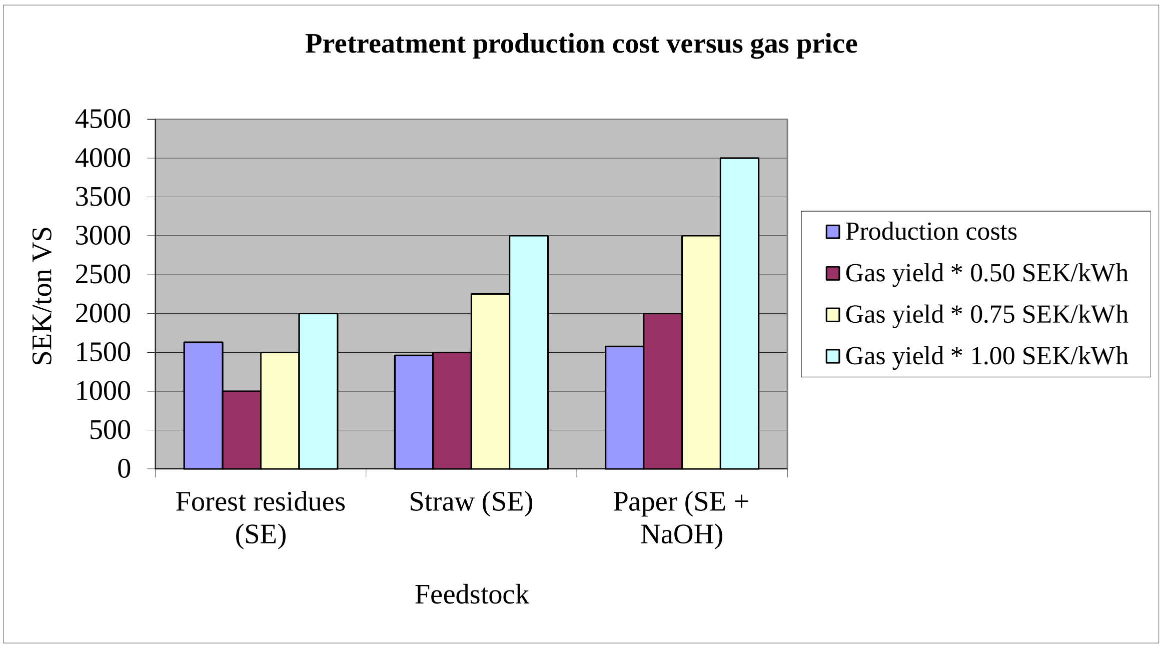


Figure 10. Pretreatment production costs versus gas price.

6.4 RESULTS AND DISCUSSION

Table 8 illustrates the result from the economic evaluation. Method refers to pretreatment methods where SE stands for steam explosion (approximately 200°C, 5-20 min) with or without chemicals referred to by their molecular formulas. The pretreatment methods considered are based on the results of the literature review.

Table 8. Method SE refers to steam explosion only, while method SE+NaOH refers to steam explosion with the addition of NaOH. The results in the table are based on 5,000 ton organic load per feedstock and a gas price of 0.50 SEK/kWh for the methane gas produced.

Feedstock	**Method**	**With pre-treatment, gas yield (Nm^3 CH_4/t VS**	**Cost of pretreatment (million SEK)**	**Total gas yield (million SEK)***	**Result (million SEK)**
Forest residues	SE	200	8.2	4.98	- 3.22
Straw	SE	300	7.3*	7.48	+ 0.18
Paper	SE + NaOH	400	8.1	9.97	+1.87

* Within 50 km from the production plant

For straw the production cost of the chosen pretreatment method(s) corresponds to the net value of the gas sold. For paper the result is positive with a net income of over 1.5 million SEK/yr. For forest residues the price of gas needs to be increased by several percent (60-70 %) to receive a positive result.

The results indicate that straw and paper are the best option when it comes to economy. To receive a significant increase in biogas yield from paper it is necessary to pretreat the current feedstock with the addition of NaOH during steam explosion (SE+NaOH). The straw probably has to be bought from a number of farmers and transported to the biogas plant, an expense which has been included in this calculation only for short distances.

Deciding on which system restrictions to use is of vital importance when it comes to economic calculations concerning the net value of a pretreatment technique. If a main part of the input of energy for steam explosion can be used for other purposes such as pasteurization, heating of other substrates and/or the digestion reactor, negative figures can become more positive, mainly feedstock that are close to breakeven (the cost of steam explosion corresponds to the increase in gas yield). This will mainly affect the operation cost, which is a minor part of the total production cost. The main portions of the costs pertain to raw material, capital costs and labor.

The effect of capital investment criteria on the final gas price is highlighted by comparing the current results with 10 % discounted cash flow rate of return (DCFROR). Increasing the DCFROR from 5 % to 10 % would result in a 16 % increase of the final production cost. However, due to the low risk of investment in this process, 5 % would be a reasonable viable discounted cash flow rate of return for such an investment.

The data is based on the pretreatment of 5,000 t/yr (organic load). The process could be much larger and handle more feedstock, which could slightly decrease the pretreatment production costs. However, the excess energy in the process from the centralized plant might be more difficult to employ if the production is centralized and the freight costs increase linearly, for straw in particular.

The sensitivity analysis illustrates that the price of sold methane gas is of central importance. With an increase of the gas price with 10-20 % the cost benefit analyses indicates a positive result, except in the case of forest residues.

7 CHALLENGES AND DISCUSSION

Reviewing the literature and research carried out on the subject, it is clear that quite a bit of work has been done regarding pretreatment of lignocellulosic rich materials for biogas production. Of course it is only natural as lignocellulosic biomass exists in the most abundant raw materials on the planet. The challenge lies in applying the correct technique to get as much energy out of the raw material as possible. This also implies that it is important to evaluate the various techniques from a wide perspective; a larger perspective than was possible within the scope of this study. It is important to optimize the entire chain and lifecycle so that materials considered waste in one process become highly sought after raw materials in another. Breaking down lignocellulosic materials in an anaerobic digestion process requires knowledge within many fields including engineering, microbiology and chemistry. Research has shown that it is possible to increase the methane yield by over 1,000 % when applying the correct techniques, the challenge lies in developing a construction that can cost efficiently attain this on the commercial/ industrial scale.

Contact with suppliers has shown that there are very few options on the market today. The high pressures and temperatures needed for an efficient steam explosion process, for example, are not available in the systems offered today. This implies that there is much to be done in terms of construction and engineering if we are to bring the pretreatment processes out of the laboratory and as an integrated part of a biogas plant. The same is true of chemicals which, today, are far too expensive to be a realistic option for pretreatment of lignocellulosic biomass.

Another important factor to consider when considering utilizing lignocellulosic biomass in an anaerobic digestion process is the flow of energy and material through the entire plant. In order to justify the costs of the pretreatment process, it is imperative that excess heat and steam are made useful to other parts of the plant or reused, that water is re-circulated as much as possible and that chemicals used in the pretreatment process are reused in the next batch. This requires coordination with engineers, contractors and suppliers at the planning stage of the process. It is only in the early stages of planning that it is possible to think ahead and create an efficient plant.

7.1 COMBUSTION AND GASIFICATION

At the moment a main part of the forest residues and paper discussed in this report are combusted to generate heat and electricity. It is, thus, interesting to briefly relate the combustion data with production of biogas from this feedstock.

Straw is not commonly used in combustion due to the high amounts of corrosive flue gases and is thus better suited for production of biogas if the economics allow that.

Another interesting use of, above all, forests residues is gasification and this will also be discussed below.

7.1.1 COMBUSTION

An important factor when considering combustion is the utilization of the energy “produced” and the cost of the raw material.

Wood chips cost about 134 SEK/MWh, including carriage with a moisture content between 50-60 % in northern Sweden (Norra Skogsägarna[125]). At Skellefteå Kraft in northern Sweden the cost is 70-80 SEK/MWh for unchipped feedstock, including carriage within 40 km from the boiler[126]. These figures are slightly lower than the figures used in the above calculations. However, the prices are somewhat higher in the south part of Sweden where a majority of the larger biogas plants are located.

The gas yield from steam pretreatment of forest residues generates about 2,000 kWh/ton VS according to the literature review. With a price of 0.50 SEK/kWh gas the value is approximately 1,000 SEK/t VS. This has to be compared to the price for the raw material (forest residues), which is approximately the same. This gives no space for an investment in a pretreatment plant. Compared to, for example, district heating with a selling price of 0.50 SEK/kWh (average price for district heating)[127] there is a much greater investment margin for combustion of the wood material. It is, however, important to consider that production of biogas instead of heat can be used to replace fossil fuels for vehicles.

Paper is not combusted separately, but as a fraction contained in household and industrial waste. Half of the paper from offices is recycled and the other half is used in energy production in a fraction called PTP (Paper-Wood-Plastic). In the case of paper and cardboard packaging, 60 % is used for energy production as fractions of waste or PTP, the rest is recycled[128].

PTP is difficult to define and is a broad term that covers virtually all combustible waste. It is an inhomogeneous fuel, with a calorific value that is generally high. The distribution between the various fractions varies but usually requires at least 20 % wood for fuel preparation to function properly[129]. It is difficult to compare the combustion value of PTP with steam pretreatment due to the inhomogeneous fuel, and we do not have any data regarding pretreatment of PTB.

Generally, straw is cheaper in chopped form, 85 SEK/MWh including carriage, hacked, and 115 SEK/MWh baled including carriage[130]. The price for straw bales in 2009 was about 155 SEK/MWh including carriage[131]. Straw is interesting to study further because of the relatively high gas yield and the difficulties concerning combustion of straw.

7.1.2 GASIFICATION

Gasification is a process that converts organic or fossil based carbonaceous materials into carbon monoxide, hydrogen, carbon dioxide and methane. This is achieved by reacting the material at high temperatures (>700°C), without combustion, with a controlled amount of oxygen and/or steam. The resulting gas mixture is called syngas (from synthesis gas or synthetic gas) or producer gas and is itself a fuel. The power derived from gasification of biomass and combustion of the resulting gas is considered to be a source of renewable energy[132]. The gasification of fossil fuel derived materials such as plastic is, however, not considered to be renewable energy.

The advantage of gasification is that using the syngas is potentially more efficient than direct combustion of the original fuel because it can be combusted at higher temperatures or even in fuel cells, so that the thermodynamic upper limit to the efficiency defined by Carnot's rule is higher or not applicable. Syngas may be burned directly in gas engines, used to produce methanol and hydrogen, or converted via the Fischer-Tropsch process into synthetic fuel. Gasification can also begin with material such as biodegradable waste, which would otherwise have been disposed of. In addition, the high-temperature combustion refines corrosive ash elements such as chloride and potassium, allowing clean gas production from otherwise problematic fuels. Gasification of fossil fuels is currently widely used on the industrial scale to generate electricity.

E.ON plans to build a large scale reactor in the south of Sweden. Table 9 summarizes some data about the plant.

Table 9. Main technical data from E.ON's gasification project (BIO2G).

Fuel input	325 MW
Biogas production	200 MW (~2,000 GWh/yr)
Biogas net efficiency	60-65 %

According to this calculation from E.ON, 60-65 % of the organic matter will be converted to biogas. E.ON plans to invest over 300-400 million Euro in the project and the production costs are estimated to 0.20-0.30 SEK/kWh (unverified data) excluding costs for feedstock (the price for forest residues could be estimated to 0.20 SEK/kWh). This indicate the production costs is less then 0.50 SEK/kWh.

The production cost for steam pretreatment of the forest residues exceeded 0.50 kr/kWh. When comparing figures, it is of vital importance to keep in mind that a significant part of this cost is feedstock, and the figure pertaining to E.ON’s project is excluding the cost of feedstock.

7.2 DIFFICULTIES CONCERNING BIOGAS FROM LIGNOCELLULOSIC BIOMASS

One of the main challenges when attempting to utilize lignocellulosic biomass in an anaerobic digestion process is to find a way to cost efficiently get the bio-accessible substrate into the digester. In order to do this, it is necessary to conduct efforts across several disciplines and fields; technique must harmonize with economics, construction with permit requirements and logistics with substrate availability to name a few.

The focus of steam explosion in this study is due to the limits of the project. There might be other techniques less costly that could increase the gas yield slightly.

For straw, an efficient pretreatment method could solely the addition of NaOH without steam explosion. Some data indicates that the cost of the chemicals and the mixing equipment could match the increase in gas yield. The relatively high cost of the raw material (straw) and the transportation cost is however a key factor for straw. Therefore, this can only be envisaged in regions with a large number of farms producing cereals. But the main problem seems to be the cost of the raw material. For wood or forest residues, for example, the cost of the raw material almost corresponds to the value of the gas yield. By adding a pretreatment method the costs exceed the gas yield significantly.

Sweden as a nation is good at producing district heating from waste and wood material and the competition for raw materials is, therefore, relatively high. This affects the cost of the raw materials and pretreatment of the current feedstock in this study may be more interesting in other parts of the world.

8 CONCLUSIONS

The study has shown that there are ways to effectively pretreat lignocellulosic biomass in order to make it more available to the microorganisms carrying out the anaerobic digestion process. The gas yield increases and the digestion process requires a shorter retention time, which are both positive effects of the pretreatment process.

Pretreatment of paper with steam explosion together with NaOH addition showed the best performance and had a positive net result. This is due to the high gas yield (400 Nm^3 CH_4/t VS) and the low cost of paper (approximately 500 SEK/t VS). Thus, paper should be evaluated further in order to assess the possibilities of utilizing it in an anaerobic digestion process. In addition, straw is worth considering further because it is a feedstock associated with few alternative uses and it is an agricultural residue produced in large amounts yearly. The pretreatment costs are, however, high for all feedstocks investigated compared to the gas price at the moment. On the other hand, a slight shift in this balance would lead to new possibilities when aspiring to utilize lignocellulosic biomass in a biogas production process.

9 LITERATURE REVIEW

The following sections summarize the results of the literature review. The substrates for which information was collected are wood, straw, paper as well as co-digestion of manure & lignocelluloses and oat straw. The tables below show the details of pretreatment processes on the chosen substrates which give highest methane yield in anaerobic digestion. The digestion process is carried out mostly in batch reactors, but there are some samples that were run as a semi continuous digestion system. The suggestions for best the pretreatment methods are depicted with red and bold font in tables.

9.1 BIOGAS PRODUCTION FROM WOOD

Substrate / Wood	**Pretreatment**	**Organic load**	**Methane yield**	**Methane yield ml/ g raw material**	**Time anaerobic digestion (day)**	**Temp. anaerobic digestion**	**Ref**
Untreated wood chips (Eucalyptus globules)	Untreated	3.4 g + 60 ml inoculum+ 240 ml inorganic solution	14 ml/ g TS	No data	14	37°C	133
	Extraction using hot water with high temperature (125°C) for 20 min	3.4 g + 60 ml in.+ 240 ml ino. sol.	124 ml/ g TS	No data	14	37°C	-“-
	Extraction using 1 % NaOH with high temperature (125°C) for 20 min	3.4 g + 60 ml in.+ 240 ml ino. sol.	134 ml/ g TS	No data	14	37°C	-“-
	Steam explosion at 25 atm for 3 min	**3.4 g + 60 ml in. + 240 ml ino. sol.**	**194 ml/ g TS**	**No data**	**14**	**37°C**	-“-
Japanese cedar chips	Untreated	1 g + 500 ml sludge	0	No data	20	37°C	134
	Steam explosion 4.5 MPa and 258°C, 5 min	**1 g + 500 ml sludge**	**180 ml/ g TS**	**No data**	**20**	**37°C**	-“-
	Fungal treatment (Cyathus stercoreus AW 03-72)	1 g + 500 ml sludge	43 ml/ g TS	No data	20	37°C	-“-
Japanese cedar wood chips	Untreated	12 g + 400 ml digested sludge	No data	2	60	35°C	135
	Fungal pretreatment *C. subvermispora* ATCC 90467+ wheat bran media for 8 weeks	12 g + 400 ml digested sludge	No data	83.5	60	35°C	-“-

	Fungal pretreatment C. subvermispora CBS 347.63 for 8 weeks	12 g + 400 ml digested sludge	No data	26.5	60	35°C	-“-
Japanese beech (Fagus crenata)	Untreated	150 mg sample and 4.9 ml water + 50 ml sludge	0	0	35	50°C	136
	• Japanese beech was soxhlet-extracted by mixture of ethanol and benzene (1:2 in volume) for 12 hours • Supercritical water treatment at 380 °C and Pressure 30 MPa →79.9 mg sample and 2.61 ml water	5 ml hydrolysate + 50 ml sludge	No data	105	35	50°C	-“-
	• Japanese beech was soxhlet-extracted by mixture of ethanol and benzene (1:2 in volume) for 12 hours • Supercritical water treatment at 380 °C and Pressure 100 MPa → 150 mg sample and 4.9 ml water	5 ml hydrolysate+ 15 ml sludge	No data	68	35	50 °C	-“-
Spruce chips (*Picea abies*)	Untreated (10 mm chips)	40 ml inoculum+ (0.2- 0.25) g substrate	13 Nml/ g VS	11	45	55°C	137
	100 g of 6 % spruce in the NMMO solution and heated in an oil bath at 130°C and 1 atm 15 h	40 ml inoculum+ (0.2- 0.25) g substrate	150 Nml/ g VS	125	45	55°C	-“-
Milled spruce	Untreated (less than 1 mm)	40 ml inoculum+ (0.2- 0.25) g substrate	80 Nml/ g VS	66	45	55°C	-“-
	100 g of 6 % spruce in the NMMO	40 ml inoculum+ (0.2- 0.25) g	295 Nml/ g	245	45	55°C	-“-

	solution and heated in an oil bath at 130°C and 1 atm 15 h	substrate	VS				
Spruce	Untreated	0.25 g dry weight of wood + 20 ml inoculum and 5 ml distilled water	30 ml/ g VS		30	55°C	138
	7 % (w/w) NaOH, at 5°C, 2 h	0.25 g dry weight of wood + 20 ml inoculum and 5 ml distilled water	50 ml/ g VS		30	55°C	139
Birch	Untreated	0.25 g dry weight of wood + 20 ml inoculum and 5 ml distilled water	250 ml/ g VS		30	55°C	-“-
	7 % (w/w) NaOH, at 100°C, 2 h	0.25 g dry weight of wood + 20 ml inoculum and 5 ml distilled water	469 ml/ g VS		30	55°C	-“-

9.2 BIOGAS PRODUCTION FROM STRAW

Substrate/ Straw	Pretreatment	Organic load	Methane yield	Methane yield ml/ g raw material	Time anaerobic digestion (days)	Temp. anaerobic digestion	Ref
Wheat straw	Untreated		189 ml/ g VS	No data			140,141
Wheat straw	Milled (0.5-1.0 mm)	Substrate inoculum DM ratio 1:3 (VDI and DIN standard)	275 ml/ g VS	235		37.5°C	142
	Steam explosion 180°C, 15 min 1 kg straw + 3 kg water	**Substrate inoculum DM ratio 1:3**	**331 ml/ g VS**	**283**		**37.5°C**	**-“-**
Oat straw	Untreated	-------	No data	No data	-------	-------	143
	Lime pretreatment	4.3 g VS/ l	287 ml/ g VS	252	98	37°C	-“-

	Steam explosion	4.3 g VS/ l	197 ml/ g VS	173	98	37°C	-“-
	Acid + steam explosion	4.3 g VS/ l	201 ml/ g VS	184.5	98	37°C	-“-
Rice straw	Untreated	400 ml swage + 1 g material (rice straw)	No data	54 *^{1}	30	35°C	144
	Acetic + propionic acid 0.75 mol/l the weight percentage of two acids (1:1), 2 hours, solid & acid ratio (1:20)	400 ml swage + 1 g material (rice straw)	No data	213.5 *^{1}	30	35°C	-“-
Rice straw hydrolysate	20 ml	400 ml swage + 20 ml hydrolysate	No data	70	30	35°C	-“-
Rice straw	Untreated (3-5 mm particle size)	12.6 g VS/ l	240 ml/ g VS	214	120	22°C	145
	Phosphate supplementation 155 mg-P/l	12.6 g VS/ l	250 ml/ g VS	223	120	22°C	-“-
Straw	Untreated	1:2.5 straw: inoc. VS	165 ml/ g VS	140	28	35°C	146
	Extruded straw	1:2.5 straw: inoc. VS	281 (+70 %) ml/ g VS	239	28	35°C	-“-
	Untreated	1:2.5 straw: inoc. VS	320 ml/ g VS	272	90	35°C	-“-
	Extruded straw	1:2.5 straw: inoc. VS	355 (+11 %) ml/ g VS	301	90	35°C	-“-
Corn straw *	Untreated	40.25 g VS/l	153.7 ml/ g VS *^{3}	118,5 *^{3}	30	35°C	147
	NaOH 8 % Wt	**40.25 g VS/l**	**472 ml/ g VS *^{3}**	**364 *3**	**30**	**35°C**	**-“-**
	Ammonia 5 % Wt	40.25 g VS/l	316 ml/ g VS *^{3}	243,5 *^{3}	30	35°C	-“-
	Urea 4 % Wt	40.25 g VS/l	178 ml/ g VS *^{3}	137 *^{3}	30	35°C	-“-

	Pleurotus florida 300 g ground corn straw +225 g distilled water then autoclaved at 121°C for 2 h	40.25 g VS/l	404.8 ml/ g VS *[3]	312 *[3]	60	35°C	-“-
	Pleurotus florida	40.25 g VS/l	380 ml/ g VS *[3]	293 *[3]	30	35°C	-“-
Wheat straw	Physical pretreatment size reduction (30 x 5) mm	160 g wheat straw (89.9 g VS) in 2 liter water + 2 liter slurry	162 ml/ g VS	91	60	37°C	148
	Physical pretreatment size reduction (0.088) mm	160 g wheat straw (89.9 g VS) in 2 liter water + 2 liter slurry	249 ml/ g VS	140	60	37°C	-“-
Rice straw	Physical pretreatment size reduction (30 x 5) mm	160 g wheat straw (79.4 g VS) in 2 liter water + 2 liter slurry	241 ml/ g VS	135	60	37°C	-“-
	Physical pretreatment size reduction (0.088) mm	160 g wheat straw (79.4 g VS) in 2 liter water + 2 liter slurry	365 ml/ g VS	205	60 days	37°C	-“-
Rice straw	Untreated	40 ml inoculum+ (0.2- 0.25) g substrate	30 Nml/ g VS	22	45 (7)	55°C	149
	100 g of 7.5 % straw in the NMMO solution, heated in an oil bath at 130°C and atmospheric pressure for 1 h, while mixing every 15 min.	40 ml inoculum + (0.2- 0.25) g substrate	212 Nml/ g VS	157	45 (7)	55°C	-“-
Triticale straw (a hybrid of rye and wheat) straw	Untreated	40 ml inoculum + (0.2- 0.25) g substrate	34 Nml/ g VS	30	45 (7)	55°C	-“-
	100 g of 7.5 % straw in the NMMO solution and heated in an oil bath at	40 ml inoculum + (0.2- 0.25) g substrate	233 Nml/ g VS	203	45 (7)	55°C	-“-

	130°C and 1 atm 15 h						
Rice straw	Untreated	50 g solid/ l	190 ml/ g VS		24	35°C	[150] APS *2
	Grounded 25 mm	50 g solid/ l	200 ml/ g VS		24	35°C	-“-
	Grounded 25 mm 110°C + NH_3 20 mg/g dry w	50 g solid/ l	245 ml/ g VS		24	35°C	-“-

*1 – (Substrate: Inoculum) ratio was not good therefore, 70-80 % methane production is from inoculums)
*2 – Anaerobic-Phased Solids Digester System (incomparable with the other batch reactors)
*3 – The yield shows the total biogas production not only methane. Methane content of carbohydrate rich material is usually 50 % of the total biogas yield.

9.3 BIOGAS PRODUCTION FROM PAPER

Substrate / Paper	Pre-treatment	Organic load	Methane yield	Methane yield ml/ g raw material	Time anaerobic digestion (days)	Temp. anaerobic digestion	Ref
Newsprint	Untreated	no data	------	No data	------	------	[151]
	Alkaline supercritical- water treatment 190°C pH= 11.2 % newsprint	0.214 g/ l day (semi-continuous)	No data	327 ml/ g. day	HRT = 40	35°C	-“-
Newsprint	Untreated	85 ml inoculum + 15 ml sample (5 g solids)	80 ml/ g COD	No data	60	35°C	[152]
	15 ml NaOH 10 % + 5 g paper 1 day at 25°C	85 ml inoculum + 15 ml sample (5 g solids)	120 ml/ g COD	No data	60	35°C	-“-

Newsprint	Untreated	100 ml total volume of solid sample, nutrient solution and inoculum was fed	100 ml/ g VS	No data	60	35°C	153
News print	Ground newsprint (0.15-0.2 g) + 10 ml (acetic acid 35 % + nitric acid 2 %) →tubes were heated for 30 min, then centrifuged at 2,500 rpm for 5 min, then supernatants were discarded	100 ml total volume of solid sample, nutrient solution and inoculum was fed	270 ml/ g VS	No data	60	35°C	-“-
Office paper	Untreated	100 ml total volume of solid sample, nutrient solution and inoculum was fed	360 ml/ g VS	No data	60	35°C	-“-
Newspaper waste	Untreated	No data	-------		-------	-------	154
	Wet oxidation 20 g hand shredded newspaper + 1 liter distilled water 190°C, 1 h	Effluent 450 ml + 300 ml inoculums + 300 ml phosphate + vitamin solution	511 ml / 100 ml effluent		60	35°C	-“-
Paper tube residual	Untreated	0.425 g VS, untreated sample +20 ml inoculum + deionized water	222 Nml/ g VS	188	30	50°C	155
	Nonexclusive pretreatment 100 ml suspension of 50 g/l dry milled paper + 2 % NaOH at 190°C for 30 min	0.425 g VS treated sample + 20 ml inoculum + deionized water to get the total volume of 30 ml	269 Nml/ g VS	228	30	50°C	-“-
	Steam explosion 3 liter suspension of 50 g/l dry milled + both 2 % NaOH and 2 % H_2O_2 at	0.425 g VS treated sample +20 ml inoculum + deionized water to get the total volume	493 Nml/ g VS	419	60	50°C	-“-

	220°C for 10 min	of 40 ml					
	Steam explosion 3 liter suspension of 50 g/ l dry milled + 2 % NaOH at 220°C for 30 min	0.425 g VS treated sample + 20 ml Inoculum + deionized water to get the total volume of 40 ml	405 Nml/ g VS	344	60	50°C	-“-
	Steam explosion **3 liter suspension of 50 g/ l dry milled + 2% NaOH at 220°C for 10 min**	**0.425 g VS treated sample + 20 ml Inoculum + deionized water to get the total volume of 40 ml**	**403 Nml/ g VS**	**342.5**	**60**	**50°C**	-“-
Pulp & paper sludge	Untreated		190 ml/ g VS	36.5	42	37°C	156
	61 g pulp & paper sludge +122 ml 0.6 % NaOH at 37°C water bath for 6 h	23 g inoculum sludge + distilled water (to keep the total amount up to 700 g)	320 ml/ g VS	61.5	42	37°C	-“-

9.4 CO-DIGESTION OF MANURE AND LIGNOCELLULOSES

Substrate	Digestion type	Organic load	Methane yield	Time anaerobic digestion (days)	Temp. anaerobic digestion	Ref
Swine manure + wheat straw	Batch	Swine manure + 40 % wheat straw, 50 g/ l VS; 20 % (w/w) inoculum	260 l/ kg VS	90	23ºC	157,158
Swine manure + wheat straw	Batch	Swine manure + 40 % wheat straw, 50 g/ l VS; 20 % (w/w) inoculum	360 l/ kg VS	90	35ºC	-“-
Swine manure + wheat straw	continuously fed and mixed digester	Swine manure + 30 % wheat straw, 15 % TS, using chemical separated manure	230 l/ kg VS	15	50ºC	159,160

		solids				
Swine manure + wheat straw	continuously fed and mixed digester	Swine manure + 30 % wheat straw, TS 15 %, using chemical separated manure solids	300 l/ kg VS	30	30ºC	-“-
Cattle manure + barley straw	continuously fed and stirred reactor	Cattle manure + 30 % barley straw	380 l/ kg VS	100	35ºC	161,162
Cattle manure + barley straw	continuously fed and stirred reactor	Cattle manure + 40 % barley straw	340 l/ kg VS	120	35ºC	-“-
Cattle manure + wheat straw	continuously fed	Cattle manure + 40 % wheat straw, 10 % TS.	140 l/ kg VS	40	28°C	163,164
	continuously fed	(Cattle manure) + 100 % rice straw	230 l/ kg VS	40	28°C	-“-
Cattle manure + wheat straw	Batch	Cattle manure + 33 % wheat straw	200 l/ kg VS	28	35ºC	165,166
Manure (beef cattle) + straw	Pilot scale (2 stages) 1- Hydrolysis 2- Fermentation (solids separation)	Manure + straw (1:1) 10- 12 % TS 0.31 m^3 CH_4 / kg VS	1.81 m^3CH_4/m^3 Fermentor. Day	8	45.5ºC	167
Swine manure + switchgrass	Dry anaerobic digestion	Manure 20 g VS, switchgrass 186 g VS + 200 g inoculum	0.337 l/ kg VS	62	55ºC	168
Manure + straw	Batch	143 g manure + 144 g straw + 945 inoculum	0.182 m^3/ kg VS	30		169
	Batch	185 g manure + 93 g straw + 927 inoculum	0.208 m^3/ kg VS	30		-“-
Ley crop silage, wheat straw	Particle size reduction	80 % silage + 20 % manure	0.31 l/ g VS	9		170

and liquid manure	(mincing, 9.5 mm hollow plate) Continuous reactor					
Ley crop silage, wheat straw and liquid manure	Particle size reduction (mincing, 9.5 mm hollow plate)	60 % silage + 20 % straw + 20 % manure	0.28 l/ g VS	9		-“-
Ley crop silage, wheat straw and liquid manure	Particle size reduction (mincing, 5-spoke plate)	70 % silage + 10 % straw + 20 % manure	0.29 l/ g VS	9		-“-
Cow manure + grass silage	Semi-continuous co-digestion	30 % VS grass silage + 70 % VS manure	268 l/ kg VS	20	35ºC	171
Cow manure	Semi-continuous co-digestion	20 % VS manure	200 l/ kg VS	20	35ºC	-“-
Straw + manure	Batch fermentation	manure /straw ration (2:1, dry weight)	0.293 l/ g raw material	30	37ºC	172
Straw + manure	Fungi pretreated manure/straw in 60 days at 25°C, subjected to batch digestion	manure /straw ration (2:1, dry weight)	0.318 l/ g raw material	30	37ºC	-“-
Straw + manure	Fungi pretreated manure/straw in 90 days at 25°C, subjected to batch digestion	manure /straw ration (2:1, dry weight)	0.343 l /g raw material	30	37ºC	-“-

9.5 CAMBI PRETREATMENT OF OAT STRAW

Substrate	Pretreatment	Organic load	Methane yield	Time anaerobic digestion (days)	Temp. anaerobic digestion	Ref
Oat straw *	Lime pretreatment (96 % $Ca(OH)_2$ and 3 % $CaCO_3$), + distilled water to final volume of 1 liter, 55°C for 24 h	3 g VS	281 ml/ g VS	35	37ºC	[173]
	CAMBI steam pretreatment, 190ºC, 10 min	3 g VS	186 ml/ g VS	35	37ºC	-“-

10 REFERENCES

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[1] Chum, H.L., et al. (1985) Evaluation of pretreatment of biomass for enzymatic hydrolysis of cellulose, *Solar Energy Research Institute. Colorado State University.*

[2] Mussatto, S.I. and J.A. Teixeira (2010) Lignocellulose as raw material in fermentation processes, *IBB – Institute for Biotechnology and Bioengineering, Centre of Biological Engineering, University of Minho.*

[3] Mosier, N., et al. (2005) Features of promising technologies for pretreatment of lignocellulosic biomass, *Bioresource Technology, 2005. 96(6),* 673-686.

[4] McKendry, P (2002) Energy production from biomass (part 1): overview of biomass, *Bioresource Technology, 2002. 83(1)*, 37-46.

[5] EES – Engineering Equation Solver: http://sel.me.wisc.edu/ees/new_ees.html. Internet access: 2011-10-13.

[6] Sun, Y., and Cheng, J. (2002) Hydrolysis of lignocellulosic materials for ethanol production: a review, *Bioresource Technology 83*, 1-11.

[7] Mosier, N., et al. (2005) Features of promising technologies for pretreatment of lignocellulosic biomass, *Bioresource Technology, 2005. 96(6),* 673-686.

[8] Cara, C., et al. (2008) Conversion of olive tree biomass into fermentable sugars by dilute acid pretreatment and enzymatic saccharification, *Bioresource Technology 99*, 1869-1876.

[9] Brun, E., (2010) Improved anaerobic digestion of energy crops and agricultural residues, *Department of Environmental Engineering, Technical University of Denmark: Lyngby*.

[10] Hahn-Hägerdal, B., et al. (2006) Bio-ethanol - the fuel of tomorrow from the residues of today*. Trends in Biotechnolog, 24,* 549-556.

[11] Sun, Y., and Cheng, J. (2002) Hydrolysis of lignocellulosic materials for ethanol production: a review, *Bioresource Technology 83*, 1-11.

[12] Palmowski, L. M., and Müller, J. A. (2000) Influence of the size reduction of organic waste on their anaerobic digestion, *A Journal of International Association on Water Pollution Research 41*, 155-162.

[13] Walpot, J. I. (1986) Enzymatic hydrolysis of waste paper, *Conservation & Recycling 9*, 127-136.

[14] Garrote, G., et al. (1999) Hydrothermal processing of lignocellulosic materials, *European Journal of Wood and Wood Products 57*, 191-202.

[15] Gregg, D., and Saddler, J. (1996) A techno-economic assessment of the pretreatment and fractionation steps of a biomass-to-ethanol process, *Applied Biochemistry and Biotechnology 57-58*, 711-727.

[16] Mok, W. S. L., and Antal, M. J. (1992) Uncatalyzed solvolysis of whole biomass hemicellulose by hot compressed liquid water, *Industrial & Engineering Chemistry Research 31*, 1157-1161.

[17] Negro, M. J., et al. (2003) Changes in various physical/chemical parameters of Pinus pinaster wood after steam explosion pretreatment, *Biomass and Bioenergy 25*, 301-308.

[18] Ramos, L. P. (2003) The chemistry involved in the steam treatment of lignocellulosic materials, *Química Nova 26*, 863-871.

[19] Gossett, J. M., et al. (1982) Heat Treatment and anaerobic digestion of refuse, *Environmental Engineering Division 108*, 437-454.

[20] Brownell, H. H., et al. (1986) Steam-explosion pretreatment of wood: Effect of chip size, acid, moisture content and pressure drop, *Biotechnology and Bioengineering 28*, 792-801.

[21] Grethlein, H. E., and Converse, A. O. (1991) Common aspects of acid prehydrolysis and steam explosion for pretreating wood, *Bioresource Technology 36*, 77-82.

[22] Brownell, H. H., et al. (1986) Steam-explosion pretreatment of wood: Effect of chip size, acid, moisture content and pressure drop, *Biotechnology and Bioengineering 28*, 792-801.

---

[23] Lawther, J. M., et al. (1996) Effects of extraction conditions and alkali type on yield and composition of wheat straw hemicellulose, *Journal of Applied Polymer Science 60*, 1827-1837.

[24] Overend, R. P., et al. (1987) Fractionation of Lignocellulosics by Steam-Aqueous Pretreatments, *Philosophical Transactions of the Royal Society of London 321*, 523-536.

[25] Chornet, E., and Overend, R. P. (1988) Phenomenological Kinetics and Reaction Engineering Aspects of Steam/Aqueous Treatments, In *Proceedings of the International Workshop on Steam Explosion Techniques: Fundamentals and Industrial Applications*, pp 21-58, Milan, Italy.

[26] Digman, M. F., et al. (2010) Optimizing on-farm pretreatment of perennial grasses for fuel ethanol production, *Bioresource Technology 101*, 5305-5314.

[27] Li, C., et al. (2010) Comparison of dilute acid and ionic liquid pretreatment of switchgrass: Biomass recalcitrance, delignification and enzymatic saccharification, *Bioresource Technology 101*, 4900-4906.

[28] Harmsen, P., et al. (2010) Literature review of physical and chemical pretreatment processes for lignocellulosic biomass, *Food & Biobased Research*, Wageningen.

[29] McMillan James, D. (1994) Pretreatment of Lignocellulosic Biomass, In *Enzymatic Conversion of Biomass for Fuels Production*, pp 292-324, American Chemical Society, Washington DC.

[30] Chen, Y., et al. (2007) Potential of Agricultural Residues and Hay for Bioethanol Production, *Applied Biochemistry and Biotechnology 142*, 276-290.

[31] Yang, B., and Wyman, C. E. (2004) Effect of xylan and lignin removal by batch and flowthrough pretreatment on the enzymatic digestibility of corn stover cellulose, *Biotechnology and Bioengineering 86*, 88-98.

[32] Cara, C., et al. (2008) Conversion of olive tree biomass into fermentable sugars by dilute acid pretreatment and enzymatic saccharification, *Bioresource Technology 99*, 1869-1876.

[33] Wyman, C. E., and Abelson, P. H., (Eds.) (1996) *Handbook On Bioethanol: Production And Utilization*, Taylor & Francis, Washington DC, USA.

[34] Sun, X. F., et al. (2005) Characteristics of degraded cellulose obtained from steam-exploded wheat straw, *Carbohydrate Research 340*, 97-106.

[35] Brown, R. (2003) *Biorenewable Resources: Engineering New Products from Agriculture*, Wiley, Ed., New York.

[36] Abdi, N., et al. (2000) Enzymatic saccharification of solid residue of olive mill in a batch reactor, *Biochemical Engineering Journal 6*, 177-183.

[37] Carrillo, F., et al. (2005) Effect of alkali pretreatment on cellulase hydrolysis of wheat straw: Kinetic study, *Process Biochemistry 40*, 3360-3364.

[38] Silverstein, R. A., et al. (2007) A comparison of chemical pretreatment methods for improving saccharification of cotton stalks, *Bioresource Technology 98*, 3000-3011.

[39] Chang, V., and Holtzapple, M. (2000) Fundamental factors affecting biomass enzymatic reactivity, *Applied Biochemistry and Biotechnology 84-86*, 5-37.

[40] Chang, V., et al. (2001) Oxidative lime pretreatment of high-lignin biomass, *Applied Biochemistry and Biotechnology 94*, 1-28.

[41] Kaar, W. E., and Holtzapple, M. T. (2000) Using lime pretreatment to facilitate the enzymic hydrolysis of corn stover, *Biomass and Bioenergy 18*, 189-199.

[42] Kim, S., and Holtzapple, M. T. (2005) Lime pretreatment and enzymatic hydrolysis of corn stover, *Bioresource Technology 96*, 1994-2006.

[43] Foster, B., et al. (2001) Enzymatic hydrolysis of ammonia-treated sugar beet pulp, *Applied Biochemistry and Biotechnology 91-93*, 269-282.

[44] Kim, T. H., et al. (2003) Pretreatment of corn stover by aqueous ammonia, *Bioresource Technology 90*, 39-47.

[45] Chang, V., and Holtzapple, M. (2000) Fundamental factors affecting biomass enzymatic reactivity, *Applied Biochemistry and Biotechnology 84-86*, 5-37.

[46] Millett, M. A., et al. (1976) Physical and chemical pretreatments for enhancing cellulose saccharification, in *Proceeding Biotechnology and Bioengineering Symposium 6*, 125-153.

[47] Bjerre, A. B., et al. (1996) Pretreatment of wheat straw using combined wet oxidation and alkaline hydrolysis resulting in convertible cellulose and hemicellulose, *Biotechnology and Bioengineering 49*, 568-577.

[48] Fan, L. T., et al. (1987) *Cellulose hydrolysis. Biotechnology monographs*, Vol. 3, Springer-Verlag, New York, NY.

---

[49] Chang, V., et al. (1998) Lime pretreatment of crop residues bagasse and wheat straw, *Applied Biochemistry and Biotechnology 74*, 135-159.

[50] Silverstein, R. A., et al. (2007) A comparison of chemical pretreatment methods for improving saccharification of cotton stalks, *Bioresource Technology 98*, 3000-3011.

[51] Fukaya, Y., et al. (2008) Cellulose dissolution with polar ionic liquids under mild conditions: required factors for anions, *Green Chemistry 10*, 44-46.

[52] Heinze, T., et al. (2005) Ionic Liquids as Reaction Medium in Cellulose Functionalization, *Macromolecular Bioscience 5*, 520-525.

[53] Feng, L., and Chen, Z.-l. (2008) Research progress on dissolution and functional modification of cellulose in ionic liquids, *Journal of Molecular Liquids 142*, 1-5.

[54] Zhu, S. (2008) Use of ionic liquids for the efficient utilization of lignocellulosic materials, *Journal of Chemical Technology & Biotechnology 83*, 777-779.

[55] Feng, L., and Chen, Z.-l. (2008) Research progress on dissolution and functional modification of cellulose in ionic liquids, *Journal of Molecular Liquids 142*, 1-5.

[56] Heinze, T., et al. (2005) Ionic Liquids as Reaction Medium in Cellulose Functionalization, *Macromolecular Bioscience 5*, 520-525.

[57] Dadi, A., et al. (2007) Mitigation of cellulose recalcitrance to enzymatic hydrolysis by ionic liquid pretreatment, *Applied Biochemistry and Biotechnology 137-140*, 407-421.

[58] Wu, J., et al. (2004) Homogeneous Acetylation of Cellulose in a New Ionic Liquid, *Biomacromolecules 5*, 266-268.

[59] Swatloski, R. P., et al. (2002) Dissolution of Cellose with Ionic Liquids, *Journal of the American Chemical Society 124*, 4974-4975.

[60] Panagiotou, G., and Olsson, L. (2007) Effect of compounds released during pretreatment of wheat straw on microbial growth and enzymatic hydrolysis rates, *Biotechnology and Bioengineering 96*, 250-258.

[61] Hon, D. N. S., and Shiraishi, N. (2001) *Wood and Cellulosic Chemistry, second ed*, New York.

[62] McGinnis, G. D., et al. (1983) Biomass pretreatment with water and high-pressure oxygen. The wet-oxidation process, *Industrial & Engineering Chemistry Product Research and Development 22*, 352-357.

[63] Palonen, H., et al. (2004) Evaluation of wet oxidation pretreatment for enzymatic hydrolysis of softwood, *Applied Biochemistry and Biotechnology 117*, 1-17.

[64] Jørgensen, H., et al. (2007) Enzymatic conversion of lignocellulose into fermentable sugars: challenges and opportunities, *Biofuels, Bioproducts and Biorefining 1*, 119-134.

[65] Schultz, T. P., et al. (1984) Similarities and differences in pretreating woody biomass by steam explosion, wet oxidation, autohydrolysis, and rapid steam hydrolysis/continuous extraction, In *Proceedings of the 8th Conference: Annual Symposium on Energy from Biomass and wastes, Lake Buena Vista, FL, USA, 30 Jan 1984*, p 28.

[66] Panagiotou, G., and Olsson, L. (2007) Effect of compounds released during pretreatment of wheat straw on microbial growth and enzymatic hydrolysis rates, *Biotechnology and Bioengineering 96*, 250-258.

[67] Schmidt, A. S., and Thomsen, A. B. (1998) Optimization of wet oxidation pretreatment of wheat straw, *Bioresource Technology 64*, 139-151.

[68] Okano, K., et al. (2005) Conversion of Japanese red cedar (Cryptomeria japonica) into a feed for ruminants by white-rot basidiomycetes, *Animal Feed Science and Technology 120*, 235-243.

[69] Sun, Y., and Cheng, J. (2002) Hydrolysis of lignocellulosic materials for ethanol production: a review, *Bioresource Technology 83*, 1-11.

[70] Tengerdy, R. P., and Szakacs, G. (2003) Bioconversion of lignocellulose in solid substrate fermentation, *Biochemical Engineering Journal 13*, 169-179.

[71] Chandler, J. A., and Jewell, W. J. (1980) *Predicting methane fermentation biodegradability.*, Solar Energy Research Institute, Golden, Colorado.

[72] Komilis, D. P., and Ham, R. K. (2003) The effect of lignin and sugars to the aerobic decomposition of solid wastes, *Waste Management 23*, 419-423.

[73] Sun, Y., and Cheng, J. (2002) Hydrolysis of lignocellulosic materials for ethanol production: a review, *Bioresource Technology 83*, 1-11.

---

[74] Akhtar, M., et al. (1992) The white-rot fungus Ceriporiopsis subvermispora saves electrical energy and improves strength properties during biomechanical pulping of wood., *Biotechnology in the Pulp and Paper Industry, Proceedings of the 5th International Conference on Biotechnology in the Pulp and Paper Industry*, 3-8.

[75] Sun, Y., and Cheng, J. (2002) Hydrolysis of lignocellulosic materials for ethanol production: a review, *Bioresource Technology 83*, 1-11.

[76] Nakamura, Y., and Mtui, G. (2003) Anaerobic fermentation of woody biomass treated by various methods, *Biotechnology and Bioprocess Engineering 8*, 179-182.

[77] Take, H., Andou, Yoshifumi., Nakamura, Yoshitoshi., Kobayashi, Fumihisa.,Kurimoto, Yasuji.,Kuwahara, Masaaki. (2006) Production of methane gas from Japanese cedar chips pretreated by various delignification methods, *Biochemical Engineering Journal 28*, 30-35.

[78] Amirta, R., et al. (2006) Methane fermentation of Japanese cedar wood pretreated with a white rot fungus, Ceriporiopsis subvermispora, *Journal of Biotechnology 123*, 71-77.

[79] Amirta, R., et al. (2006) Methane fermentation of Japanese cedar wood pretreated with a white rot fungus, Ceriporiopsis subvermispora, *Journal of Biotechnology 123*, 71-77.

[80] Mirahmadi, K., et al. (2010) Alkaline pretreatment of spruce and birch to improve bioethanol and biogas production, *Bioresources 5*, 928-938.

[81] Teghammar, A., et al. (2011) Enhanced biogas production from rice straw, triticale straw and softwood spruce by NMMO pretreatment, *Biomass and Bioenergy* In Press.

[82] Sharma, S. K., et al. (1988) Effect of particle size on biogas generation from biomass residues, *Biomass 17*, 251-263.

[83] Sharma, S. K., et al. (1988) Effect of particle size on biogas generation from biomass residues, *Biomass 17*, 251-263.

[84] Dererie, D. Y., et al. (2011) Improved bio-energy yields via sequential ethanol fermentation and biogas digestion of steam exploded oat straw, *Bioresource Technology 102*, 4449-4455.

[85] Panagiotou, G., and Olsson, L. (2007) Effect of compounds released during pretreatment of wheat straw on microbial growth and enzymatic hydrolysis rates, *Biotechnology and Bioengineering 96*, 250-258.

[86] Panagiotou, G., and Olsson, L. (2007) Effect of compounds released during pretreatment of wheat straw on microbial growth and enzymatic hydrolysis rates, *Biotechnology and Bioengineering 96*, 250-258.

[87] Zhang, R., and Zhang, Z. (1999) Biogasification of rice straw with an anaerobic-phased solids digester system, *Bioresource Technology 68*, 235-245.

[88] Zhong, W., et al. (2011) Comparison of chemical and biological pretreatment of corn straw for biogas production by anaerobic digestion, *Renewable Energy 36*, 1875-1879.

[89] Xiao, W., and Clarkson, W. W. (1997) Acid solubilization of lignin and bioconversion of treated newsprint to methane, *Biodegradation 8*, 61-66.

[90] Xiao, W., and Clarkson, W. W. (1997) Acid solubilization of lignin and bioconversion of treated newsprint to methane, *Biodegradation 8*, 61-66.

[91] Clarkson, W. W., and Xiao, X. (2000) Bench-scale anaerobic bioconversion of newsprint and office paper, *Water Science and Technology 41*, 93-100.

[92] Lin, Y., et al. (2009) Alkali pretreatment enhances biogas production in the anaerobic digestion of pulp and paper sludge, *Journal of Hazardous Materials 170*, 366-373.

[93] Fox, M., and Noike, T. (2004) Wet oxidation pretreatment for the increase in anaerobic biodegradability of newspaper waste, *Bioresource Technology 91*, 273-281.

[94] Teghammar, A., et al. (2010) Pretreatment of paper tube residuals for improved biogas production, *Bioresource Technology 101*, 1206-1212.

[95] Teghammar, A., et al. (2010) Pretreatment of paper tube residuals for improved biogas production, *Bioresource Technology 101*, 1206-1212.

[96] Lehtomaeki, A. (2006) Biogas Production from energy Crops and Crop Residues, *PhD Thesis in department of Biological and Environmetal science of University of Jyvaeskylae, Finland*.

[97] Mata-Alvarez, J., et al. (2000) Anaerobic digestion of organic solid wastes. An overview of research achievements and perspectives, *Bioresource Technology 74*, 3-16.

---

[98] Lehtomäki, A., et al. (2007) Laboratory investigations on co-digestion of energy crops and crop residues with cow manure for methane production: Effect of crop to manure ratio, *Resources, Conservation and Recycling 51*, 591-609.

[99] Lehtomäki, A., et al. (2007) Laboratory investigations on co-digestion of energy crops and crop residues with cow manure for methane production: Effect of crop to manure ratio, *Resources, Conservation and Recycling 51*, 591-609.

[100] Lehtomaeki, A. (2006) Biogas Production from energy Crops and Crop Residues, *PhD Thesis in department of Biological and Environmetal science of University of Jyvaeskylae, Finland*.

[101] Demirbas, A. (2006) Biogas Potential of Manure and Straw Mixtures, *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects 28*, 71-78.

[102] Müller, H. W., and Trösch, W. (1986) Screening of white-rot fungi for biological pretreatment of wheat straw for biogas production, *Applied Microbiology and Biotechnology 24*, 180-185.

[103] Cambi. www.cambi.no. Internet access: 2011-09-21.

[104] Holte, Rasmus. 2011. Process Engineer. Cambi. Personal correspondence: 2011-10-09.

[105] Biorefinex. www.biorefinex.com. Internet access: 2011-07-21.

[106] Smith, Stephen. 2011. CEO. Biorefinex. Personal correspondence: 2011-09-21.

[107] Brodén, Henrik. Senior technical consultant, Grontmij AB. Personal correspondence: 2011-08-30.

[108] Fritz, Lars. 2011. Process Ingenjör. NBE Sweden AB. Personal correspondence: 2011-11-21.

[109] Rundvik Masonite. www.masonite.se. Internet access: 2011-11-22.

[110] EES – Engineering Equation Solver: http://sel.me.wisc.edu/ees/new_ees.html. Internet access: 2011-10-13.

[111] Jönsson, Mikael. 2011. Technical consultant. Grontmij AB. June, 2011.

[112] Manhag, Kjell. 2011. Senior technical consultant. Grontmij AB. 2011-06-09.

[113] Zimbardi, et al. (2002). Technoeconomic study on steam explosion application in biomass processing, *Applied Biochemistry and Biotechnology 98-100, Numbers 1-9, 89-99, DOI: 10.1385/ABAB:98-100:1-9:89.*

[114] Schell, D., et.al. (1999) A technical and economic analysis of acid-catalyzed steam explosion and dilute sulfuric acid pretreatments using wheat straw or aspen wood chips, *Applied Biochemistry and Biotechnology 28-29, 87-97, DOI: 10.1007/BF02922591.*

[115] Seider, W.D.,et al. (2004) *Product and Process Design Principles – Synthesis Analysis and Evaluation, second ed.* John Wiley and Sons Inc., New York.

[116] Wingren, A., et al. (2003) Techno-Economic Evaluation of Producing Ethanol from Softwood: Comparison of SSF and SHF and Identification of Bottlenecks. *Biotechnol. Prog. 19 (4),* 1109–1117.

[117] Nasdaq OMX Commodities. www.nordpool.se. Internet access: 2011-10-12.

[118] Mänd, Björn. 2011. Scandicore. Nordens pappersindustri AB. Personal correspondence: 2011-12-01.

[119] Wooley, R.J., et al. (1999). Lignocellulosic biomass to ethanol process design and economics utilizing concurrent dilute acid prehydrolysis and enzymatic hydrolysis current and futuristic scenarios. *NREL/TP-580-26157*

[120] Seider, W.D.,et al. (2004) *Product and Process Design Principles – Synthesis Analysis and Evaluation, second ed.* John Wiley and Sons Inc., New York.

[121] Zimbardi, et al. (2002). Technoeconomic study on steam explosion application in biomass processing, *Applied Biochemistry and Biotechnology 98-100, Numbers 1-9, 89-99, DOI: 10.1385/ABAB:98-100:1-9:89.*

[122] Kumar, A., et al. (2005) Pipeline transport and simultaneous saccharification of corn stover. *Bioresource. Technology. 96*, 819–829.

[123] Kumar, A., et al. (2005) Pipeline transport and simultaneous saccharification of corn stover. *Bioresource. Technology. 96*, 819–829.

[124] Wooley, R.J., et al. (1999) Lignocellulosic biomass to ethanol process design and economics utilizing concurrent dilute acid prehydrolysis and enzymatic hydrolysis current and futuristic scenarios. *NREL/TP-580-26157*

[125] Haaker A. (2011) Priser och marknad för biobränsle, *Bioenergi nr 1 2011*. http://bioenergitidningen.se/Priser%20och%20marknad

---

[126] Haaker A. (2011) Priser och marknad för biobränsle, *Bioenergi nr 1 2011*. http://bioenergitidningen.se/Priser%20och%20marknad

[127] EI, 2011 (Energimarknadsinspektionen). URL: http://www.ei.se/upload/Rapporter/Fjv/EIR201004.pdf. Internet access: 2011-09-01.

[128] Strömberg, B. (2005) *Bränslehandboken*, Värmeforsk, rapport 911, Stockholm, Sverige.

[129] Strömberg, B. (2005) *Bränslehandboken*, Värmeforsk, rapport 911, Stockholm, Sverige.

[130] Strömberg, B. (2005) *Bränslehandboken*, Värmeforsk, rapport 911, Stockholm, Sverige.

[131] Arkelöv O., et al. (2010) *Grödor från åker till energi*, Värmeforsk, rapport 1139, Stockholm, Sverige.

[132] Clean Energy: http://www.clean-energy.us/facts/gasification.htm. Internet access: 2011-12-01.

[133] Nakamura, Y., and Mtui, G. (2003) Anaerobic fermentation of woody biomass treated by various methods, *Biotechnology and Bioprocess Engineering 8*, 179-182.

[134] Take, H., et al. (2006) Production of methane gas from Japanese cedar chips pretreated by various delignification methods, *Biochemical Engineering Journal 28*, 30-35.

[135] Amirta, R., et al. (2006) Methane fermentation of Japanese cedar wood pretreated with a white rot fungus, Ceriporiopsis subvermispora, *Journal of Biotechnology 123*, 71-77.

[136] Yoshida, K., et al. (2010) Methane production from organic acids obtained by supercritical water treatment of Japanese beech, *Journal of Wood Science 56*, 160-165.

[137] Teghammar, A., et al. (2011) Enhanced biogas production from rice straw, triticale straw and softwood spruce by NMMO pretreatment, *Biomass and Bioenergy* In Press

[138] Mirahmadi, K., et al. (2010) Alkaline pretreatment of spruce and birch to improve bioethanol and biogas production, *Bioresources 5*, 928-938.

[139] Dererie, D. Y., et al. (2011) Improved bio-energy yields via sequential ethanol fermentation and biogas digestion of steam exploded oat straw, *Bioresource Technology 102*, 4449-4455.

[140] Bauer, A., et al. (2009) Analysis of methane potentials of steam-exploded wheat straw and estimation of energy yields of combined ethanol and methane production, *Journal of Biotechnology 142*, 50-55.

[141] KTBL. (2005) Faustzahlen für die Landwirtschaft. Kuratorium für Bauwesen in der Landwirtschaft e.V., Darmstadt.

[142] Bauer, A., et al. (2009) Analysis of methane potentials of steam-exploded wheat straw and estimation of energy yields of combined ethanol and methane production, *Journal of Biotechnology 142*, 50-55.

[143] Dererie, D. Y., et al. (2011) Improved bio-energy yields via sequential ethanol fermentation and biogas digestion of steam exploded oat straw, *Bioresource Technology 102*, 4449-4455.

[144] Zhao, R., et al. (2010) Methane production from rice straw pretreated by a mixture of acetic-propionic acid, *Bioresource Technology 101*, 990-994.

[145] Lei, Z., et al. (2010) Methane production from rice straw with acclimated anaerobic sludge: Effect of phosphate supplementation, *Bioresource Technology 101*, 4343-4348.

[146] Hjorth, M., et al. (2011) Extrusion as a pretreatment to increase biogas production, *Bioresource Technology In Press, Accepted Manuscript*.

[147] Zhong, W., et al. (2011) Comparison of chemical and biological pretreatment of corn straw for biogas production by anaerobic digestion, *Renewable Energy 36*, 1875-1879.

[148] Sharma, S. K., et al. (1988) Effect of particle size on biogas generation from biomass residues, *Biomass 17*, 251-263.

[149] Teghammar, A., et al. (2011) Enhanced biogas production from rice straw, triticale straw and softwood spruce by NMMO pretreatment, *Biomass and Bioenergy* In Press

[150] Zhang, R., and Zhang, Z. (1999) Biogasification of rice straw with an anaerobic-phased solids digester system, *Bioresource Technology 68*, 235-245.

[151] Fox, M. H., et al. (2003) Alkaline subcritical-water treatment and alkaline heat treatment for the increase in biodegradability of newsprint waste, *Water Science and Technology 48*, 77-84.

[152] Clarkson, W. W., and Xiao, X. (2000) Bench-scale anaerobic bioconversion of newsprint and office paper, *Water Science and Technology 41*, 93-100.

---

[153] Xiao, W., and Clarkson, W. W. (1997) Acid solubilization of lignin and bioconversion of treated newsprint to methane, *Biodegradation 8*, 61-66.

[154] Fox, M., and Noike, T. (2004) Wet oxidation pretreatment for the increase in anaerobic biodegradability of newspaper waste, *Bioresource Technology 91*, 273-281.

[155] Teghammar, A., et al. (2010) Pretreatment of paper tube residuals for improved biogas production, *Bioresource Technology 101*, 1206-1212.

[156] Lin, Y., et al. (2009) Alkali pretreatment enhances biogas production in the anaerobic digestion of pulp and paper sludge, *Journal of Hazardous Materials 170*, 366-373.

[157] Oosterkamp, W. J. (2008) Enhancement of biogas production from straw and manure, *Draft to be submitted to Waste and Biomass Valorization*.

[158] Llabrés-Luengo, P., and Mata-Alvarez, J. (1988) Influence of temperature, buffer, composition and straw particle length on the anaerobic digestion of wheat straw--Pig manure mixtures, *Resources, Conservation and Recycling 1*, 27-37.

[159] Oosterkamp, W. J. (2008) Enhancement of biogas production from straw and manure, *Draft to be submitted to Waste and Biomass Valorization*.

[160] Moeller, H. B., and Andersen, G. (2006) How to double the gas production through the addition of solid biomass, *Bioenergy Research no 13.*, 6-7.

[161] Lehtomaeki, A. (2006) Biogas Production from energy Crops and Crop Residues, *PhD Thesis in department of Biological and Environmetal science of University of Jyvaeskylae, Finland*.

[162] Oosterkamp, W. J. (2008) Enhancement of biogas production from straw and manure, *Draft to be submitted to Waste and Biomass Valorization*.

[163] Oosterkamp, W. J. (2008) Enhancement of biogas production from straw and manure, *Draft to be submitted to Waste and Biomass Valorization*.

[164] Somayaji, D., and Khanna, S. (1994) Biomethanation of rice and wheat straw, *World Journal of Microbiology and Biotechnology 10*, 521-523.

[165] Demirbas, A. (2006) Biogas Potential of Manure and Straw Mixtures, *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects 28*, 71-78.

[166] Oosterkamp, W. J. (2008) Enhancement of biogas production from straw and manure, *Draft to be submitted to Waste and Biomass Valorization*.

[167] Hashimoto, A. G., and Robinson, S. A. (1982) Pilot-scale conversion of manure--straw mixtures to methane, *Resources and Conservation 8*, 19-28.

[168] Ahn, H. K., et al. (2010) Evaluation of biogas production potential by dry anaerobic digestion of switchgrass--animal manure mixtures, *Applied Biochemistry and Biotechnology 160*, 965-975.

[169] Demirbas, A. (2006) Biogas Potential of Manure and Straw Mixtures, *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects 28*, 71-78.

[170] Nordberg, Å., and Edström, M. (1998) Co-digestion of ley crop silage, straw and manure, *Swedish Institute of Agricultural Engineering*

[171] Lehtomäki, A., et al. (2007) Laboratory investigations on co-digestion of energy crops and crop residues with cow manure for methane production: Effect of crop to manure ratio, *Resources, Conservation and Recycling 51*, 591-609.

[172] Müller, H. W., and Trösch, W. (1986) Screening of white-rot fungi for biological pretreatment of wheat straw for biogas production, *Applied Microbiology and Biotechnology 24*, 180-185.

[173] Dererie, D.Y. (2010) Integrated Production of Bioethanol and Biogas from Agricultural Residue: Comparison of Pretreatment Methods Using Mass low and Energy Yields Analysis, *M.Sc. Thesis for the Master Programme in Sustainable Technology, Royal Institute of Technology (KTH), Stockholm.*

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