BIOGAS : Combined biogas and bio-ethanol production for optimal energy utilization

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PROJECT 2010

Title of the project	Combined biogas and bio-ethanol production for optimal energy utilization
Acronym	BIOGAS
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Duration	Two years 2010- 2012

Summary

Until now, much research work has been dealing with facilitating the production of bio-ethanol from 2nd generation feedstocks (i.e. lignocellulosic materials such as wood or straw) with the natural focus on bio-ethanol production. However, environmental sustainability is necessary; the process is generating waste streams that could possibly be converted into biogas which could be used as vehicle fuel to replace fossil fuels. At the same time as biogas is produced, a wastewater handling problem could be solved. This solution is expected to work out well, but so far, not much research work can be found on this matter… therefore, the aim of this R&D project is to evaluate parameters needed to develop an environmental sustainable wastewater treatment process that uses the waste stream from the 2nd generation bio-ethanol production. Anaerobic treatment will substantially reduce the organic content, but there will still be too high levels of organic matter in the wastewater for internal recirculation and/or direct discharge to any recipient. Hence, combinations of aerobic wastewater treatment and advanced oxidation methods (e;g. ozonation) will be applied after the anaerobic digestion(AD) process. Different combinations of aerobic treatment and advanced oxidation will thus be evaluated. The aim is to reach a water quality that fulfills outlet demands and/or recirculation demands. The research work will include the investigation of: 1Stillage characterization/content; nutrients, toxic substances, organic content, variations in flow and content, etc…,2Adaptation of anaerobic applications3Process parameters,4Combination of AD and aerobic wastewater treatment.

Results

This experimental work aimed to evaluate possibilities for combining bio-ethanol production with anaerobic and aerobic treatment. Some parameters should be characterized.

Nitrogen and phosphorus contents of the waste streams are rather low, and there is a risk of lack of N and P in anaerobic digestion. This lack could be recovered by co-digestion with e.g. food waste. This combination was tested with good results.

Significant amounts of biogas production from bioethanol waste streams are possible, with different biogas production rates and final biogas potentials from different process configurations.

Both mesophilic and thermophilic digestion is possible with no difference in biogas potential.

The overall energy potential from biogas production from different process configurations is about the same for the cases evaluated.
Bio-ethanol residues are inhibiting nitrification, but less after anaerobic digestion. Anaerobic step should precede an eventual aerobic step, and in that way, brings another benefit: the organic content of the waste streams can primarily be used for biogas production, instead of demanding energy for aerobic degradation.

Deliverables

Å. Davidsson, O Wallberg, K Jönsson, G Zacchi (2012) Optimal Biogas Production from Bioethanol Process. Poster presented at the 8th International Conference on Renewable Resources & Biorefineries, 4-6 June, 2012, Toulouse, France
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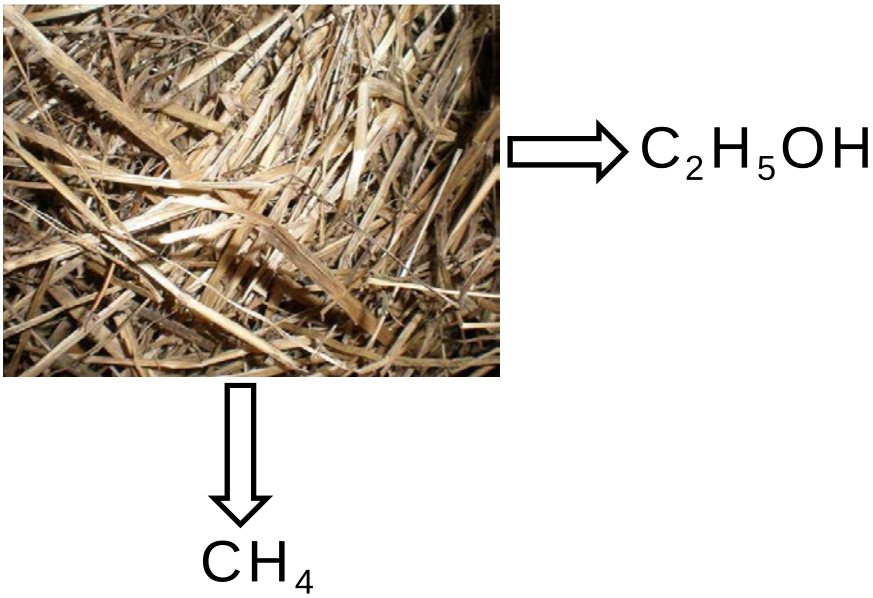
Combined biogas and bio-ethanol production for optimal energy utilization



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TUCK Foundation / ENERBIO R&D-project

Pre-face

This work was done within an ENERBIO R&D-project with the financial help from the TUCK Foundation. The work within this project which is summarized in this report was performed with the assistance from several colleagues at the Department of Chemical Engineering, Lund University.
The project group consisted of: Åsa Davidsson, Ola Wallberg, Karin Jönsson and Guido Zacchi. Other staff members and students that have contributed are: Elin Johansson, Pia-Maria Bondesson, Fredrik Nielsen, Christian Roslander, Elisabeth Joelsson, Mahan Amani Geshnigani and Gertrud Persson. All involved are acknowledged for their assistance.
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Lund 2013-01-12

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Summary of results

When using biomass for energy production, as 2nd generation bio-ethanol production, economic and environmental sustainability is necessary. To fulfil this it is important to have an energy efficient process configuration (with a high yield per biomass) and also to take care of the waste streams generated in the process (i.e. wastewater treatment). Anaerobic treatment of the waste streams could be a potential method which both increases the energy yield and improves the quality of the waste stream. However, anaerobic treatment will not be sufficient as sole treatment step, but could possibly be combined with for example an aerobic step.

So far very little has been published regarding the downstream processing of the wastewaters from 2nd generation bio-ethanol production and this is an issue which must be handled before any complete plants can be constructed and permitted. It was therefore the aim of this research project to evaluate important parameters to be able to suggest an environmental sustainable wastewater treatment process (including anaerobic digestion) for the 2nd generation bio-ethanol production. The main findings are summarized below:

A review showed that the content of the waste streams from bioethanol production are important for the development of a process including biogas production and further wastewater treatment. Especially organic content (for estimation of biogas production), nutrient content (microbiological needs of anaerobic and aerobic processes) and possible toxicant (that could affect biological processes) should be characterized.

Nitrogen and in some case also phosphorus content is rather low in some substrates generated in the two alternative process configurations studied in this project. There is subsequently a risk of lack of N and P in anaerobic digestion. This lack could be recovered by co-digestion with e.g. food waste, a combination which was tested experimentally with good results in the study.

Significant amounts of biogas production from all bioethanol waste streams are possible. However the waste stream from the different ethanol process configurations results in different biogas production rates and different final biogas potentials.

Both mesophilic and thermophilic digestion is possible. Almost no difference in biogas potential was seen. However thermophilic temperature could be favorable since the bioethanol process involves high temperatures already.

The overall energy potential from biogas production considering the mass flows expected from different process configurations is about the same for the two cases evaluated. However, if solids are separated and burnt after fermentation the biogas potential is reduced compared to distillation of the whole fraction.

Bioethanol residues are inhibiting nitrification – but less after anaerobic digestion. Therefore it is suggested that the anaerobic step should precede an eventual aerobic step. This brings about another benefit as well; the organic content can primarily be used for biogas production – instead of demanding energy (oxygen) for degradation aerobically.

Content

Introduction

Background

The European Parliament has set targets to be achieved during 2020 to reduce the problem of greenhouse gas emissions. These greenhouse gases must be reduced by 20% and 10% of the fuel used must be biofuel (EC, 2007). One way to achieve this goal might be to invest in the combined production of bioethanol and biogas. Using wheat straw as raw material is a good choice because wheat is the most produced crop in Sweden and throughout Europe, and it is not competitive in food.

The major components of wheat straw are cellulose, hemicellulose and lignin (Sun et al., 1998). Cellulose consists of densely packed glucose chains whereas hemicellulose consisting of a branched network in which xylose is predominant (Sun et al, 1998). Since hemicellulose is composed of mostly pentose sugars and most techniques for ethanol production is enhanced for hexoses, it is desirable to separate the hemicellulose and cellulose and having an alternative use of the hemicellulose, which could be anaerobic degradation and biogas production.

The production of ethanol from lignocellulosic material consists of five main steps: pretreatment, enzymatic hydrolysis of cellulose, fermentation of hexoses, separation and wastewater treatment (Galbe and Zacchi, 2007).Steam explosion is a pretreatment method, where the material is treated with saturated steam at high pressure during a time period from seconds to several minutes, after which the material is suddenly depressurized. The hemicellulose is solubilized and the cellulose is exposed, which enhances the enzyme accessibility during hydrolysis. When the hemicellulose is solubilized, acetyl groups are cleaved off and forms acetic acid. The main disadvantages of steam explosion are the partially sugar degradation to 5-hydroxymethylfurfural (HMF) and furfural and the generation of other toxic compounds, which could have a negative effect on the following hydrolysis and fermentation steps. The steam explosion can be combined with dilute acids. The most commonly used acid, sulphuric acid, has though a negative effect on the anaerobic digestion (AD) in case the stillage is used in AD, leading to less produced methane. Using organic acids has a potential in high hydrolysis yields and lower degradation products compared to sulphuric acid. In addition to that, organic acids have the advantage that they can be used as raw material in the anaerobic digestion step, resulting in a higher biogas production (Alvira et al, 2009). During enzymatic hydrolysis the cellulose is converted into glucose monomers, which are fermented to ethanol during the fermentation. By combining these steps in simultaneous saccharification and fermentation (SSF), a shorter residence time is needed and also problem with glucose inhibition in the hydrolysis step is avoided (Linde, 2007)

The production of bio-ethanol from 2nd generation feedstocks (i.e. lignocellulosic materials such as wood or straw) can be facilitated in several different ways. One commonly cited process layout (Sassner et al., 2007) starts with acidic pretreatment of the biomass to hydrolyze the hemicellulosic part to monomeric sugars(Figure 1). The pretreated slurry is then subjected to enzymatic hydrolysis and fermentation, often combined into an SSF (simultaneous saccarification and fermentation) operation. One large challenge appears downstream of these operations when the fermentation broth needs to be distilled and the stillage is to be handled to reduce the environmental impact of the bio-ethanol production and in order to utilize the energy content of the raw material in an effective way. The stillage contains a substantial portion of the original biomass, both as solid lignin and as low molecular weight substances which has been solubilized during the upstream operations. The solid part can be filtered from the solution and subsequently burnt in the heat and power generation part of the bio-ethanol plant. The liquid part of the stillage has low total solids content, but it still contains much higher levels of organic compounds than would be permitted to let out in any recipient. One relatively easy treatment alternative is to evaporate the stillage and burn it to utilize the energy content.

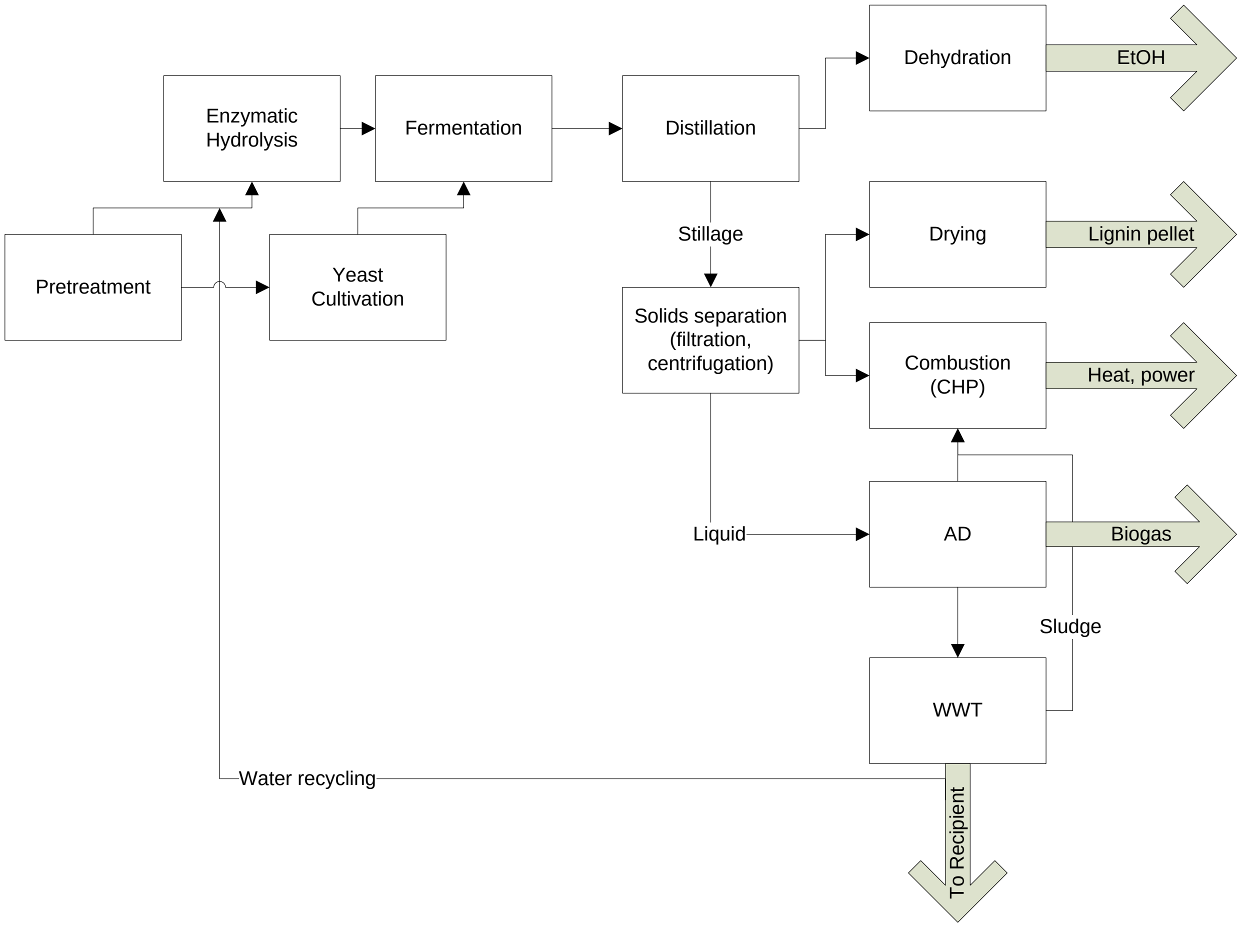

Figure 1. Process layout for bio-ethanol production from 2nd generation feed stocks

However, recent techno-economical evaluations suggest the energy demand for the evaporation would be very high (Wingren et al., 2008; Sssner et al., 2008). A better option would therefore be to treat the liquid part of the stillage in a wastewater treatment operation, preferably starting with an anaerobic step to produce biogas in addition to ethanol. The liquid from this operation would then be treated in aerobic waste water treatment facilities to reduce the organic content of the waste water to levels which would be permitted to let into the recipient. So far very little has been published regarding the downstream processing of the wastewaters from 2nd generation bio-ethanol production and this is an issue which must be handled before any complete plants can be constructed and permitted. It is the aim of this research project to suggest and validate an environmental sustainable wastewater treatment process (including anaerobic digestion) for the 2nd generation bio-ethanol production.

Treating the stillage by anaerobic digestion (AD) could be beneficial both economically and environmentally compared to evaporation. Instead of using energy for evaporating lots of water, the AD step will produce biogas, which can be used for production of vehicle fuel, electricity or heat, thus replacing fossil fuels. Anaerobic digestion is a well-known process that has been used during many years for stabilization of municipal sewage sludge and in industrial applications for treatment of wastewater. The AD process includes a microbial degradation and conversion of organic matter. The potential for using AD for reduction of organic content in stillage is expected to be high. Some recent initial tests conducted at the department indicate a high biogas potential (Dienes, 2009; Jacsina & Kiriakov, 2009). The state of the art in this subject was studied by Wilkie et al. (2000). It was concluded that the data on cellulosic stillage characteristics and treatment parameters are extremely limited and highly variable. It is therefore suggested that much more research work is needed to be able to include AD as a step in the bio-ethanol production process.

The biogas potential is depending on the substrate being applied to anaerobic digestion. Monomer sugars are easy to digest, but since the methanogens have a slow growth the digestion of the fatty acids are limited, which can result in a lower alkalinity. Stillage from ethanol production can have high protein content since almost all sugar has been fermented, which can result in inhibition by ammonia. Combining stillage with sugars like not fermentable pentoses from wheat straw could improve the biogas production (Jarvis & Schnürer, 2009). In Bondesson (2010), three different soaking materials were tested combined with the steam pretreatment, water, 1 % acetic acid and 0.4 % phosphoric acid. The pretreated slurry was then investigated in two different process configurations. In the first configuration, the SSF was done on the whole slurry from the pretreatment. The slurry after SSF was stripped so the ethanol was separated from the slurry. The residue was filtered and the liquid part was taken to the AD. In the second configuration, a separation was made after the pretreatment and the liquid part was taken for the AD and the solid part to the SSF. The results showed that the highest yield regarding the energy recovery, 60 % in ethanol and in methane, was obtained with phosphoric acid when using the whole slurry in the SSF. In the acetic acid configurations the recovery was 42% respectively 40%. The low methane yield for the phosphoric acid pretreated material where the cake is used for SSF and the hydrolysate for the AD could probably increase a lot if another base (instead of ammonia) or a pH controlled reactor had been used for the AD.

Project tasks

This project has focused on bio-ethanol and biogas production from 2nd generation feedstocks (i.e. lignocellulosic materials such as wood or straw). The bio-ethanol production process is generating waste streams that could possibly be converted into biogas which could be used as vehicle fuel to replace fossil fuels. At the same time as biogas is produced, a wastewater handling problem could be solved. In this project, parameters needed to develop a process that uses the waste stream from bio-ethanol production for generation of biogas, are studied. The aim is also to further treat the waste stream to reach a water quality that fulfills outlet demands and/or recirculation demands. Hence, aerobic wastewater treatment is needed in combination with the AD process. The research work mainly included the investigation of:

Stillage characterization/content; nutrients, toxic substances, organic content

Adaptation of anaerobic applications; mesophilic, thermophilic, co-digestion

Process parameters: temperature, retention time

Combination of AD and aerobic wastewater treatment; inhibition on aerobic treatment

The main part of the results found is presented in the following chapters and includes two parts 1) literature studies and 2) experimental work

Literature review

The aim of this part was to review the area of bio-ethanol stillage treatment to find suitable anaerobic digestion processes and process combinations.

Focus and limitations

The focus of the study was wheat straw-based bio-ethanol production and the waste streams of interest are marked as substrate 1-5 in the process scheme below (Fig. 2). Two different process configurations were mainly evaluated; either fermentation of the whole slurry or fermentation of the solid fraction only, where the liquid fraction goes directly to a treatment system of some sort. The first configuration results in one major waste stream consisting of residual material after distillation, while the second configuration gives both the waste stream from the separation step and the residual material after distillation. The fermented broth can either be distilled as a whole or separated into solid and liquid fraction where the liquid fraction is distilled while the solid fraction is combusted. The different configurations give rise to five different waste streams in total, where substrates nr 3 and 4 or 3 and 5 are to be treated together.

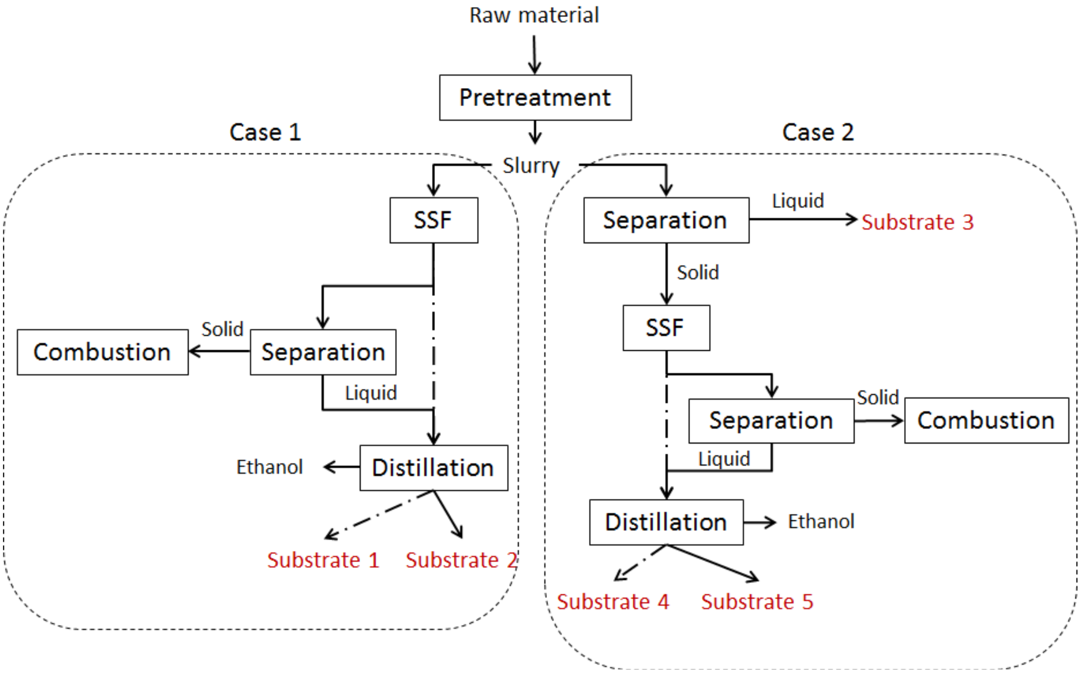

Figure 2. Process scheme of the bioethanol process

Characterization of stillage

The amount of organic matter is generally high in stillage, especially for whole stillage. The content of organics is usually measured as total organic carbon (TOC), chemical oxygen demand (COD) or biochemical oxygen demand (BOD) (Strong, et al., 2008). The COD load of the liquid phase of stillages can range from 10 to 100 g O_2/l, depending on process characteristics and treatment of stillage (Kaparaju, 2010). Because of additions of strong acids in the pretreatment of the material, the liquid fraction denoted as substrate 3 has a low pH. The pH optimum for anaerobic systems is around 7, which makes process control and monitoring of pH highly important when using different wastewaters from ethanol production as substrate.

Stillage is generally very rich in color, which mainly comes from phenolics, melanoidins from Maillard reaction, caramels from overheated sugars and furfurals from acid hydrolysis (Pant, 2007). Phenolic compounds generally form a small portion of the total COD of the stillage, but can be inhibitory to biological treatment systems as well as toxic to organisms in low concentrations (Strong, et al., 2008). Studies have shown that phenols and their intermediates are used as sole substrate at low concentration but induce inhibition at high concentrations in anaerobic treatment. Concentrations of phenols in stillage have been analyzed by recognizing specific substances with GC or HPLC (Kaparaju, 2010; Dienes, 2009) as well as total phenols by the Folin Ciocalteau method (Béltran, 2004).

Nutrient concentrations are highly dependent on the type of raw material used in the process; the concentration of nitrogen, phosphorous, sulfate and potassium are commonly analysed (Wilkie, et al., 2000). Methanogenic bacteria are quite sensitive in general, mainly because of their slow growth, and are generally said to require a COD: N: P ratio of 250:5:1. Recent studies showed that filtrated stillage from wheat straw had a ratio of 250:1.1:0.4 (Dienes, 2009). As a comparison, in the pulp and paper industry pulping effluents are generally nutrient deficient and P and N are added to receive a COD:N:P ratio of 350:5:1 (Jahren, et al., 1999).

Wilkie et al. (2000) summarized stillage characteristics for cellulosic feedstocks from literature values and found a large variation in data from different sources. The BOD and COD values displayed standard deviations that were more than 50% of the average value while the nitrogen concentration was 2.8 g/l in average with a standard deviation of as much as 4.6 g/l.

Kaparaju et al. (2010) studied the production of biogas from wheat straw stillage in an UASB reactor. The stillage was produced in a laboratory setup of bioethanol production with hydrothermal pretreatment, enzymatic hydrolysis, fermentation with baker´s yeast and vacuum distillation. The stillage was the effluent from the distillery and therefore had a quite high TS and VS content. The stillage was characterized as shown in table 1. The concentrations of volatile fatty acids (VFA) and NH_4^+-N were well below 1 and 2 g/l respectively, values that have been reported to cause inhibition. The COD values in the study were within the range reported in other studies made on similar stillages. Furfurals, HMF, phenols and lignin were all present in undetectable or very low amounts, and should therefore not cause inhibition on the microorganisms. The main phenolic compounds and its precursors present in the stillage were acetovanillone, ferulic acid and syringic acid.

(Kaparaju, 2009) have also characterized whole stillage from a Swedish bioethanol plant based on wheat straw and grain, see Table 1. Since the substrate originally contained more protein, the stillage also had a higher ammonia and protein content than the whole stillage based on wheat straw only. Hydrolysate from hydrothermal pretreatment of wheat straw was characterized in the same study, which can be found in Table 1. Furfurals, HMF and phenols could be found in higher concentrations in the hydrolysate and the xylose content was high while the glucose content was low.

Dienes (2009) characterized filtered stillage derived from spruce, see table 1. The color of the filtered stillage was brown and the result show higher concentrations of HMF than for the other stillage’s. The distribution between the measured pentoses and hexoses was also different compared to the other stillage’s, with more five than six carbon sugars.

Table 1. Characterization of wastewaters from bioethanol production

	Whole stillage (Kaparaju, 2010)	Whole stillage (Kaparaju, 2009)	Hydrolysate (Kaparaju, 2009)	Filtered stillage (Dienes, 2009)
pH	3.6±0.1	4.0±0.1	4.9±0.1	4.61
TS (%)	12.0±0.03	19.6±0.18	4.4±0.01	1.38
VS (%)	10.2±0.03	17.8±0.18	3.3±0.01	0.90
Ash content (%)	1.8±0.03	1.8±0.18	1.1±0.01	0.48
TSS (g/l)	1.4±0.2	-	-	-
VSS (mg/l)	69.1±2.5	-	-	-
TCOD (g/l)	150±3.59	170.7±0.38	37.9±1.31	28.5
SCOD (g/l)	61±4.36	85.05±0.13	32.05±2.22	-
VFA (g/l)	0.18±0.02	0.37±0.02	0.7±0.14	-
Ethanol (g/l)	2.3±0.13	0.8±0.10	N.D.	1.3
TKN (g/l)	1.4±0.02	6.2±0.20	0.2±0.01	0.12
NH_4^+-N (g/l)	0.16±0.01	1.3±0.02	0.03±0.01	3.4e-4
Proteins (g/l)	7.7±0.09	38.8±1.15	1.1±0.03	-
Lipids (%)	0.99	0.93±0.12	0.24±0.01	-
Carbohydrates (g/l)	84.5	129.3	30.5	-
Furfurals (g/l)	N.D.	N.D.	0.25±0.04	0
HMF (g/l)	N.D.	0.02±0.01	0.14±0.02	0.10
Phenols (g/l)	0.061	0.08±0.02	0.14±0.12	-
Lignin (g/l)	75.6	-	N.A.	-
Arabinose (g/l)	0.00	6.9±0.04	1.3±005	0.64
Xylose (g/l)	6.9	21.3±0.12	11.3±0.15	2.6
Glucose (g/l)	10.3	29.9±0.21	2.9±0.21	0.07

Combinatory treatment systems

It is evident that stillage in general has a very high organic content which makes anaerobic treatment interesting for energy recovery, and that the effluent has a still too high organic content to be discharged directly after the anaerobic digestion. The effluent is also generally still rich in color that needs to be removed before water discharge or recovery (Ryan, et al., 2009). Aerobic digestion as initial treatment step is insufficient in treating stillage's, mainly because of the high energy consumption needed for aeration and the large production of sludge. When treating molasses stillage by aerobic digestion as an initial step, 50% of the COD in the stillage was converted to sludge (Satyawali, et al., 2008).

As additional treatments of stillage after anaerobic and aerobic digestion, several biological, chemical, thermal and filter systems have been evaluated (Satyawali, et al., 2008). Biological treatment options are generally much cheaper than chemical alternatives both regarding investment and operational costs, why these are more popular (Ryan, et al., 2009). The biological systems ability to adapt to different substrates and conditions is also highly beneficial.

A combination of anaerobic and aerobic systems is popular for treatment of molasses stillage (Satyawali, et al., 2008), in which case the combinatory system generally is unable to decolorize the wastewater. Tertiary treatment is therefore needed to fit quality requirements of the treated water. Travieso et al. (2006) developed a treatment system for molasses stillage, consisting of an anaerobic fixed bed reactor (AFBR) followed by an aerobic trickling filter reactor (TFR) and finally a stabilization pond. The distillery waste had an initial

COD of 77 g/l which was firstly reduced to 16 g/l in the AFBR and then down to 5 g/l in the TFR. The stabilization pond gave a COD reduction of 50% when the inlet COD was over 5 g/l and the retention time was 30 days, while only a retention time of 15 days was required to remove 50% of the COD when the inlet had a COD of 3 g/l.

The activated sludge process is the most common aerobic treatment option after anaerobic digestion, when treating molasses based distillery waste (Satyawali, et al., 2008).

Melanoidins are not affected by conventional biological treatment and multistage biological treatment might also intensify color because of re-polymerization of colored compounds (Peña, et al., 2003). When biological treatment is insufficient in removing coloring and associated COD, physico-chemical tertiary treatment options are for example membrane filtration, electrocoagulation and chemical flocculation. These tertiary methods have been stated as the most cost-effective ones (Ryan, et al., 2009). Ozonation is another alternative, either as a finishing step or as a treatment step or before biological treatment. It is often ruled out as a treatment option because of high investment costs, but has been proven effective in degrading phenolics (Amat, et al., 2003) and melanoidins (Peña, et al., 2003), which contribute to COD and color and might act inhibitory on biological degradation.

To enable water recovery in the process, further treatment is generally needed. Reverse osmosis in combination with nanofiltration or electrocoagulation as tertiary treatment for water recovery has been calculated to require a COD reduction of approximately 69% in the preceding anaerobic step (Ryan, et al., 2009). Ryan et al. (2009) stated that it was realistic to power aerobic COD reduction, color removal and meaningful water reuse from electricity generated from biogas production only.

Experimental work

The experimental work included lab-scale pre-treatment (with acetic acid) and processing of wheat straw according to the scheme in Figure 2 to establish the Substrates 1-5. Characterization of substrates concerning organic content, eventual inhibiting substances and content of nutrients was done by HPLC analysis, spectro-photometrical analyses and other standardized methods. The generated waste streams were further evaluated for anaerobic treatment, biogas potential, post-treatment and final handling.

Characterization of stillage

Previous to the initial anaerobic tests, the following parameters were analyzed on substrate 1-5 (see Fig. 1): TS, VS, N-tot, P-tot, NH_4-N (on some), TOC, COD, pH, VFA (acetic+ propionic acid) and alkalinity. Additionally, the usual bioethanol production parameters were provided by HPLC measurement: cellobiose, glucose, XyGaMa, arabinose, lactic acid, glycerol, formic acid, acetic acid, ethanol, HMF (hydroxymethyl furfural) and furfural. The results are found in Table 2 and Table 3 as well as in Figure 3. The presence of other phenolic compounds is left unexplored for now, since they generally seem to be of minor importance for treatment of wheat straw stillage.

Table 2. Content of Substrates 1-5 and C:N:P –ratios (on weight basis).

Substrate	pH	COD (mg/l)	TOC (mg/l)	NH_4-N (mg/l)	N_{tot} (mg/l)	P_{tot} (mg/l)	TS (%)	VS (% av TS)
1	5.04	166400	50200	133.4	560	249.2	12.2	89%
2	5.02	63500	21800	96.2	288	162.4	6.1	70%
3	3.47	79600	29000	25.7	195.6	43.6	6.24	97%
4	4.89	101800	33000	48	700	201.6	6.89	87%
5	4.96	30400	10100	11.5	161.2	103.6	2.62	71%

Substrate	TOC	N	P	TOC/N
1	250	2.8	1.2	90
2	250	3.3	1.9	76
3	250	1.7	0.4	148
4	250	5.3	1.5	47
5	250	4.0	2.6	63

Table 3. Content of raw material (wheat straw) and pre-treated (acetic acid) slurry. For the Case 1 two batches were produced.

	Raw material (Wheat straw)		Wheat slurry		Wheat SSF case 1 batch 1		Wheat SSF case 1 batch 2		Wheat SSF case 2	
	AVERAGE	STD DEV	AVERAGE	STD DEV	AVERAGE	STD DEV	AVERAGE	STD DEV	AVERAGE	STD DEV
Glucan	35,29%	0,52%	55,14%	0,33%	38,33%	1,75%	29,71%	1,75%	17,79%	0,75%
Xylan	21,34%	0,28%	8,25%	0,11%	4,53%	0,03%	3,85%	0,03%	3,07%	0,08%
Galactan	0,80%	0,00%	0,00%	0,00%	0,00%	0,00%	0,00%	0,01%	0,00%	0,01%
Arabinan	2,66%	0,04%	0,10%	0,00%	0,04%	0,00%	0,06%	0,01%	0,05%	0,02%
Mannan	0,11%	0,06%	0,09%	0,07%	0,80%	0,00%	0,87%	0,02%	1,33%	0,07%
ASL	1,60%	0,01%	1,68%	0,07%	1,41%	0,02%	1,38%	0,01%	1,60%	0,02%
AIL	23,11%	0,36%	19,95%	0,10%	38,84%	0,95%	43,82%	0,78%	52,19%	0,74%
Lignin Ash	4,02%	0,10%	3,58%	0,43%	7,25%	0,27%	9,09%	0,46%	11,15%	0,80%
Total determined compounds (corrected)	88,93%		88,67%		91,09%		88,69%		87,05%	

The results show that the waste streams contain a lot of water (88-97%). The organic content in terms of VS is varying from 70-97%. The nitrogen content in some streams (Substrate 1-3) and the phosphorus content in one (Substrate 3) are rather low and might lead to lack of nutrients in the anaerobic digestion process. The optimal nutrient relation for the anaerobic digestion process is 250:5:1 (COD:N:P) (Henze & Harremoes, 1983).

The content of sulfate, ammonia and magnesium would also be interesting to analyze since they, if present at too large concentrations (400, 60, 300 mg/l), might affect the piping network if the waste streams are transported to a municipal wastewater treatment facility (Publikation P95, Svenskt Vatten). However this study did not evaluate effects on pipe network, but focused on possibilities for treatment.

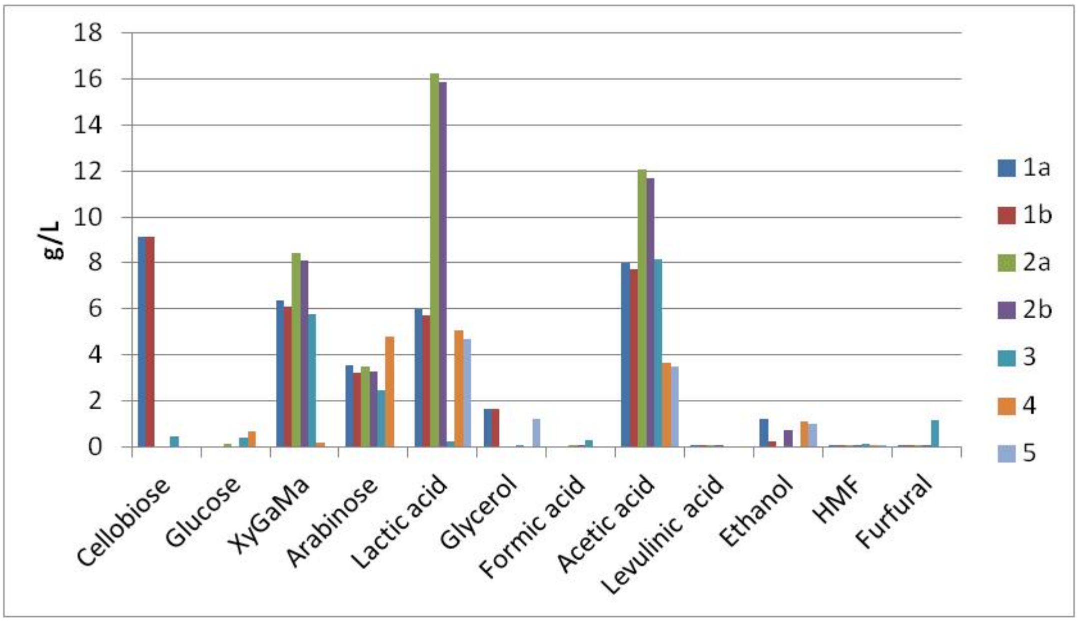

Figure 3. Content of the different streams 1-5 (see Fig. 1). Two different batches were produced for Case 1 generating Substrate 1a and b and 2a and b.

Anaerobic digestion tests

Methane potential tests were prepared with the aim of determining the methane potential of the waste streams present and evaluating possible inhibitory problems and/or nutrient deficiency that could disturb biogas production. The substrates were tested individually and substrate 3 was also combined with 4 and 5 to investigate any potential co-digestion effects. The results show significant methane potentials in most of the waste streams, but also that there are some differences, see Figure 4 and 5. The biogas production rate is higher for some of the substrates. For Substrates 1, 2 and 5 around 80% of the methane potential is already obtained after 10 days, whereas for Substrates 3 and 5 only 66% and 55% of the potential is reached within that period.

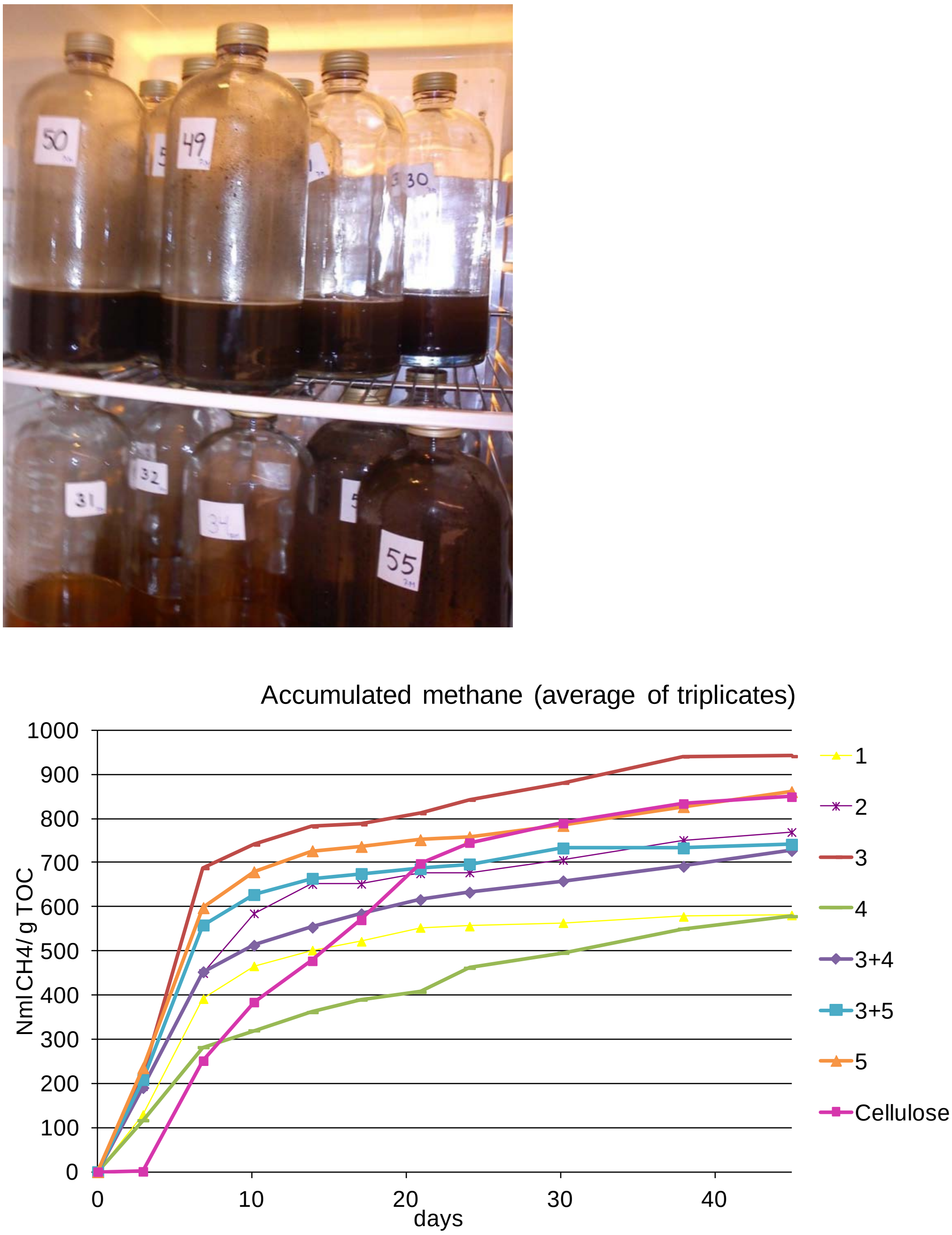

Figure 4a and b. a) Methane potential tests and b) Results (produced accumulated methane per added amount of organic matter (TOC) during 45 days of anaerobic digestion of the different waste streams (1-5) and combinations of waste streams (3+4 and 3+5).

The combinations of waste streams 3+4 and 3+5 gave reasonable methane production, but no additional co-digestion effect was seen. Digestion at different temperatures (Figure 6) resulted in about the same methane potentials for both substrates tested (1 and 2), with slightly higher potential for substrate 2 at thermophilic temperature. This indicates that both operating temperatures could be used for these substrates. However the choice will be dependent on the bioethanol process temperature and the possibility to recover the energy by heat exchangers when substrate temperatures are lowered to desired digestion temperature. Co-digestion of Substrate 3 together with food waste (source separated and pre-treated food waste originating from households) was assessed and resulted in a methane potential that corresponded to the expected value from calculations (based on single-substrate digestion of food waste and Substrate 3 respectively), Figure 7. This induces that the ethanol waste streams could be used for biogas production together with food waste at existing plants with unused capacity, which is the case at some biogas plants in e.g. Sweden. The co-digestion could have positive effects on the nutrient balance, since food waste usually is a bit low in carbon content (Davidsson et al., 2007) , but high in N and P and the ethanol waste streams showed out to be low in N and P.

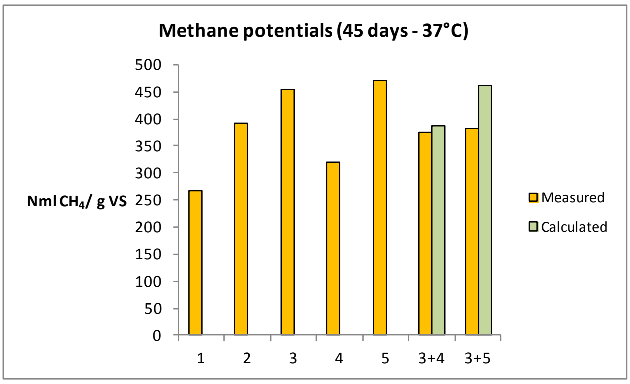

Figure 5. Methane potential for substrates 1-5 and combinations (3+4 and 3+5), 50:50 on VS-basis, in mesophilic digestion for 45 days.

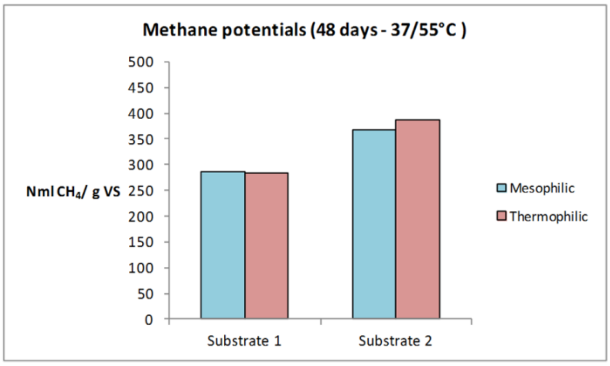

Figure 6. Methane potential for substrates 1 and 2 in both mesophilic and thermophilic digestion for 48 days.

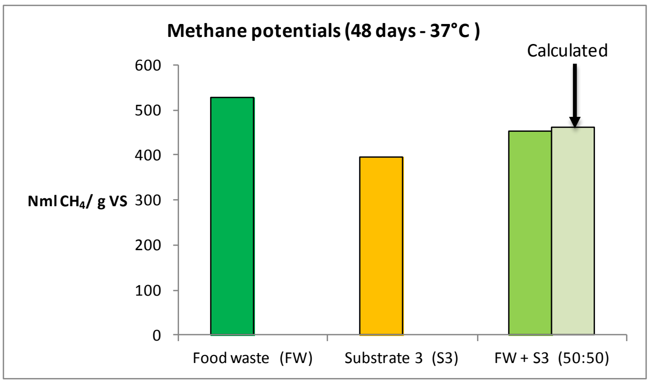

Figure 7. Methane potential for separate digestion and co-digestion (50:50 on VS-basis) of substrate 3 and food waste at mesophilic temperature for 48 days.

Energy potential

The energy potential from biogas production of the waste streams in the two cases (with two alternative process lay-outs within each case) shown in Figure 2, were compared by combining data on mass flows (using a potential plant producing bioethanol and biogas from wheat straw) and the outcomes from the experimental biogas tests. It should be noted that the final methane potential was used for the calculations, which will probably overestimate the realizable energy potential in full-scale operation. The results, shown in Figure 8 (Case 1) and Figure 9 (Case 2), show that a substantial energy potential will not be used in the alternative where solids are separated after SSF. However, if this solids fraction can be used for production of heat by combustion some of the energy potential may be recovered. Comparing the two cases (1: fermentation of the whole slurry and 2: fermentation of solid fraction only) shows that the biogas potential from Case 1 and Case 2 is equal (~ 22 000 kWh/hr) if no separation is done after SSF (Substrate 1 gives the same as 3+4). Furthermore, if the process configuration includes a separation of solids after SSF a slightly higher biogas potential is expected from the Case 2 (Substrate 3+5 ➔ 15000 kWh/hr) than for Case 1 (substrate hr2 ➔ 11 000 kWh/).

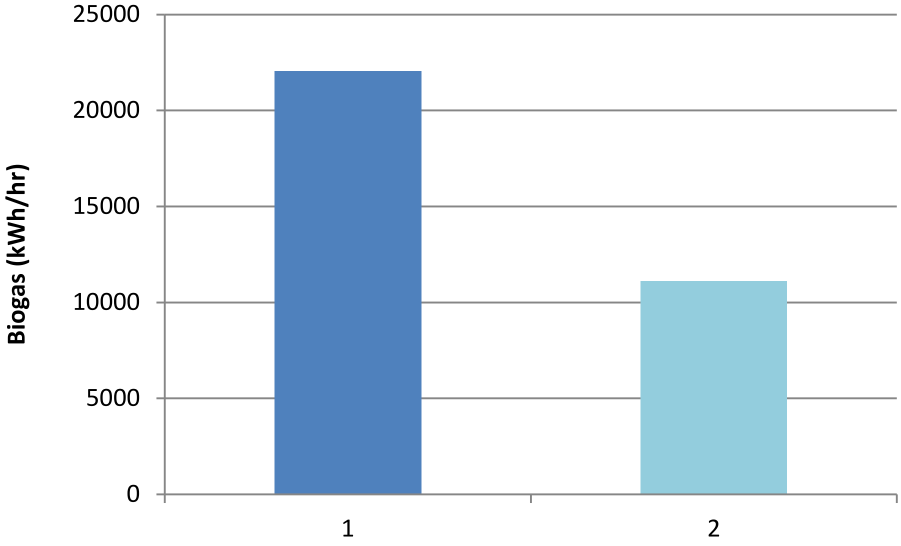

Figure 8. Energy potential for Case 1: Biogas from Substrate 1 (without solids separation after SSF) or from Substrate 2 (solids separation after SSF)

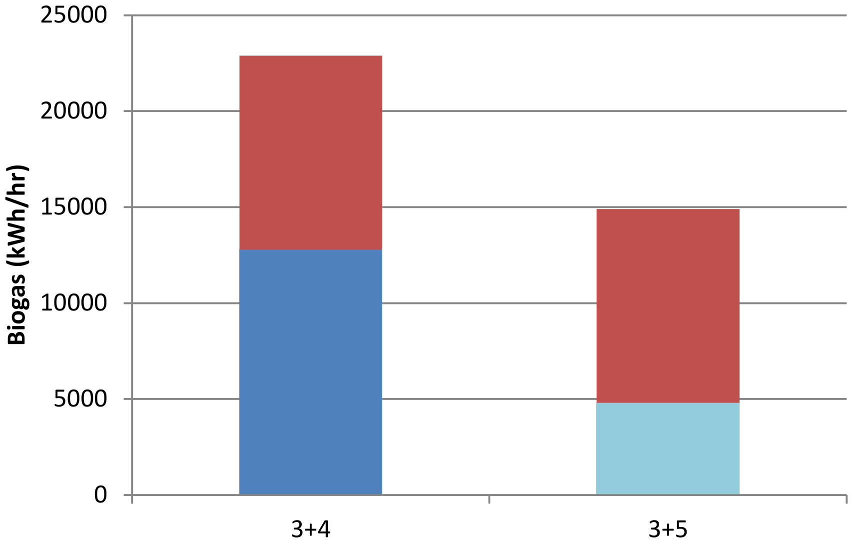

Figure 9. Energy potential for Case 2: Biogas from Substrate 3 together with either Substrate 4 (without solids separation after SSF) or Substrate 5 (solids separation after SSF).

Post-treatment

Evaluation of the possibilities for using/handling the residues after anaerobic digestion has been done. The following possibilities are identified as the most sustainable alternatives:

- Recirculation in plant which means the need for fresh water in the production process is reduced. To obtain this an internal treatment is needed to quite a high extent. This treatment could be a combination of biological, chemical and mechanical treatment.
- Directly to recipient. It is not clear what outlet demand that is required, but it would mean that an extensive treatment step at the plant is needed. This treatment could be a combination of biological, chemical and mechanical treatment.
- To further treatment at a municipal wastewater treatment plant. This alternative requires that the wastewater is accepted at the WWTP. Especially WWTP:s including a biological treatment step are restrictive in accepting industrial wastewater since they could possibly be toxic and affect the biological processes. The wastewater should therefore be tested for toxicity. One such method is the test of nitrification inhibition.

In spite of the alternative for handling the residues, the need for aerobic biological treatment is seen, since biological methods are economic compared to other methods and usually requires less chemicals and energy input compared to other methods. However, biological methods are sensitive to toxicants and may therefore be inhibited by the content of the residues. Toxicity of the waste streams from bioethanol production were therefore tested by a screening method for nitrification inhibition (Swedish EPA, 1995; Jönsson, 2001). This method determines the short term inhibitory effect of test substances on nitryfing bacteria in activated sludge. In general, nitryfing bacteria are more vulnerable to toxic substances than heterotrophic bacteria (Blum and Speece, 1991). The nitrification method is an appropriate method to evaluate if a waste stream from an industry is likely to be permitted at a municipal wastewater treatment plant. However this method cannot alone be used to conclude about the total toxicity of the waste streams. In addition, other toxicity methods are needed to evaluate the effect on a recipient if the waste stream is supposed to be directly emitted to natural recipients. The method for screening of inhibition on nitrification is described in short below.

Nitrification inhibition screening method

The basic principle of the screening method is that nitryfing activated sludge is mixed with a nutrient solution and the suspension is shaken together with, in this case, the waste streams from ethanol production from wheat straw (Jönsson, 2001). All five Substances (1-5) were tested before digestion and Substances 1 and 2 were also tested after digestion. Different concentrations of the substances were tested in duplicate. The samples were shaken/aerated for 120 min and then the reaction was stopped by filtering and cooling the samples. The degree of nitrification inhibition was determined by comparing the total oxidized nitrogen produced in the test tubes containing the tested substances with control tubes containing tap water. For samples without inhibiting compounds the inhibition will vary around zero. This reflects the uncertainties of the NO_x analysis and in the general performance of the test.

Toxicity results

The inhibition results for the different substances tested in different concentrations are summarized in Figure 10.

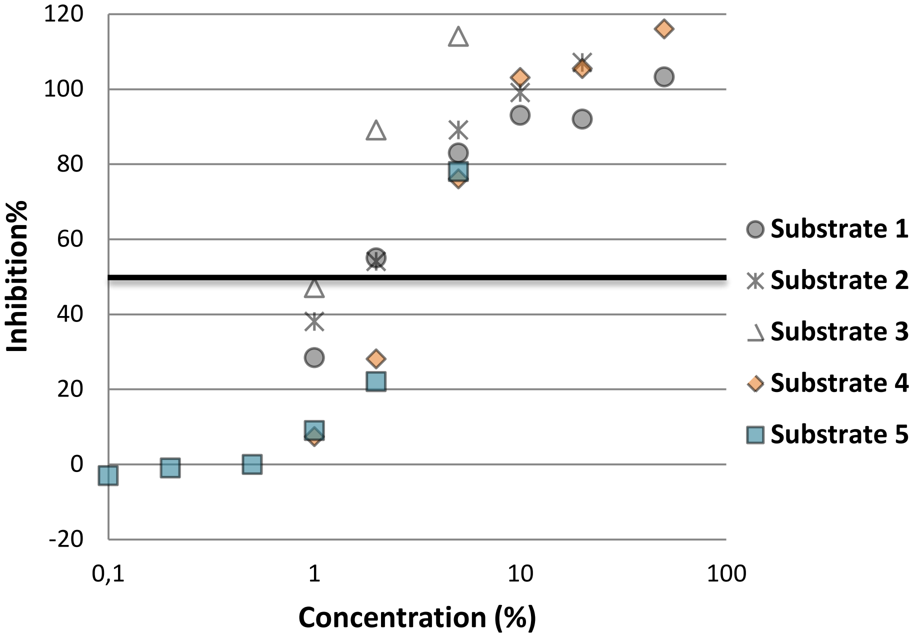

Figure 10. Inhibition on nitrifying bacteria at different concentrations of Substances 1-5. The level of inhibition corresponding to the EC50 level is indicated with a black line.

It is seen that the EC50 value (the percentage of the test substance that results in 50% inhibition of the nitrification) is varying from 1% up to 4% for the tested ethanol waste streams (untreated). Most toxic is the Substrate 3 (hydrolysate) and least toxic are the Substrates 4 and 5. However none of these waste streams are expected to be accepted at Swedish or Danish wastewater treatment plants without any pre-treatment. A commonly accepted guideline for these kinds of toxicity results is that the inhibition should be less than 20% at a concentration of 20% of the substance to be admitted at the inlet of a municipal wastewater treatment plant with biological treatment (Jönsson, 2001). None of the substrates could fulfill these recommendations. It is sometimes accepted that the wastewater is resulting in 20-50% inhibition at 20% concentration if the reason for the inhibition is known and can be regarded as harmless. However all of the Substrates 1-5 resulted in >50% inhibition at 20% concentration. It should be noted that values showing > 100% inhibition are not normal, but were seen in this tests. The reason for this is probably that the color in the samples (the substrates) were interfering with the spectrophotometric measurements of nitrite and nitrate.

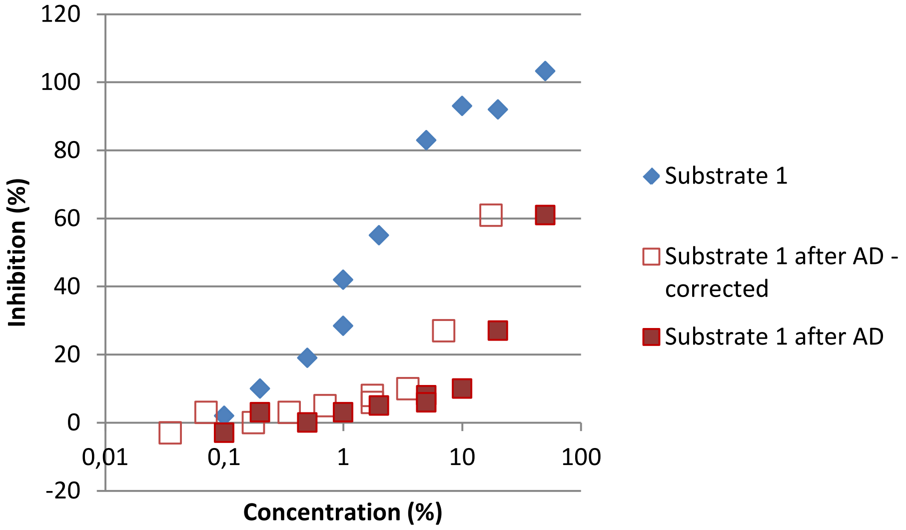

Figure 11. Inhibition at different concentrations of Substrate 1 before and after anaerobic digestion. Both original inhibition values and values corrected for (effect of dilution with inoculum has been withdrawn by correcting the substrate concentration).

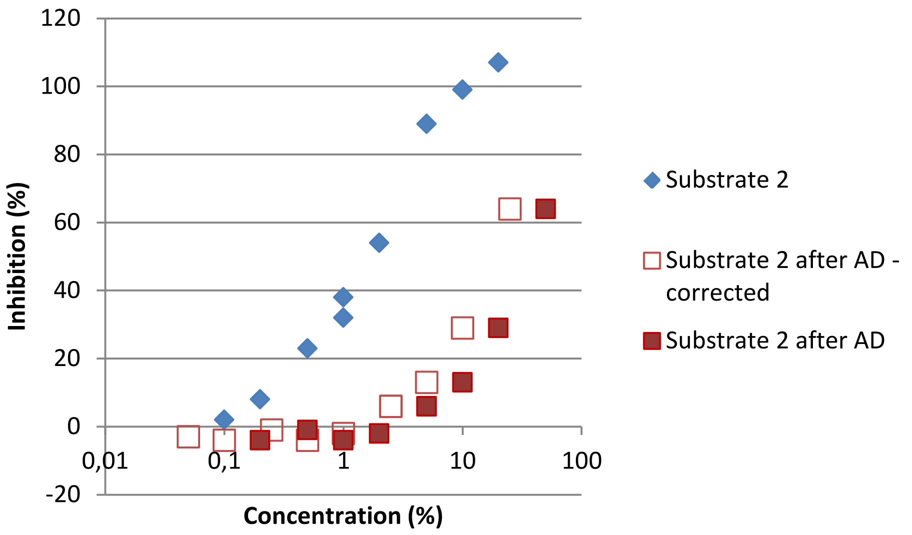

Figure 12 Inhibition at different concentrations of Substrate 2 before and after anaerobic digestion. Both original inhibition values and values corrected for (effect of dilution with inoculum has been withdrawn by correcting the substrate concentration).

It is seen in both Figure 11 and 12 that the anaerobic digestion step reduces inhibition substantially. This indicates that the anaerobic digestion process is degrading one or several organic compounds which are inhibitory for nitrifying bacteria. If the results after AD is compared to the commonly used recommendations for admitting industrial wastewater at municipal wastewater treatment plants, mentioned before (Jönsson, 2001) it can be concluded that the inhibition at 20% substrate concentration is slightly over the recommendation of < 20% inhibition. This means that there is a possibility of allowing the wastewater to a municipal plant after digestion, but it would probably imply more investigations and analyses. Is should be noted that the Substrate 1 and 2 after AD contained not only Substrate 2, but also some inoculating digested sludge. Part of the inoculum was previously digested Substrate 1 and 2 respectively, but some inoculum (used in the beginning of the biogas testings) origined from an external biogas plant, digesting other types of substrates and could therefore be considered to dilute the actual substrate and thereby decreasing the inhibition. On VS-basis this external inoculum made up about 7% of the substrate after digestion, but on wet weight basis it made up about 50%. However, the difference in inhibition between the digested and non-digested substrates are much bigger than what could be explained by dilution with inoculum. Even if the original inoculum is considered to dilute the substrate and this effect of dilution has been withdrawn by correcting the substrate concentration (see corrected data in Fig. 11 and Fig. 12) there is still much lower inhibition from the substrate after anaerobic digestion.

Conclusions

This study included literature review and experimental work to evaluate possibilities for combining bio-ethanol production with anaerobic and aerobic treatment. The main findings are summarized in the following conclusions:

- Existing experiences showed that the content of the waste streams are important for the development of a process including biogas production and further wastewater treatment. Especially organic content (for estimation of biogas production), nutrient content (microbiological needs of anaerobic and aerobic processes) and possible toxicant (that could affect biological processes) should be characterized.
- Nitrogen and in some case also phosphorus content is rather low in some substrates generated in the two alternative process configurations studied in this project. There is subsequently a risk of lack of N and P in anaerobic digestion. This lack could be recovered by co-digestion with e.g. food waste, a combination which was tested experimentally with good results in the study.
- Significant amounts of biogas production from all bioethanol waste streams are possible. However the waste stream from the different ethanol process configurations results in different biogas production rates and different final biogas potentials.
- Both mesophilic and thermophilic digestion is possible. Almost no difference in biogas potential was seen. However thermophilic temperature could be favorable since the bioethanol process involves high temperatures already.
- The overall energy potential from biogas production considering the mass flows expected from different process configurations (Case 1 or Case 2 and the choice of solids separation or not before SSF) is about the same for the two Cases evaluated. However, if solids are separated and burned after SSF the biogas potential is reduced compared to distillation of the whole fraction.
- Bioethanol residues are inhibiting nitrification – but less after anaerobic digestion. Therefore it is suggested that the anaerobic step should precede an eventual aerobic step. This brings about another benefit as well; the organic content can primarily be used for biogas production – instead of demanding energy (oxygen) for degradation aerobically.

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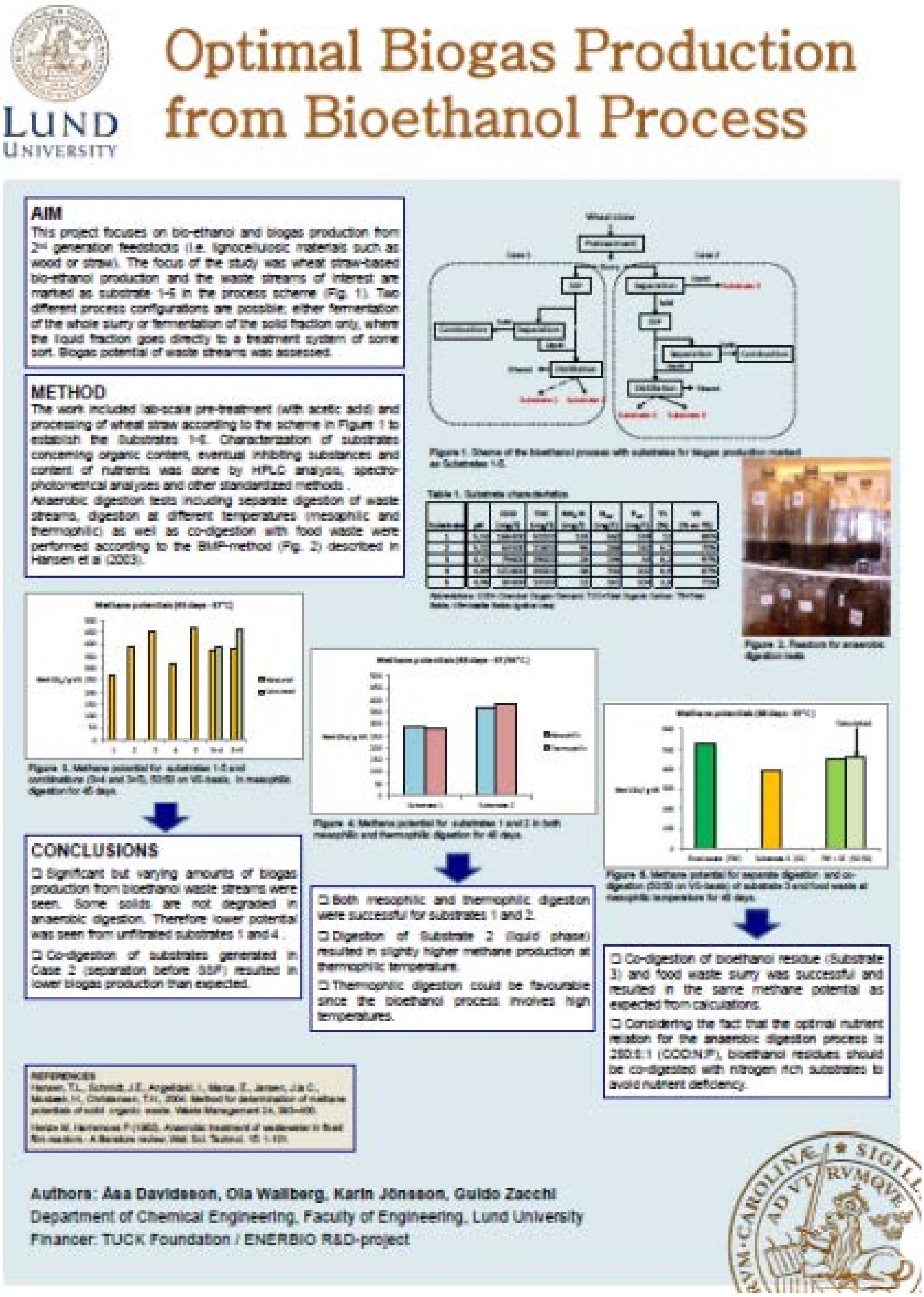
Publications so far within the project

Mahan Amani (2013). Toxicity screening of wastewaters from bioethanol production. Project course report (VVA920).

Åsa Davidsson, Ola Wallberg, Karin Jönsson, Guido Zacchi (2012). Optimal biogas Production from Bioethanol Process. Poster presented at the 8th International Conference on Renewable Resources & Biorefineries , 4 – 6 June, 2012 – Toulouse, France. *See attachment.*

Åsa Davidsson, Ola Wallberg, Karin Jönsson, Guido Zacchi. (2012) . COMBINED BIOGAS AND BIOETHANOL PRODUCTION FOR OPTIMAL ENERGY UTILIZATION. Paper presented at the ENERBIO seminar 21 June 2012.

Attachment 1: Poster presented at the 8th International Conference on Renewable Resources & Biorefineries , 4 – 6 June, 2012 – Toulouse, France.



LUND UNIVERSITY

Optimal Biogas Production from Bioethanol Process

AIM

This project focuses on bio-ethanol and biogas production from 2nd generation feedstocks (i.e. lignocellulosic materials such as wood or straw). The focus of the study was wheat straw-based bio-ethanol production and the waste streams of interest are marked as substrate 1-5 in the process scheme (Fig. 1). Two different process configurations are possible: either fermentation of the whole slurry or fermentation of the solid fraction only, where the liquid fraction goes directly to a treatment system of some sort. Biogas potential of waste streams was assessed.

METHOD

The work included lab-scale pre-treatment (with acetic acid) and processing of wheat straw according to the scheme in Figure 1 to establish the Substrates 1-5. Characterization of substrates concerning organic content, eventual inhibiting substances and content of nutrients was done by HPLC analysis, spectro-photometrical analyses and other standardized methods .

Anaerobic digestion tests including separate digestion of waste streams, digestion at different temperatures (mesophilic and thermophilic) as well as co-digestion with food waste were performed according to the BMP-method (Fig. 2) described in Hansen et al (2003).

Figure 1. Scheme of the bioethanol process with substrates for biogas production marked as Substrates 1-5.

Table 1. Substrate characteristics

Substrate	pH	COD (mg/l)	TOC (mg/l)	NH_4-N (mg/l)	P_{tot} (mg/l)	K_{tot} (mg/l)	TS (%)	VS (% av TS)
1	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
2	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
3	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
4	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
5	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

Abbreviations: COD=Chemical Oxygen Demand, TOC=Total Organic Carbon, TS=Total Solids, VS=Volatile Solids (ignition loss)

Figure 2. Reactors for anaerobic digestion tests

Figure 3. Methane potential for substrates 1-5 and combinations (3+4 and 3+5), 50/50 on VS-basis, in mesophilic digestion for 40 days.

Figure 4. Methane potential for substrates 1 and 2 in both mesophilic and thermophilic digestion for 40 days.

Figure 5. Methane potential for separate digestion and co-digestion (50/50 on VS-basis) of substrate 3 and food waste at mesophilic temperature for 40 days.

CONCLUSIONS

☐ Significant but varying amounts of biogas production from bioethanol waste streams were seen. Some solids are not degraded in anaerobic digestion. Therefore lower potential was seen from unfiltrated substrates 1 and 4 .

☐ Co-digestion of substrates generated in Case 2 (separation before SSF) resulted in lower biogas production than expected.

☐ Both mesophilic and thermophilic digestion were successful for substrates 1 and 2.

☐ Digestion of Substrate 2 (liquid phase) resulted in slightly higher methane production at thermophilic temperature.

☐ Thermophilic digestion could be favourable since the bioethanol process involves high temperatures.

☐ Co-digestion of bioethanol residue (Substrate 3) and food waste slurry was successful and resulted in the same methane potential as expected from calculations.

☐ Considering the fact that the optimal nutrient relation for the anaerobic digestion process is 250:5:1 (COD:N:P), bioethanol residues should be co-digested with nitrogen rich substrates to avoid nutrient deficiency.

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