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ABSTRACT

To meet the increasing need for bioenergy three lignocellulosic materials: raw hay, pretreated wheat straw and pretreated household waste were considered for the production of bioethanol and biogas. Several mixtures of household waste supplemented with different fractions of wheat straw and hay in fermentation process with *Saccharomyces cerevisiae* were investigated. Wheat straw and household wastes were pretreated using IBUS technology, patented by Dong Energy, which includes milling, stem explosion treatment and enzymatic hydrolysis. Methane production was investigated using stillages, the effluents from bioethanol fermentation experiment. Previous trial of biogas production from above mentioned household wastes was enclosed.

INTRODUCTION

At present the largest part of energy market take up bioethanol and biomethane production. First is produced in fermentation process and other in anaerobic digestion process, respectively. As fermentation of sugars included in starch is very good known, lignocellulosic materials are big challenge. The reason is because of very tough chemical structure of cellulose, hemicelluloses and lignin. These compounds are very strong connected, so different kinds of technologies were developed to split it. Millions tones of different materials, including plants, food and agricultural residuals, waste water and many others are promising source for biofuels production (Goettemoller J., Goettemoller A., 2007).

There are recognized many separation techniques, but any of them is sufficient to isolate all cellulose from this strongly connected structure. The new IBUS technology solves this problem much more than the others. In general these are few steps physical and thermo-chemical conversion of biomass into simple chemical compounds, which are ready to fermentation or anaerobic digestion processes (Ibicon, hydrothermal treatment, Jan.2010).

AIM OF PROJECT

The focus was on household wastes efficiency as a substrate for biofuels production, both bioethanol and biogas, and relations between household wastes and two other materials.

MATERIALS AND METHODS

Materials

Lignocellulosic materials are now in focus around the world. It is because is promising material for biofuels industry. The most significant material in project was household wastes, but also wheat straw and hay are good to focus on them.

Mentioned HHW it's a mixture of wastes collected from residual sector. It includes papers, metals, plastics elements and non-degradable hygienic wastes. The material was delivered by Dong Energy after pre-treatment step with IBUS Technology.

Wheat Straw is lignocellulosic material comes from middle Denmark. It has been harvested from fields cultivated for industrial needs. This material consists approximately 38% of cellulose, 20% of lignin, 20% of xylose and a little of arabinose and ash. The total dry matter reaches 24,3%. Wheat

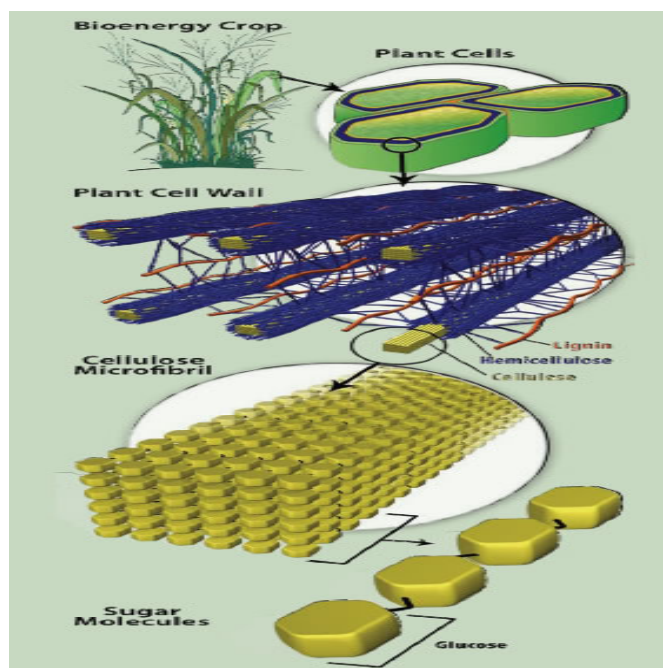
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straw has been delivered by Dong Energy after pre-treatment step.

The hay is also lignocellulosic material comes from middle Denmark. It contains more than 88% of dry matter. Harvested 2-3 months before experiment was the freshest and non-treatment material in project.



(C&EN, Chemical and Engineering News, Jan.2010)

Thermophilically digested animal manure from a biogas plant (Ribe, Denmark) was applied as inoculums. The total dry matter content was cr. 4,25%. Animal manure is used there as raw material for biogas production at 53°C.

Enzymes and yeasts were used for hydrolysis and fermentation steps. Traditional baker's yeast *Saccharomyces cerevisiae* was applied in fermentation processes to convert sugars into alcohol. To decrease activation energy, in consequence make it more economical, Cellulase and β -glucosidase were used. Both kinds of enzymes were delivered by Novozymes.

Pre-treatment

Pretreatment of substrate is a very significant step to destroy lignocellulosic structure and make cellulose more available for microorganisms. This preprocessing is carried out in few steps, first and the easiest one is milling and grinding. Material is cut into small pieces, because it enables easier and faster destroys chemical structure in further steps. Milled material is transported continuously to next step. At his stage water steam treatment is applied. In special reactor substrate is mixed with hot water (approx. 180°C) for short period of time. That temperature causes formation of water steam, that this step is called steam water explosion. The pretreated material is transported continuously into last reactor, where is hydrolyzed. The enzymatic hydrolysis is carried out with enzymes decreasing activation energy. Addition of enzymes makes process faster and less demanding. This technology is named IBUS Technology and it is patented by Dong Energy.

Hydrolysis

In main experiment was added third substrates-hay which haven't been pre-treatment like two others substrates. It was needed to make hydrolysis step before fermentation. The total hydrolysis time has gone for 24 hours and has place in incubator with 50 °C and 200 rpm. In experiment were used 10 BluCup flasks, 250 ml each with traditional bottles cups.

Fermentation

Separate fermentation took place in Aalborg University Esbjerg laboratory. Process was carried out in special incubator with rotation plate. During the process stable conditions with 32°C and 180 rpd were maintained. Fermentation step took

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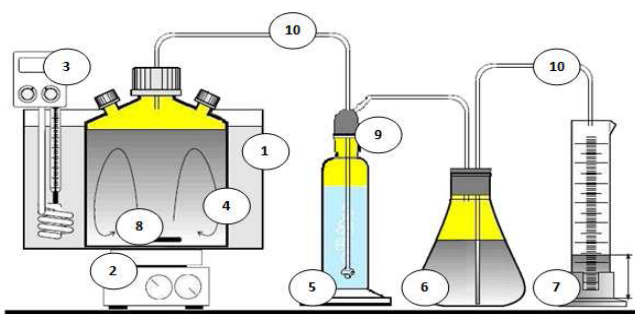
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approx. 150 hours. Substrates were split into BlueCaps with volume 250 ml, sealed with a loop trap filled with glycerol. In order to initiate alcohol production, fermentation bottles were inoculated with *Saccharomyces cerevisiae* after supply with an adequate amount of substrates.

Anaerobic Digestion

Anaerobic digestion process took place at the same laboratory. It was started in spring semester 2009, from the same substrate as fermentation in autumn 2009 -household wastes. The main difference is in pretreatment method of this material, which was milled, stem explosion treated and hydrolyzed but not continuously. IBUS Technology was used in autumn semester project only. Anaerobic digestion was carried out in the water bath with 6 flasks each, at a stable temperature 53°C for approximately 300 hours. First inoculum was divided into flasks with precisely measured weight. Flasks were filled up with warmed in incubator material from fermentation process. In experiment were used magnetic stirrers to keep mixing during all experimental time.

Standard setup to AD experiment should include the following elements presented in Picture 3.



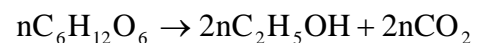
Picture 3: Schematic biogas setup:

1-water bath, 2-magneticstirrer, 3-thermostat, 4-fermentation vessel, 5-gas washing bottle, 6-displacement bottle, 7-collecting cylinder, 8-magnetic bar stirrer, 9-gas proof stoppers, 10-gas proof rubber tubes

Analysis

Analyze of Total Solid contents has been carried out on few steps of experiment. First prediction of dry matter was made for pre-treatment materials delivered from Dong Energy (household waste slurry and wheat straw slurry) before fermentation step. Second one was made for characterization of raw hay as a material for main experiment before pre-treatment and after this step. The total solid analysis has been also carried out after hydrolysis of hay for prepared this substrate on fermentation.

In order to monitor the fermentation process, gravimetric ethanol analysis was prepared. The method is based on equation of glucose fermentation process.



Where n is number of moles.

During fermentation carbon dioxide is produced and released, decreasing weight of flasks. This is base for ethanol estimation. From the equation it can be seen that from 1 mole of glucose can be obtained 2 moles of ethanol and 2 moles of carbon dioxide. The ethanol amount can be calculated from equation bellow.

$$m_{EtOH} = m_{CO_2} \times \frac{M_{EtOH}}{M_{CO_2}} = m_{CO_2} \times \frac{46,0688[g/mol]}{44,01[g/mol]} = m_{CO_2} \times 1,045$$

The relation between ethanol and carbon dioxide is:

$$\frac{m_{EtOH}}{m_{CO_2}} = 1,045 [gEtOH / gCO_2]$$

Where:

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m_{EtOH} is mass of ethanol produced [g]
 m_{CO_2} is mass of carbon dioxide produced and released [g]
 M_{EtOH} is molecular weight of ethanol [g/mol]
 M_{CO_2} is molecular weight of carom dioxide [g/mol]

RESULTS

Bioethanol formation

In order to obtain the ethanol yield, alcohol production was monitored gravimetrically. Carbon dioxide production was followed by measuring the weight loss indicating the ethanol yield.

For experiment I proportions of two substrates used in fermentation stage (wheat straw slurry – S, and household waste slurry – HHW) and obtained results from gravimetric analysis can be presented graphically as is easily seen in Figure 1.

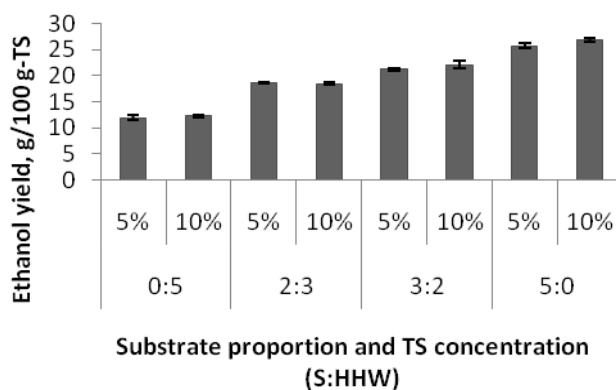


Figure 1: Ethanol production measured gravimetrically, experiment I

It can be seen that with growing value of dry matter content amount of ethanol was rising. Important thing is that bigger dry matter content is connected with bigger costs, so if this difference in amount of ethanol is not significant, then is not valuable to use more substrates.

Experiment II was conducted using three different kinds of material, wheat straw, household waste slurry and hay. Combinations of ingredients were prepared according to STAVEX software experimental plan. In this case the same gravimetric analysis has place. Composition of analyzed mixtures, substrate concentration and ethanol yield are plotted in Figure 2.

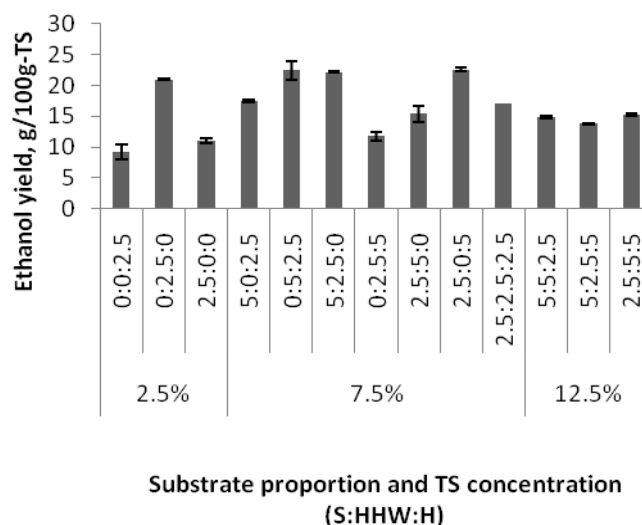


Figure 2: Ethanol production measured gravimetrically, experiment II

Very complicated results have been obtained from second trial of fermentation. There is no correlation between ethanol production and dry matter content rise in the first moment watching graph above. In more carefully looking it can be seen that very good production of ethanol has place from single materials samples. In mixtures the same materials gives less alcohol.

Biogas production

Household waste was used as a source of biomass for methane production. Thermophilically digested animal manure from a biogas plant (Ribe, Denmark) was applied as inoculum.

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Methane production was investigated using stillages as well. Effluents from bioethanol fermentation were obtained from experiment II.

Methane formation progress was followed by measuring the volume of gaseous products evolved, what was equivalent to the repressed amount of water. Final results obtained in AD test can be presented as cumulative methane productivity expressed in $\text{dm}^3 \text{CH}_4/\text{g-VS}$. This relationship is estimated by dividing the overall volume of generated methane by the volatile solid content. The dependence is defined as biogas potential. Final results obtained in AD investigation are plotted for different VS concentration in Figure3.

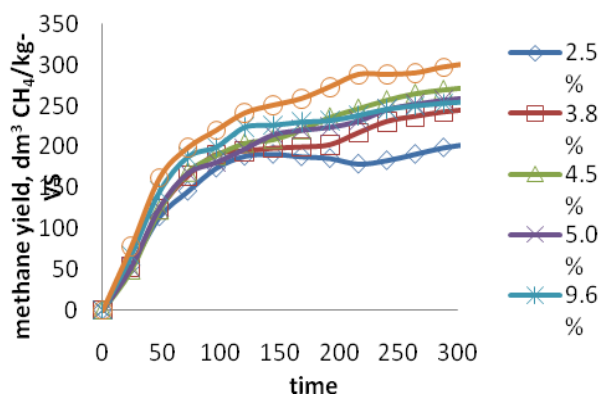


Figure 1: Methane yield curves

The final estimation of methane yields for each waste concentration used in the experiment is shown in above potential graph. There can be observed upward trend that increasing VS content of waste in trial results in increase of methane yield. The highest growth of methane potential is observed at the beginning of conducted process and decreases in the next hours. The shapes of curves, which achieved maximum value indicates that biogas production was finished

CONCLUSION

The following major conclusion can be drawn from this study:

- bioethanol can easily be produced from mixture of household waste, wheat straw and hay.
- supplementing household waste with wheat straw has a much more positive effect on the ethanol yield in fermentation experiments than with hay.
- the highest ethanol productivity can be obtained while household waste is supplemented with high fraction (67.7%) of wheat straw;
- pretreated household waste is promising source in biogas generation,
- effluents from bioethanol processes can be further used to produce methane, although not so high gas yields.

It is promising solution to increase the efficiency for material and energy through multiple biofuel production and it can presumably be more beneficial economically process for biomass utilization.

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