Final report

1.1 Project details

Project title	Industrial scale straw-to-biofuel conversion – by high mechanical pressure and hydrolysis
Project identification (program abbrev. and file)	Journalnr. 64011-0302
Name of the programme which has funded the project	EUDP-2011 II
Project managing company/institution (name and address)	C. F. Nielsen A/S, Solbjergvej 19, DK-9574 Bælum
Project partners	C. F. Nielsen A/S Aarhus University BioFuel Technology
CVR (central business register)	21483974
Date for submission	December 31, 2015

1.2 Short description of project objective and results

DANSK

Vi har udviklet og demonstreret en ny mekanisk briketteringsteknologi til indsamling, håndtering, forbehandling og indfødning af halm i form af høj densitets briketter direkte i bioreaktorer for produktion af bioenergi, enten som biogas eller bioethanol.

Teknologien er demonstreret i industriel skala, heraf titlen på projektet: Industriel storskala konvertering af halm til biogas – via højt mekanisk tryk og hydrolyse. Demonstrationen blev udført på Århus Universitets fuldskala testanlæg, hvor hvedehalm effektivt blev forbehandlet og sam-udrådnet med gylle i kommerciel skala biogas reaktorer. Resultatet var væsentligt forøget biogasproduktion og væsentligt bedre driftsøkonomi.

Under projektet blev det endvidere demonstreret i laboratorie og semi-skala, hvordan halmbriketter kan integreres med lignocellulose – dvs. halmbaseret – ethanol produktion, og hvordan briketteringen medfører både en logistikløsning og en procesløsning for produktion af ethanol.

Jordbrugets afgrøderester skal nødvendigvis indsamles over store geografiske afstande og transporteres til centrale anlægsfaciliteter. Mekanisk brikettering ved hjælp af reciprokerende stempler på decentrale briketterings-stationer forøger bulk densiteten 4 gange i forhold til typiske bigballer. Transportomkostninger til ethanolanlæg reduceres dermed og halmen bliver effektivt sikret mod mikrobiel nedbrydning under lagring. Briketteringen ændrer også halmens fysiske egenskaber på en sådan måde, at den bliver langt letter at behandle via autohydrolyse i en sluttelig damp for-behandling. Helt enkelt via anvendelse af briketteret halm, overvindes adskillige udfordringer for markeds introduktion af autohydrolyse baseret 2G ethanol, herunder proces flaksehalse og kapital og produktionsomkostninger.

ENGELSK
We have developed and demonstrated a new mechanically based briquetting technology for collecting, handling, pre-treating, and injecting straw in the form of high density briquettes directly into bioreactors for production of biofuel, whether biogas or bioethanol.

We have demonstrated the technology on an industrial scale, hence the title of the project: "Industrial scale straw-to-biofuel conversion – by high mechanical pressure and hydrolysis". The demonstration was performed at Aarhus University full scale test facility at Foulum, where cereal straw was effectively pretreated and co-digested with animal manures in the commercially sized biogas reactors. The result is substantially increased methane production and gross revenues of the biogas plant.

The project has furthermore demonstrated in laboratory and semi-scale how straw briquettes can be smoothly integrated with a cellulosic ethanol production, and how the briquetting constitute a logistics as well as a process solution for cellulosic ethanol production.

Agricultural residues as feedstocks must be gathered over a disparate geographic area and transported to centralized facilities. Mechanical pretreatment by reciprocating piston compression at de-centralized "briquetting stations" increases density 4-times greater than typical feedstock bales. Transportation costs to ethanol plants are thereby reduced and feedstocks effectively sterilized against bacterial rot during storage. Briquetting also physically alters feedstocks so as to significantly improve performance in autohydrolysis steam pretreatment. Simply through use of briquetted feedstocks, several medium term challenges to market penetration of autohydrolysis-based cellulosic ethanol can be overcome including pretreatment processing bottlenecks, and capital and production costs.

1.3 Executive summary

The project has been carried out in full accordance with the project plan and has yielded excellent results both in full scale and in the form of scientific output.

One of the main results is the fact that the briquetting demonstration unit at Aarhus University test site in Foulum has worked perfectly for more than 3 years, and daily, or with few days interval, has injected dry straw briquettes directly into the main reactor of the biogas plant, and with a high and stable biogas production as the result.

We have never over this 3-year period seen any issues with the running of the biogas plant due to floating covers, dead volumes, or clogging as a result of the straw addition. On the contrary, we have measured a substantial reduction in the hydrogen sulfide content of the biogas and a stable co-digestion of not only the straw, but also the animal manure.

We have further demonstrated that addition of a catalyzer in the form of potassium hydroxide during the actual briquetting results in substantially increased biogas yields.

On average, it is possible to produce app. 250 Nm^3 methane per tons straw and with addition of lye up to app. 300 Nm^3 methane per tons straw, assuming a sound biogas process and a high straw quality.

Finally, we have optimized the technology understood as a complete straw line system with a view to reducing the specific consumption of power. We erected one plant in Havndal with this technology. The C. F. Nielsen A/S also developed a prototype press with a capacity of the order of 3.5 tons straw per hour rather than earlier presses with a capacity of the order of 1.5 tons straw per hour.

With these updates we have arrived at a total power consumption of 60-70 kWh per tons straw processed.

The briquetting technology is therefore the most cost effective solution for pre-treating straw for biogas. This is particular evident in light of the fact that this technology also provides a logistic solution for collecting and processing straws. One straw line at a decentral satellite station situated near the crop producers may thus serve several biogas pants with straw briquette supplies.

The technology has further proven an effective first pre-treatment of straw before a bio-ethanol process. During the actual briquetting, the straw achieves dramatically altered properties. Among other things, it becomes highly water absorbent, which is of major advantage during hydrothermal final pre-treatment. It means that final pre-treatment can be achieved in very simple unagitated reactors with substantial reduced installation, energy, and running costs, i.e. of the order of 50%.

This is particularly useful in the context of very large cellulosic ethanol plants where 0.5 to 1.5 million tons straw annually must be collected. Here, the briquetting is not only useful; it is simply a necessity in order to manage such quantities of straw residues.

This is why the total concept beginning with briquetting and leading to the simple final pre-treatment has been selected by large commercial actors in China and with one potential project in Denmark pending.

We have achieved large commercial pre-orders on several briquetting lines to large projects in China and expect to receive pre-order for an ethanol project in Denmark.

We have achieved international patent on the method and submitted additional patents on, among other things, the new hydrothermal final pre-treatment.

The project group is convinced that the method will manifest itself as a breakthrough within the field of cellulosic ethanol as well as cellulosic (straw based) biogas.

Under Danish conditions it is unequivocally demonstrated that it is possible to produce biogas based on the total annual production of animal manures of app. 30 million tons and app. 50% of the total Danish straw production (app. 6 million tons) producing 60-70 PJ biogas (Peta Joule).

This can be planned for with virtually no unknowns! The supply of animal manures and straw can be based on 10-15 year long contracts; the gas yield is known, installation and running costs are known for the biogas plants as well as for the straw plants, and it is possible to formulate a complete business model based on the co-digestion of animal manure with straw. The model can include all direct and indirect advantages for agriculture, animal husbandry, climate, environment, society etc. Hence it is possible to develop a national action plan based on this model.

The project group recommends to the Government and the Parliament that this sustainable business model is agreed and implemented to the benefit of green growth, agriculture, climate and environment and for the branding of Denmark internationally.

1.4 Project objectives

The objective of the project was to establish the entire treatment line consisting of a conveyor band for big bales or round bales, and equipped with a shredder and mixer. The shredder cuts the straw into pieces of 5-10 cm and the mixer homogenizes the straw from the various bales. The mixer is equipped with a trap for impurities such as gravel or stones. The straw is air assisted to a hammer mill, where the straw is milled to about 2 cm before it is conveyed to the mechanical press. The press includes a mixer allowing for addition of any catalyzes.

Two complete lines were developed and demonstrated in the project, one at Foulum and one at Havndal.

The objectives were further to achieve full scale continuous running of the pre-treatment line and the associated biogas plant. During the running, the mechanics of the treatment line was corrected and optimized as was the chemical process with respect to use of catalyzes. Similarly, we observed how the treated straw physically behaved in the digester in terms of suspension in the liquid, possible formation of floating covers or sediments, need of stirring and potential clogging of pipes and pumps. Biochemical parameters such as gas production, gas composition, concentration of organic acids and volatile fatty acids, ammonia, pH etc. was monitored to assess the state of the biochemical process.

We also evaluated the biogas yield that can be obtained from different cultivars of cereal straw and grasses straw by the pre-treatment, and to make a technical and economical evaluation. In this task the treatment by mechanical pressure was optimized by determining the effect on biogas yield by different adjustments of the press and different additives. Furthermore the technique was compared with other technologies like extrusion. The energy consumption was measured and a complete energy balance of the technology made.

The final objective was to develop final conditioning before final enzymatic liquidation of processed straw before an ethanol process. We demonstrated that the processed straw becomes very hygroscopic and thus absorb added water and swells accordingly. This trait was used to formulate a final ethanol concepts beginning with briquetting of the cereal straw at decentral satellite stations before final transport to the central ethanol facility. Here, by use of a simple unagitated bioreactor we were able to finally condition the briquettes to a state were enzymatic hydrolysis and therefore full ethanol yield could be achieved.

The further objectives included commercial exploitation of the demonstration which is ongoing and successful.

1.5 Project results and dissemination of results

Demonstration line at Århus University biogas facility in Foulum.

In the middle of 2012, the projecting of a straw downsizing and briquetting line for installation on the research-site of Aarhus University in Foulum. The purpose of this installation was to achieve practical operational experience in the concept of adding briquetted straw into an existing biogas reactor, and extract valid data on the increase in gas yield, resulting of the additive.

The line was projected by C.F. Nielsen, taking into account local conditions, after which the briquetting part of the line was put into production. At the time, no supplier were able to quote a financially viable, complete system for the downsizing of straw, in the needed (low) capacity range, which is why the downsizing equipment was pieced together from several, separate danish suppliers. Especially the straw shredder was a challenge, and a newly developed model, with the addition of a stone trap was chosen. On figure 1, layout no. 90000139 is displayed, showing the line in Foulum.

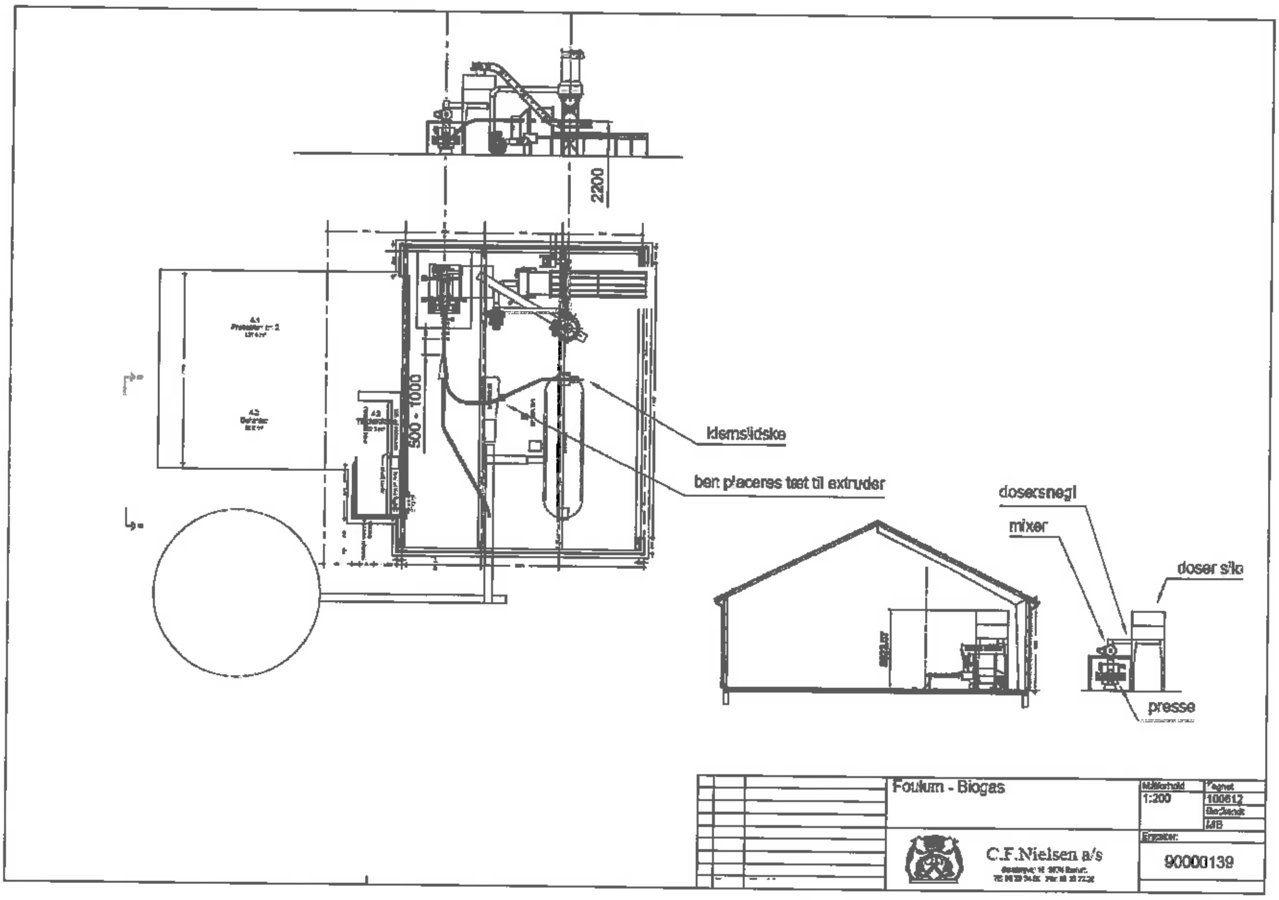
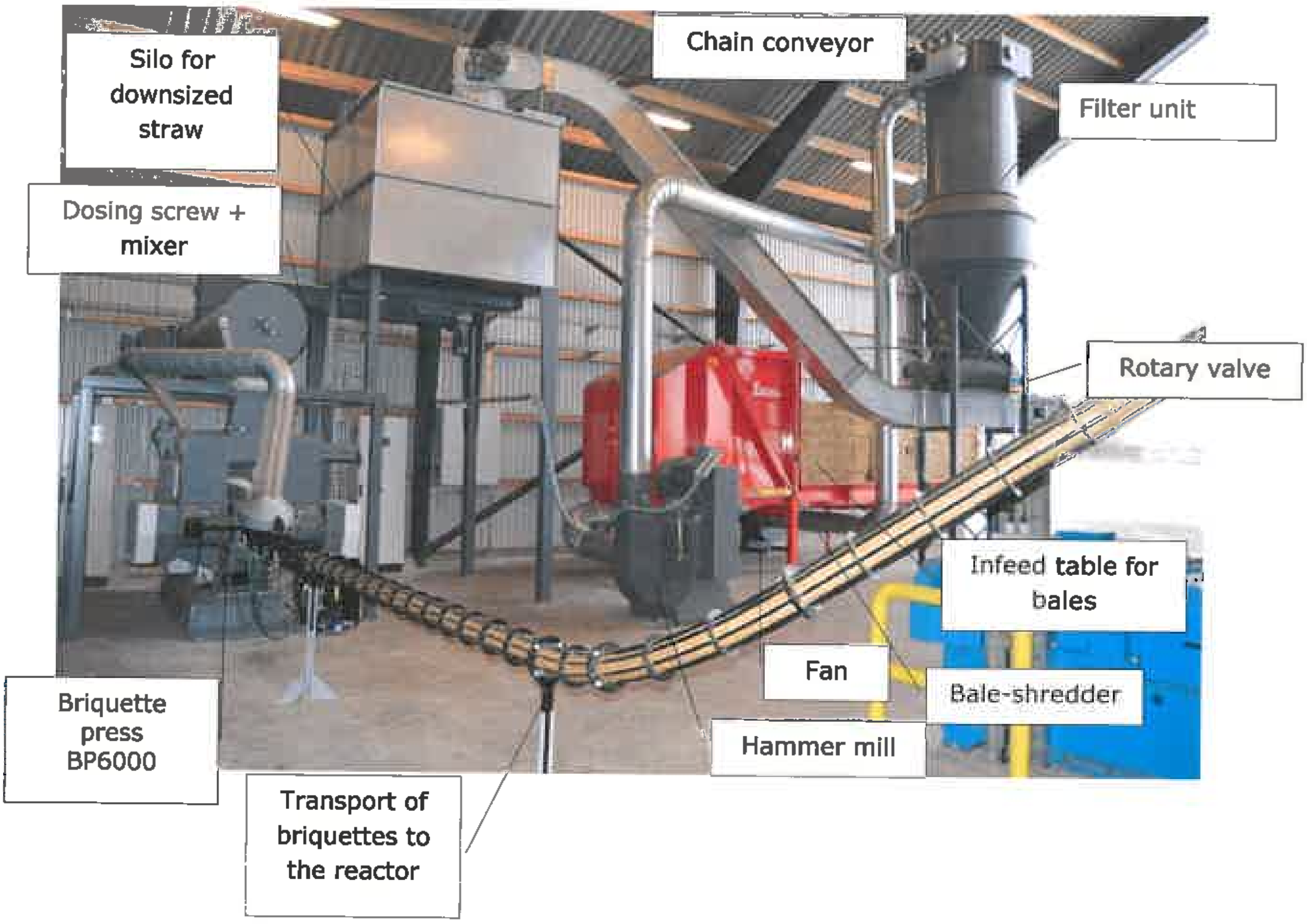


Figure 1

The line was commissioned towards the end of 2012. In figure 2 below, the installed equipment is seen.



Quite quickly, problems occurred with operational stability, since the filter unit in particular, had a tendency to create "plug" and overfill. In figure 3, the filter unit is shown, with the plug.

To downsize straw is markedly different than many other species of biomass, due to the long, ductile structure of the straw. Downsized straw also has a more pronounced tendancy to "bridge", meaning bind together and form layers/plugs in silos and other cavities. Therefore, it was necessary to optimize some of the machines, and achieving continuous operation was difficult for the first few months of 2013.

After a focused effort by the project group members, the equipment was optimized, and continuous operation became possible, in the beginning with a reduced capacity. Most importantly was, that the line demonstrated in actual scale, that dry straw can be added directly into a biogas reactor in large quantities with a good gas yield, without any negative influences on reactor operation, like floating crust, foam-formation or inhibiting the biogas proces itself. The mechanical operation of the reactor was neither affected, no increased plugging of valves, pipes, need of stirring or other was detected.
Aarhus University continued the operation of the line with support from C.F. Nielsen and initiated comparative long-term tests of gas yield with addition of downsized straw, straw bedding and briquettes into the biogas reactor. In the fall of 2013, capacity on the

line was increased without compromizing stability. Achieved capacity was 0,6-1,0 ton/hour, depending on straw quality.

At the time of completion of the project, the line has been in operation for 3 years without any issues, and as such has proven the practical implementation of the main concept of adding (briquetted) straw to a biogas reactor.

Figure 3

Development of new, high-capacity press (Task 3.2)

During the project, it has become very clear, that the capacity needs for feeding biogas reactors are so high, that briquette presses from C.F. Nieslen's existing product range can not fulfill the demands, without resulting in a financially, and technically unatractive solution.

The capacity of a briquette press is limited by the power of it's main motor, the transport-capacity of it's infeed system and the diameter of the die. The diameter of the die, determins the diameter of the end product, and historically, C.F. Nielsen has encountered very few customers, who could accept larger briquettes than 90mm. diameter. That is the reason why, the biggest press in the existing product range produced 90mm briquettes and as such, has a capacity of 12-1800kg/hour, depending on raw material. This limitation on dimensions of the end product is not present in a biogas reactor. Contradictory, a large diameter is an advantage, since there is a larger surface area to absorb the slurry.

C.F. Nielsen set out to develop a new line of presses, with capacities between 2 and 3 ton/hour and a lower specific power consumption, than the existing models. The development was begun during first quarter of 2013, where necessary specifications were agreed upon, and an brainstorming process was carried out.

A prototype was designed, to help determine the best design for an infeed system, especially optimized for lightweight materials, such as straw. This prototype went through trials in C.F. Nielsen's factory in the 4th quarter of 2013 while simultaneously dynamic calculations and dimensioning of the full-size machine were carried out. Figure 4 shows a cross section of the machine design.

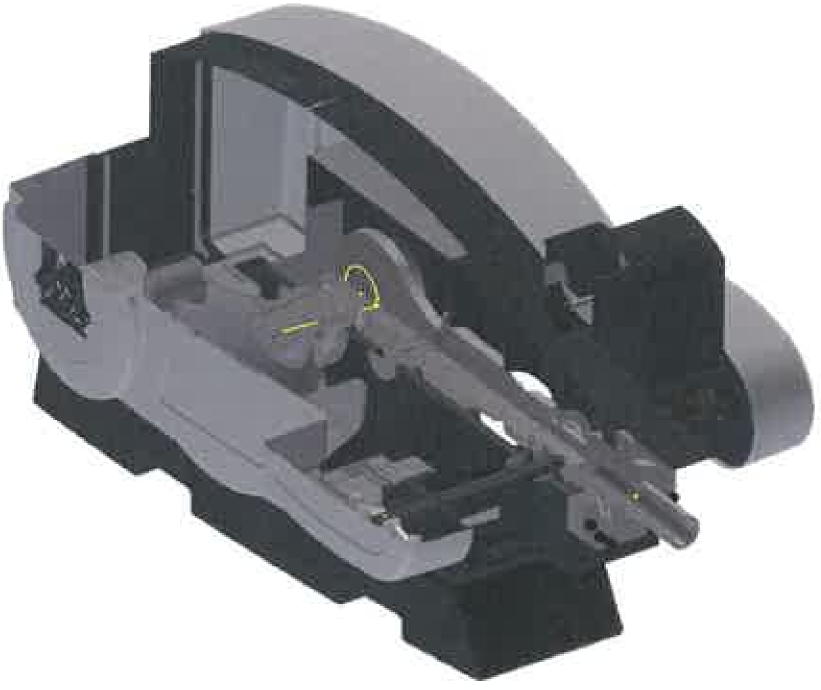


Figure 4

In the 1st half of 2014, the overall design ideas were further refined and in the second half of 2014, the production drawings for the first prototype of the complete press, named BP7510HD, were made. The machine was manufactured during the winter, and assembled in time to be displayed on the Ligna fair in Hannover in May 2015. In figure 5, finished internal parts can be seen, along with the press on the Ligna fair. Figure 5 shows the finished press.

Figure 5

In the second half of 2015, a test site was designed at C.F. Nielsen's headquarters, where power supply and raw material storage was adequate.

Simultaneously, design of the big press's smaller brother, BP7010HD, was begun, in order to fill the gap between the previous and current largest press models. It was put into production in October 2015, but manufacturing was not completed within the framework of the project.

In the end of 2015, the BP7510HD was tested in a production environment, established at C.F. Nielsen, with great succes and an achieved capacity comfortably above 3 ton/hour. Figure 7 shows the installation at C.F. Nielsen: The press is placed under a deck in a big silo, with sufficient capacity to hold enough raw materials for prolongued operation.

Figure 6

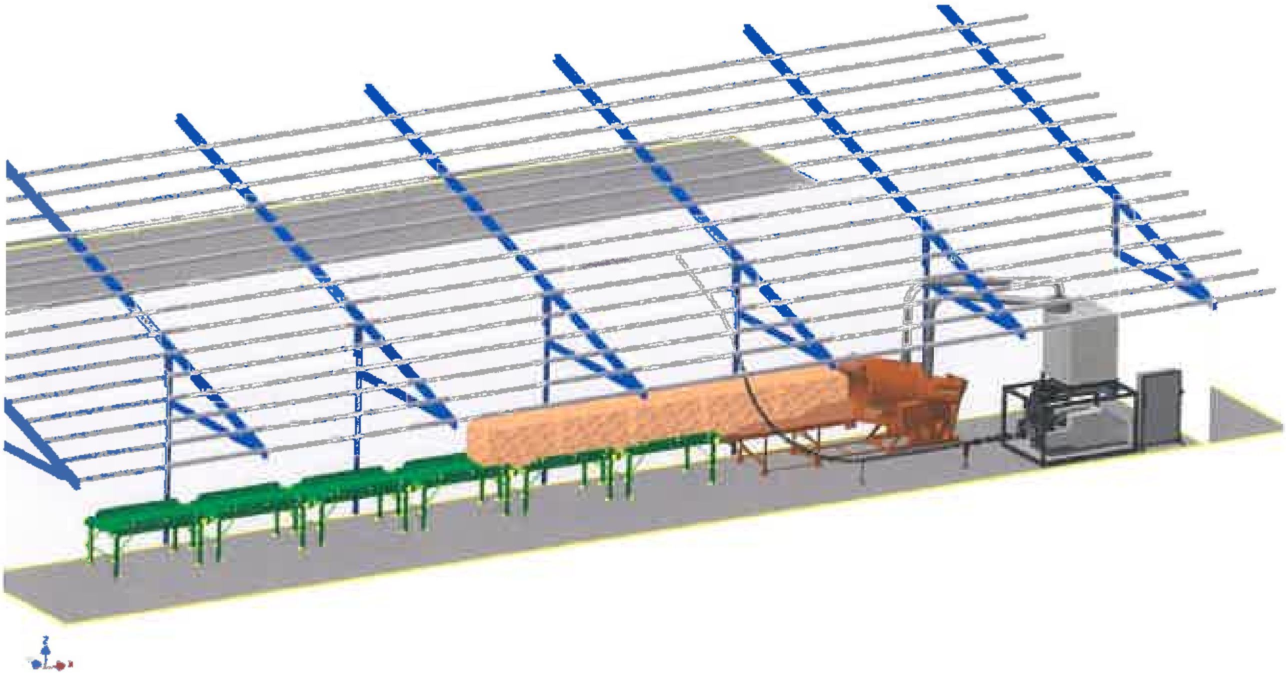
Optimizing of energy consumption and straw downsizing: Test line no. 2 in Havndal (Task 4.1)

One of the lessons from the demonstration line in Foulum, was that specific energy consumption could be optimized, and the capital cost of the straw downsizing equipment was too large for small scale projects (up to 3 ton/hour). A development was commenced in corporation with Danish company Ribers Maskinimport, where an existing straw shredder, designed for hydraulic/PTO drive with a tractor, was modified for a stationary installation, and drive through an electrical motor. Brain storming and meetings were held together with representatives from Ribers Maskinimport, and a prototype was manufactured, see figure 7.

Figur 7

Another purpose of the line was to explore a mobile unit, which could be moved around, depending on the location of the straw. The briquetting press and the new downsizing equipment were installed on special skids, with framework for support of silo, dosing screw, etc.

The location for the equipment was carefully selected, in order to find a place, where the operation of the equipment would be as close to reality as possible, in terms of operating hours, operator skill, focus on up-time, etc. In Havndal, a big farm is located, with a very large annual amount of straw. An agreement was made with the owner of the farm, and the line was installed in April 2014. In figure 9, the layout of the line can be seen.



As seen in figure 10, the line was installed with a long infeed conveyor for bales, enabling unmanned operation for several hours.

Figure 8

Monitoring of moisture content in the bales upon unloading is critical, since a bale with excessive moisture (above 15%) will clog up the cooling line, which routes the briquettes to the storage area.
In figure 11, the storage area can be seen, ready for pickup with a wheel loader.
The power consumption of the 2nd generation straw downsizing equipment is much improved, in particular because an actual hammer mill is not used, and the air stream for pneumatic transport is generated by the system itself, meaning there is no need to introduce additional pressure with a fan. This means that specific power consumption is down to around 65-70kWh/ton for downsizing and briquetting combined.

Figure 9

Biogas results

In the project several research tasks have been carried out resulting in new knowledge for optimizing the briquetting process and documenting the impact and efficiency on straw degradation in biogas plants.

The results have been disseminated in national and scientific papers. The most important results can be found in scientific papers focusing on the use of briquetted straw in co-digestion with manure, documentation of gas yield, optimal adjustments and use of additives in the briquetting process.

Co-digestion:

Anaerobic co-digestion of cattle manure (CM) with shredded or briquetted wheat straw (SS and BS, respectively) was evaluated in thermophilic continuously stirred tank reactors (CSTR) in two experiments (lab and full-scale).

Three lab-scale CSTR (15 L) were used with 20 days hydraulic retention time (HRT); one was fed with CM and the other two with mixtures of CM (95% of fresh matter, FM) and SS or BS (5% FM). Anaerobic digestion of CM, CM+SS and CM+BS in lab-scale reactors yielded 165; 214 and 217 L_{STP} CH_4 kg^{-1} VS (Fig 10.).

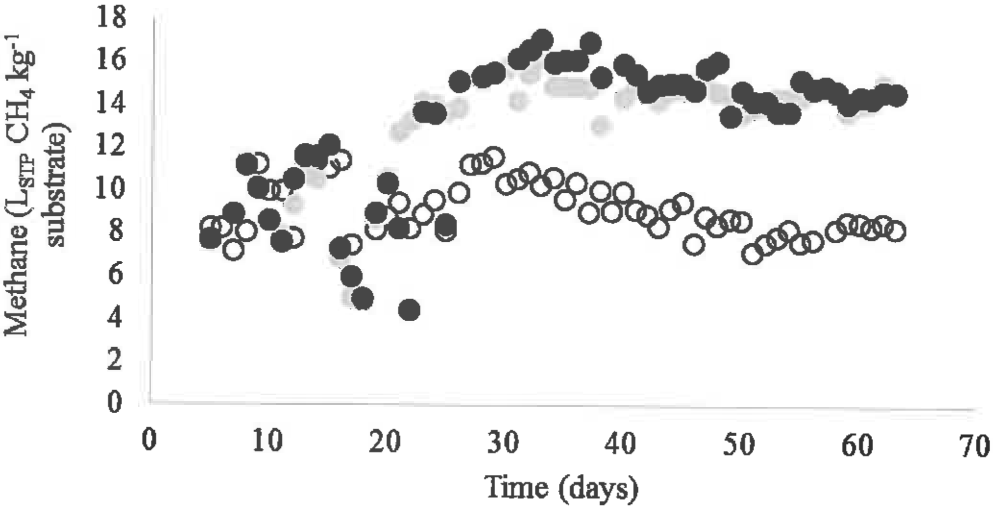


Figure 10. Volumetric methane yield obtained in the lab-scale CSTR from cattle manure (o), cattle manure and shredded wheat straw (●) and cattle manure + briquetted wheat straw (●).

In the second experiment, two full-scale CSTR (30 m^3) were operated with 25 days HRT; one reactor was fed with CM and the other with CM+BS (9% FM). Ultimate CH_4 yield was analyzed from each substrate. In full scale-reactors, CM and CM+BS yielded 264 and 351 L_{STP} CH_4 kg^{-1} VS. Co-digestion of cattle manure and straws led to higher CH_4 yield than digestion of cattle manure alone. In full-scale reactors, the mixture of cattle manure and briquetted wheat straw presented 33% higher specific CH_4 yield compared to cattle manure and 158% in terms of volumetric CH_4 yield (Fig. 11).

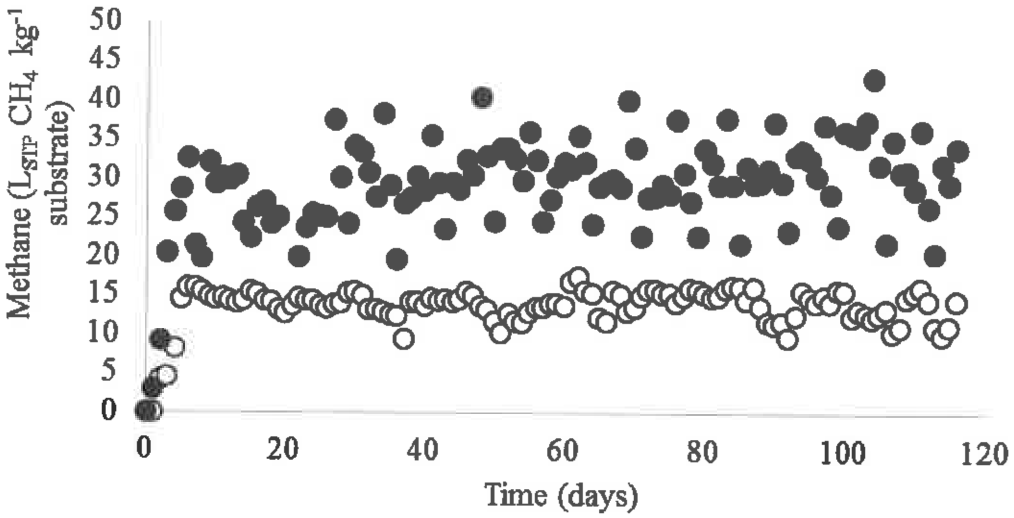
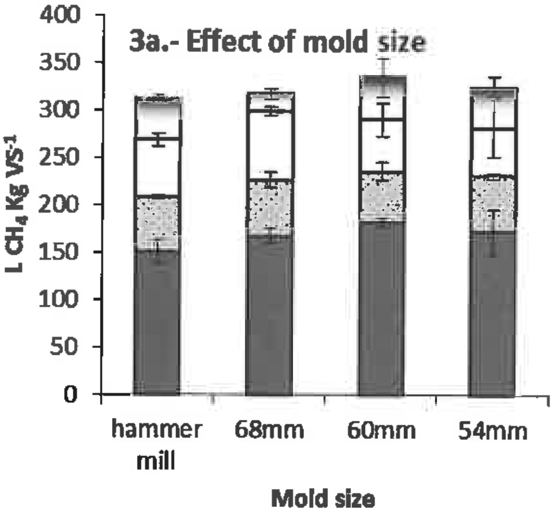


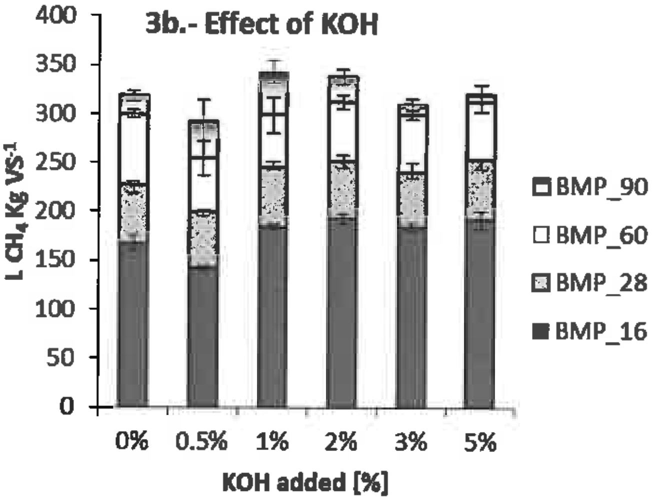
Figure 11. Volumetric methane yield obtained in full-scale CSTR from cattle manure (o) and cattle manure and briquetted wheat straw (•).

In general the CH_4 yield of the briquetted straw results in 19% higher energy yield compared to shredding in terms of substrate mass at the given retention time. The use of straw for co-digestion results in a very positive energy balance for both technologies and the extra energy consumption used for briquetting is more than compensated by extra energy production.

Optimal adjustments and use of additives:

A combination of briquetting and chemical additives to promote lignocellulosic biodegradability was examined and two experiments were designed. In the first experiment briquetting equipment configuration in terms of mold inner diameter (58mm, 60mm and 68mm) and additive addition (KOH, NaOH and acetic acid) at different concentrations (0%, 0.5%, 1%, 2%, 3% and 5%) were evaluated as a combined pretreatment to promote ultimate methane yield (B_0) and hydrolysis rate (k) of the straw. Briquetting configuration in terms of mold inner diameter didn't show a clear effect on B_0 (Fig. 12). Alkali addition has a higher effect on B_0 than acetic acid addition at all concentration tested. The best alkali concentration was 2-3% of KOH.


3a.- Effect of mold size
L CH$_4$ Kg VS^{-1}
400
350
300
250
200
150
100
50
0
hammer mill
68mm
60mm
54mm
Mold size


3b.- Effect of KOH
L CH$_4$ Kg VS^{-1}
400
350
300
250
200
150
100
50
0
0%
0.5%
1%
2%
3%
5%
KOH added [%]
BMP_90
BMP_60
BMP_28
BMP_16

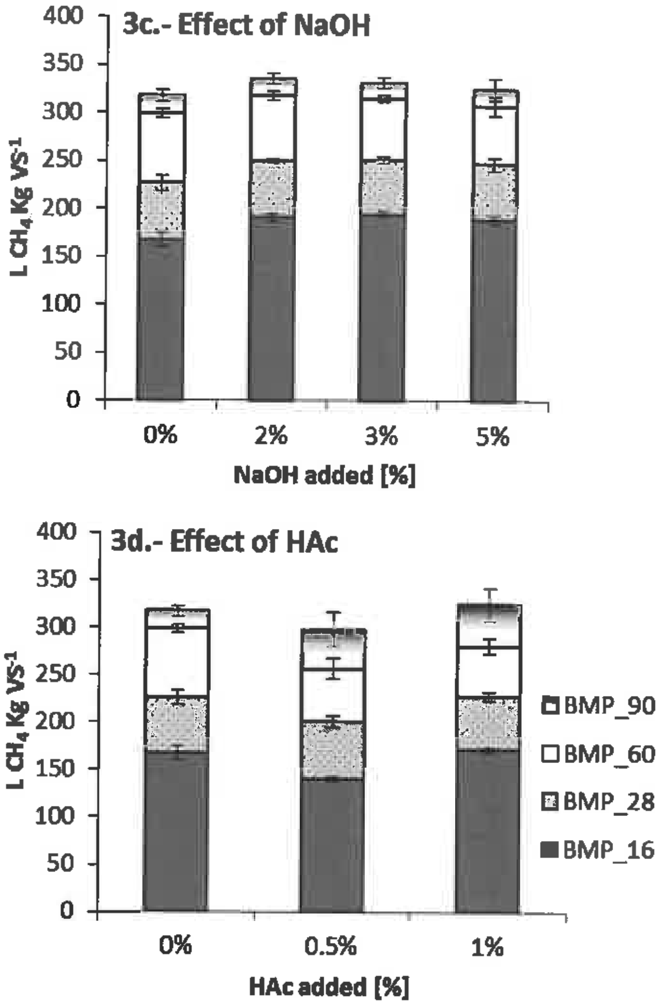


Figure 12. Average of the cumulative methane production (BMP) at 16, 28, 60 and 90 days of the briquetted wheat straw made with different mold sizes and different concentrations of additives: KOH (Figure 12b), NaOH (Figure 12c) and acetic acid (HAc) (Figure 12d). Bars show standard deviation of the cumulative methane production at different times (N=3).

The addition of alkali to BWS in anaerobic plants had higher effect on the hydrolysis constant k than on the B_0 promotion as shown in figure 4. Increasing the alkali concentration had a very significant impact on the hydrolysis rate meaning that the speed at which the straw is converted to methane is higher by increasing alkali concentrations up to around 3%.

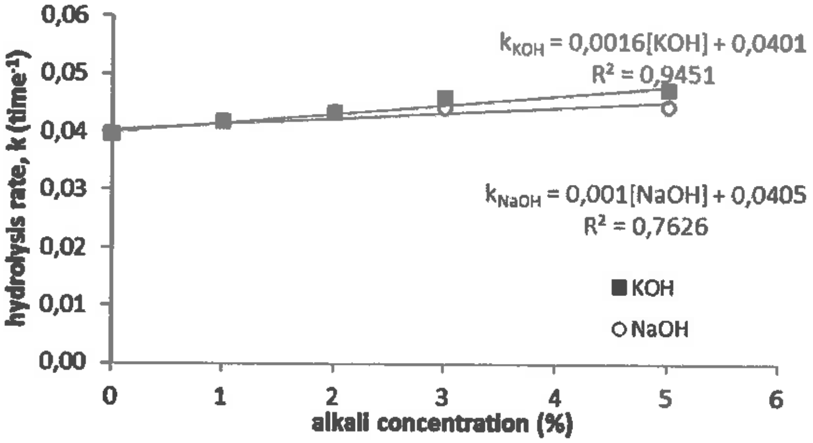


Figure 13. Correlation between hydrolysis rate and alkali (KOH and NaOH) concentration. Hydrolysis rate calculated from model fit of the cumulative specific bio-methane potential (BMP) curve measured in L CH_4 kg VS^{-1} as a function of time $BMP_t = B_0 (1-exp^{-k \cdot t})$.

In a second experiment, the effect of one selected combination was evaluated in continuous stirred tank reactors (CSTR) by co-digestion the briquetted wheat straw (BWS) with cattle manure (CM), not only by measuring CH_4 yield, but also reactors performance and residual CH_4 production after the anaerobic digestion process.

Figure 14 shows the evolution in CH_4 yield in reactors throughout the experimental period. The average specific CH_4 yield (± standard deviation) in the last 30 days was 239.7 (± 17.95) L CH_4 $kgVS^{-1}$ in the reactor fed CM + BWS_{RAW} and 291.9 (± 15.69) L CH_4 $kgVS^{-1}$ in reactors fed CM + $BWS_{3\%KOH}$. This means that around 22% more CH_4 per kg VS can be expected when BWS is pretreated with 3% KOH in the CSTR. Similar results were obtained in terms of volumetric CH_4 yield; in this case a 20% higher volumetric CH_4 yield was obtained in reactors fed CM + $BWS_{3\%KOH}$ than with CM + BWS_{RAW} (26.3 ± 1.42 and 21.7 ± 1.59 L CH_4 kg^{-1} of mixture added to the reactors, respectively) during the last 30 days of the experimental period. These results reflect the higher VS degradability found in reactors fed CM + $BWS_{3\%KOH}$. Compared with the batch assay results, higher promotion in CH_4 yield was achieved with alkali addition in the CSTR than in the batch experiment, probably, as previously stated, because of an attenuation of the effect of alkali addition at increasing retention times, and therefore the effects of alkali addition could be higher at shorter retention times.

In the CSTR experiment, an economical and energetic comparison between treatments was made to evaluate the consequences of alkali addition. For this, the extra energy input and economical cost is only related to the alkali addition itself, since this is the only difference between the treatments. The energy balance was made with an assumption that the energy consumption of the potassium is 7 MJ kg^{-1} K corresponding to. 1.31 g KOH Kg^{-1} f mixed substrate added to the reactor (5.5% of BWS with 3% of KOH addition on a dry matter basis). This corresponds to an energy demand of 9.17 J kg^{-1} mixed substrate added to the digester. The extra CH_4 gained in the reactors with the addition of alkali is 4.6 L CH_4 extra kg^{-1} of mixture (26.3-21.7). The specific energy of methane is 36.63 MJ L^{-1}, which means an extra energy gain 168.5 MJ Kg^{-1} of mixed substrate. This value is much higher than the calculated energy demand of alkali addition (9.17 J kg^{-1} of mixed substrate). and there is an energy surplus of more than a factor 15.

It is assumed that the costs for KOH is 7 DKK Kg^{-1}, which means an extra cost of 9.17 DKK ton^{-1} of mixed substrate added to the reactors (assuming 1.31 Kg KOH ton^{-1} of mixture added). Furthermore it is assumed that the investment in a piston pump for alkali addition is negligible in the overall economical evaluation. When calculating the extra income by using alkali it has been assumed that the value of methane coming from for biogas is around 5 DKK m^{-3} CH_4. This means an extra income of 23 DKK ton^{-1} of mixed substrate (assuming 4.6 m^3 CH_4 extra ton^{-1} of mixture) and a net benefit of 13.83 DKK ton^{-1} of mixed substrate added to the reactor or around 255 kr/ton of straw

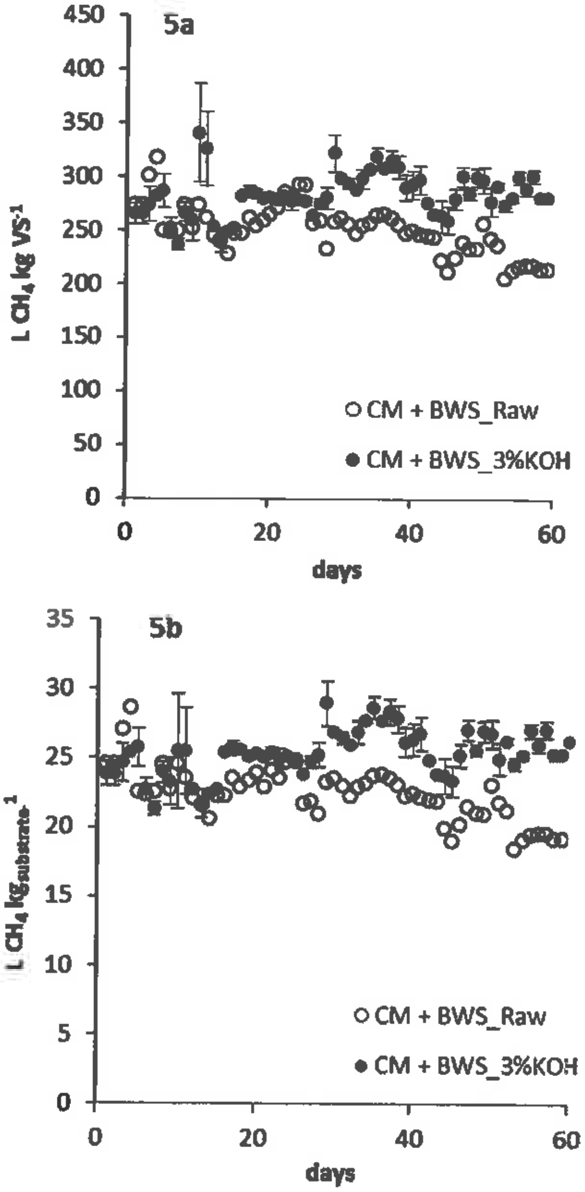


Figure 14. Methane production in reactors in terms of L CH_4 per kg volatile solids introduced in the reactors (CH_4 kg VS^{-1}) (Figure 4a) and in terms of L CH_4 per kilo of substrate introduced in the reactors (L CH_4 $kg_{substrate}^{-1}$) (Figure 4b). *CM + BWS_Raw* reactor fed with a mixture of cattle manure and briquetted wheat straw, *CM + BWS_3%KOH* average from two reactor fed with a mixture of cattle manure and briquetted wheat straw pre-treated with 3%KOH. Bars in *BWS_3%KOH* indicate the standard error of the mean from the two reactors.

Enzymatic hydrolysis and ethanol production

The flowing overall results were achieved in the program:

Feedstock supply

The use of de-centralized briquetting stations as the central feature of an efficient and safe logistical system for biomass feedstock supply to a cellulosic ethanol facility was demonstrated. Use of briquetted feedstocks significantly reduces risk of feedstock supply problems. Briquettes can be safely stored with reduced risk of rot, while ordinary feedstocks are prone to rot, with significant loss of fermentable sugars. Briquettes are easily handled, more homogenous and much cheaper to transport than ordinary feedstocks. Sand and stones, which have proved a significant source of maintenance problems in cellulosic ethanol plants, are removed at the briquetting stage.

Pretreatment of briquettes and enzymatic hydrolysis and ethanol

Through the simple expedient of using briquetted feedstock in a low-cost, unagitated steam pretreatment system, the following improvements in business case for autohydrolysis-based processing will be demonstrated relative to the current industry standard:

Significantly reduced capital cost for the pretreatment system

Because briquetted feedstocks exhibit dramatically enhanced water absorbing properties, heat transfer during steam pretreatment is significantly more efficient. As a consequence, there is no requirement for agitation to achieve homogenous pretreatment at high mass loads. This makes it possible for biomass to be handled at high capacity with reduced incidence of processing bottlenecks using a simple, low-cost, unagitated, gravity fed pretreatment system. Further, because briquetted feedstocks are greatly compressed, it is possible to feed a large quantity of biomass to the reactor using a simple, inexpensive sluice feed system rather than a conventional screw plug feeder.

Significantly reduced tendency for processing bottlenecks at large scale

The steam heat exchange and water retention properties of ordinary raw feedstocks at reactor temperatures are such that the greater the mass of feedstock, i.e. the greater the capacity of the pretreatment reactor, the more inhomogeneous the pretreatment will be, in the absence of agitation above and beyond that provided by a transport screw alone. Because of improved steam heat transfer and water absorption properties, briquetted feedstocks do not suffer from this significant source of processing bottlenecks. Pretreatment of briquetted feedstock using an unagitated reactor is homogenous without dependency on the mass load.

Significantly reduced operating cost from pH adjustment

The chemistry of autohydrolysis pretreatment occurs differently with unagitated briquettes compared with ordinary raw feedstocks pretreated in agitated conventional systems. As a consequence, pH of pretreated briquette whole slurry is much higher - 4.4-4.5 compared with 3.8 and less using ordinary feedstocks. The need for pH adjustment to bring process streams within the pH optima of ethanol producing microorganisms and/or enzyme preparations is correspondingly reduced.

The cost of pH adjustment chemicals can be extraordinarily high. Current market prices for caustic soda (NaOH) vary between 288 - 405 euro/ton. Acids in the soluble component of pretreated biomass include primarily acetic acid, which is inevitably released from hemicellulose during either hydrothermal or enzymatic hydrolysis. Conventional autohydrolysis pretreatment also produces some quantities of "by-product" acids derived from unwanted by-product reactions involving lignin and C5 degradation products.[1] Even where the only concern is the inherent acetate content, which must be accounted for in enzymatic hydrolysis and in C5/C6 yeast fermentation, pH adjustment costs can be very significant. Table 1 shows the estimated cost of NaOH per ton DM[2] for whole slurry hydrolysis and fermentation of pretreated wheat straw at both initial pH 4.4 (e.g, briquettes) and initial pH 3.8 (e.g., ordinary feedstocks in conventional autohydrolysis). As shown, where GMO yeast fermentations are conducted at pH 5.5, pH ad-

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[1] *Yelle, D. et al. "Two-dimensional NMR evidence for cleavage of lignin and xylan substituents in wheat straw through hydrothermal pretreatment and enzymatic hydrolysis," Bioenerg. Res. (2013) 6:211.*

[2] *Assumes NaOH cost of 315 euro/ton and that no pH adjustment is required with pretreated briquette slurry at pH 4.4 with 3 g/L acetate, as has been observed experimentally.*

justment costs can reach levels as high as 5.99 euro / ton DM, which is more than 25% of enzyme costs projected for 2016.

Process pH	3g/L acetate		5g/L acetate		7g/L acetate	
	Briq	Raw	Briq/	Raw	Briq/	Raw
4.4	0	0.667	0.322	1.114	0.644	1.555
4.5	0.117	0.801	0.541	1.337	0.965	1.867
5.0	0.978	1.660	1.993	2.772	2.999	3.868
5.5	1.624	2.575	2.943	4.300	4.262	5.999

Table 1. Estimated cost of pH adjustment at 17% DM in EU/ton DM

Significantly improved recovery of C5 sugars

The chemistry of autohydrolysis pretreatment occurs differently with unagitated briquettes compared with ordinary raw feedstocks pretreated in agitated conventional systems. As a consequence, loss of C5 sugars to unwanted byproduct reactions is significantly reduced with briquettes. C5 loss during pretreatment has been cited by industry leaders INBICON (Tm)[3] and BETA RENEWABLES (Tm)[4] as a very significant problem with autohydrolysis-based cellulosic ethanol production that their technologies seek to mitigate. Simply by using briquetted feedstock in an unagitated reactor, C5 recovery can be increased by at least 20% relative to these current industry standard technologies.

In the experimental system, comparing ordinary raw wheat straw with briquetted straw pretreated by autohydrolysis to equivalent severity log Ro 3.76 at equivalent water content, without agitation and without steam explosion, pH values in the liquid fraction are significantly lower (*t, $p<0.00001$) with ordinary straw, pH 4.05 +/- 0.08 (N=7), than with briquetted straw, pH 4.43 +/- 0.02 (N=16).

Note that when small quantities of feedstock are pretreated by autohydrolysis without agitation at similar or even lower severity, with steam explosion, pH values are reportedly comparable to those observed with large quantities of wheat straw at equivalent severity in agitated commercial hydrothermal pretreatment systems, i.e. on the order of 3.8. See e.g. Jurado et al. (2009)[5] [ca 20% DM; log Ro 3.6; pH 3.8]; Ballesteros et al. (2006)[6] [ca 20% DM; log Ro 3.6; pH 3.8]; Alvira et al. (2011)[7] [ca 20% DM; log Ro 3.6; acetate+formate 5.7 g/L].

In the experimental system, comparing ordinary raw wheat straw with briquetted straw pretreated by autohydrolysis to equivalent severity log Ro 3.76 at equivalent water content, the water content of pretreated briquettes (N=11) is significantly increased (*t, $p<0.006$) after pretreatment compared with ordinary straw (N=5), relative increase +27.0% +/- 5.3%.

[3] *See WO2014/019589*

[4] *See WO2010/113129.*

[5] *Jurado, M. et al. "Laccase detoxification of steam-exploded wheat straw for second generation bioethanol," Bioresource Technology (2009) 100:6378-6384.*

[6] *Ballesteros, I. et al. "Ethanol production from steam-explosion pretreated wheat straw," Applied Biochemistry and Biotechnology (2006) 129-132:4996-5008.*

[7] *Alvira, P. et al. "Effect of endoxylanase and alpha-L-arabinofuranosidase supplementation on the enzymatic hydrolysis of steam exploded wheat straw," Bioresource Technology (2011) 102:4552-4558.*

Briquetted wheat straw was repeatedly tested at identified optimal severity conditions of severity log Ro 3.76 at 60% water content. Glucan and arabinan content of fibers recovered from whole slurry were washed to remove >98% of soluble solids and xylan and arabinan content was determined by NREL method of strong acid hydrolysis. Washed fibers were observed to have xylan + arabinan content within the range 12.8 - 13.3%. The xylan content of solid fraction recovered from raw straw pretreated using conventional autohydrolysis to the same severity log Ro 3.76, as reported by INBICON, was less than 9.%. (See note 26; note that "xylan number" reflects both xylan + arabinan content and that the value of 9% as reported includes the contribution from liquid fraction, such that the actual xylan content of solid fraction was considerably less than 9%). Xylan and arabinan content in the reaction buffer was determined after enzymatic hydrolysis using an excess of CELLIC CTEC2 (Tm) from Novozymes for 96 hours at 50o C using both washed fiber and also soluble component pressed from a whole slurry of the same pretreated briquettes, with an applied pressure of 8 bar. The total C5 recovery from enzymatically hydrolysed washed fibers combined with enzymatically hyrolysed soluble component, correcting for increased molecular weight of free monomers compared with xylan monomers, was between 88% and 92% of theoretical. Total glucan conversion obtained after 96 hours hydrolysis of a whole slurry of the pretreated briquettes at 50o C using CELLIC CTEC2 (Tm) at the dose 0.07 ml/g glucan was 68.0% (N=4), which is experimentally indistinguishable from the equivalent value reported by INBICON using whole slurry of ordinary straw pretreated to equivalent severity at the dose 0.08 ml/g glucan (see WO2014/019589, example 4, Figure 5). When washed fibers from the pretreated briquetted straw were hydrolysed under the same conditions, and soluble component added back to assess toxicity, the observed inhibition of CELLIC CTEC2 (Tm) activity as 4% compared with an inhibitory effect of 14% reported by INICON using the same enzyme preparation and wheat straw pretreated to the same severity.

Significantly reduced toxicity of the soluble component of pretreated biomass against enzyme preparations

The chemistry of autohydrolysis pretreatment occurs differently with unagitated briquettes compared with ordinary raw feedstocks pretreated in agitated conventional systems. As a consequence, toxicity of the soluble component of pretreated biomass is significantly reduced with briquettes. Toxicity of the soluble component has been cited by industry leader INBICON (Tm) as a very significant problem with autohydrolysis-based cellulosic ethanol production that their technology seeks to mitigate. Simply by using briquetted feedstock in an unagitated reactor, toxicity of the soluble component can be reduced at equivalent pretreatment severity by at least 60% relative to this current industry standard technology.

Reduction of energy consumption during pretreatment

Because of enhanced water absorbing properties of briquetted feedstock, water content can be added to feedstocks *inside the reactor* at reactor temperature. In this manner, energy cost of bringing the 60-65% water content of the feedstock to reactor temperature can be significantly reduced.[8]

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[8] *With ordinary raw feedstocks, steam is condensed to water during pretreatment in order to heat the material and its 60-65% water content. If briquettes, which absorb steam condensate, can be wetted inside the reactor, the consequence will be that the total quantity of heated water can be kept to precisely the 60-65% required. In contrast,*

1.6 Utilization of project results

Lately the project partners – BioFuel Technology and C.F. Nielsen – have marketed the concept through a new company – Kinetic Biofuel A/S. Please see the web-site www.kineticbiofuel.com for more information.

The new company is in contact with several of the major potential customers in Denmark and a new design for a complete line – BP7510 with straw processing equipment (capacity 3-4 t/hour) is under development. The prototype line is shown in figure 15.

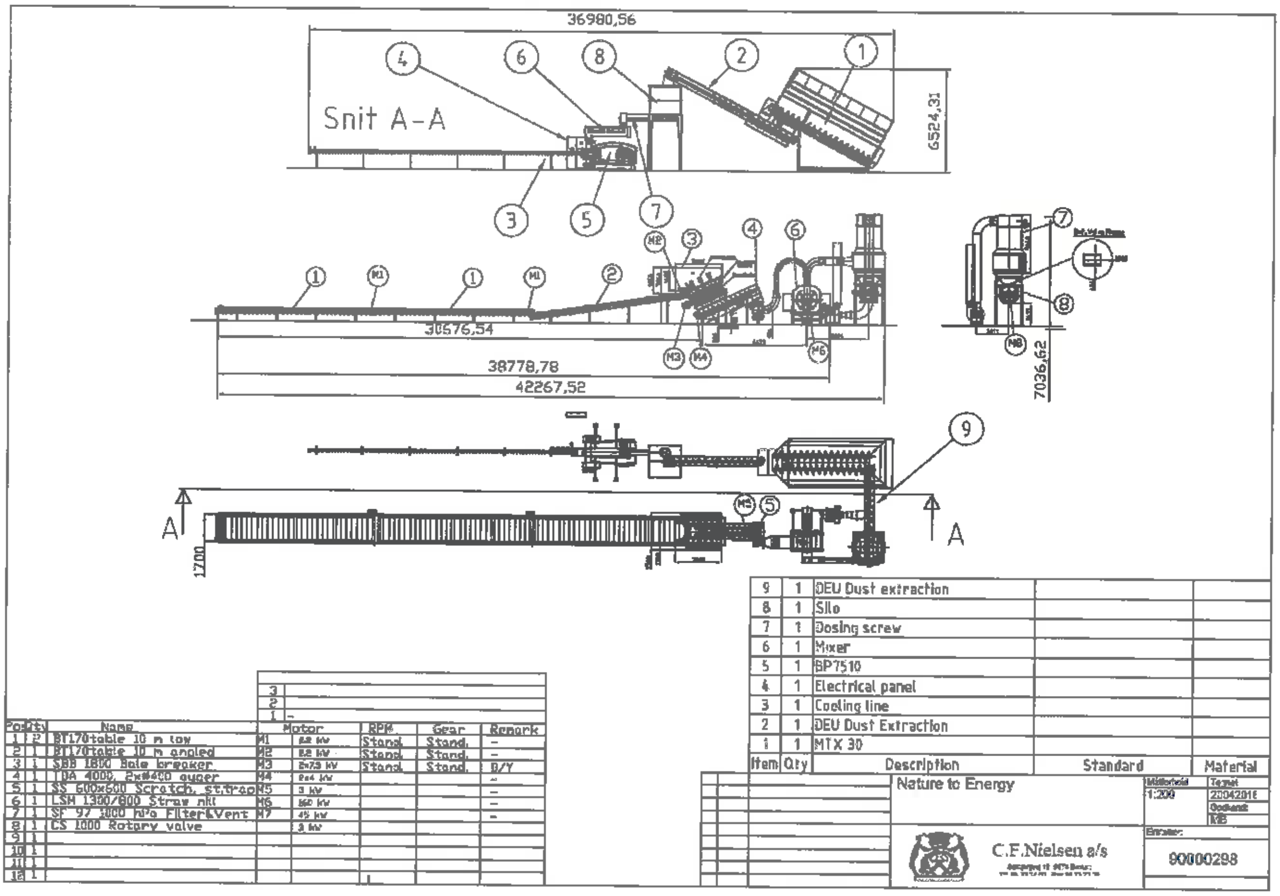

Figure 15

As seen, the larger scale enables inclusion of a large buffer with mixing capabilities, between the downsizing and briquetting parts of the line. This is an advantage, since it increases operational stability. Furthermore, the buffer contains and mixes an amount of downsized straw equivalent to several bales, meaning smaller moisture peaks in lumps on individual bales are evened out.

The technology has been patented and patent has been obtained in Denmark and Europe. The patent is pending in other countries.

with raw feedstocks, the total quantity of heated water is the 60-65% required plus the amount of condensate produced during steam heating.

The results will further be used for producing an entire new front end system for cellulosic ethanol production. We will continue developing a plug flow reactor designed to benefit from the pre-treatment of the straw during briquetting –the s-called CELLEBRIQ^{TM} technology.

Subsequently we will

(a). Propose zero- or low-capital retrofits supporting CELLEBRIQ technology with existing steam pretreatment equipment.

(b). To submit, in all public tender offers made under EU rules for cellulosic ethanol projects, a detailed engineering package for the pretreatment and feedstock handling system based on a modular 10 ton/hour pretreatment reactor.

(c). To manufacture and test the modular 10 ton/hour pretreatment reactor as the first of 15 planned processing lines in a complete, full scale autohydrolysis-based cellulosic bioethanol facility to be constructed in Harbin, China.

The commercial project in Harbin is being developed systematically, beginning with establishment of the feedstock supply system. A total of 60 briquetting stations are planned to be established to form a network of nodes in a feedstock supply chain to a central biomass processing facility which will eventually produce cellulosic bioethanol. This facility will initially process briquetted feedstocks primarily to biogas, to support a dedicated green energy plant running gas turbines on biogas. The cellulosic ethanol component will be introduced as the technology is brought to speed. After two rounds of intensive national exporters' technology evaluations, the provincial government issued official authorization for a joint venture company involving BIOFUEL TECHNOLOGY and Heilongjiang JianYe Fuel Co. to build a biomass processing facility based on briquetting supply having capacity 1.3 million tons annually using local corn straw. The Chinese partner in the joint venture has organized a farmers' union which owns the planned network of briquetting stations. Several briquetting stations have already been constructed in Harbin, with municipal leaders participating in ground breaking ceremonies. Local news has extensively reported such events. For example, see Harbin city, Bin County, government site

http://www.chinabx.gov.cn/News_View.asp?NewsID=4178. Figure 11 shows a photo of such a ground breaking ceremony

The expected commercial impact of introducing this system is, thus, a general improvement relative to the current industry standard of any business case for an autohydrolysis-based plant as follows:

1. An increase in ethanol production from C5 by at least 20%
2. An increase in overall ethanol yield as function of the entire new front end process by at least 10% and more likely 20%.
3. An increase in methane output by 200% due to conversion of lignin to biomethane.
4. Reduced anaerobic digester maintenance and operation cost by at least 20%
5. A reduction in capital cost for pretreatment by at least 50%
6. A reduction in operating cost for pH adjustment chemicals by at least 25%
7. Eliminating processing bottlenecks arising from pretreatment to achieve continuous operation maintained at high capacity.
8. A reduction in energy consumption in pretreatment by at least 15%.

1.7 Project conclusion and perspective

We are convinced that we have developed a new technology with a substantial potential to boost biogas production as well as bioethanol production.

We have the technology to assist in developing the biogas industry with up to 1 million tons straw annually by year 2020 and in the longer run with up to 3 million tons annually. The biogas output from app. 3 million tons straw and app. 30 million tons animal manures is of the order of 60-70 PJ i.e. about 10% of the gross energy use in Denmark and about 50% of the present use of natural gas.

The technology is very solid in the sense that both the supply of animal manure and straw can be based on 10-15 year contracts; the biogas yields are known, installation and running costs are known for the biogas plants as well as for the straw plants. It is therefore possible to base an entire business model for substantially increased biogas production in Denmark solely on use of manure and straw. The business model may include direct and indirect advantages for agriculture, livestock production, climate, environment, society, etc. A national action plan can be based on this model.

The new front end system for cellulosic ethanol production is yet an additional booster for a combined ethanol and biogas production. We have provided general improvements to the industry to an extent that cellulosic ethanol becomes much more technological viable and economically interesting.

We have worked with a preliminary design of a cellulosic ethanol facility with a supply of 400.000 tons wheat straw briquettes. The production of ethanol and biogas in combination, and based on the new front end system, is promising. It is estimated that in time several large bioethanol facilities will benefit from this technology.

Annex
www.kineticbiofuel.com

Annex

Biogaspublications partly or fully funded by the project:

Moset, Veronica, Nawras Al-zohairi, and Henrik B. Møller. 2015. The impact of inoculum source, inoculum to substrate ratio and sample preservation on methane potential from different substrates. *Biomass and Bioenergy* Vol. 83, 2015, s. 474-482. .

Moset, Veronica, Cristiane de Almeida Neves Xavier and Henrik Bjarne Møller. 2015. Optimization of methane yield by using straw briquettes- influence of additives and mold size. Submitted in *Industrial Crops and Products.* Vol. 74, 05.11.2015, s. 925-932.

Xavier, Cristiane de Almeida Neves, Verónica Moset, Radziah Wahid and Henrik Bjarne Møller 2015. The efficiency of the shredded and briquetted wheat straw in anaerobic co-digestion with dairy cattle manure. *Biosystems Engineering* Vol. 139, Nr. November, 2015, s. 16-24.

Møller, Henrik Bjarne; Møller Hansen, Mogens. 2014. **Briketter af halm og tørt græs kan fordoble gasproduktionen.** /. I: Forskning i Bioenergi, Brint & Brændselsceller, Vol. 47, 2014, s. 3-5

Conferences etc. where the results from the project has been disseminated:

Xavier de Almeida Neves, Cristiane; Hernandez, Veronica Moset; Wahid, Radziah; Møller, Henrik Bjarne **Methane production from cattle manure co-digested with briquetted and macerated wheat straw.** .2014. Poster session presented at Solid Waste World Congress, Sao Paulo, Brasilien

1.6 **Møller, H.B. 2015. Forbehandling i praksis: erfaringer og sammenligninger af nye teknologier. Konkrete forsøg og nye resultater. 25 august 2015, Workshop. Halmbaseret biogas-status og perspektiver, Korsør.**

1.7 **Møller, H.B. 2015. Optimizing pre-treatment of biomass and biogas technology to produce more gas and reduce GHG emissions. 4 Nov. 2015, Workshop in Brasil, BIOGREEN,**

1.8 **Møller, H.B. 2015. Gas af halm og dybstrøelse, hvordan kan det gøres i praksis? 7 dec. 2015, Seminar, Foreningen for Danske biogasanlæg, Århus.**

1.9 **Møller, H.B. 2015. Mere gas på anlæggene med forbedret miljø- og klimagevinst. 7 dec. 2015. Seminar, Foreningen for Danske biogasanlæg, Århus.**

1.10 **Møller, H.B. 2015. Hvordan kan anlæggene lave mere gas og få en endnu bedre miljøprofil - foreløbige erfaringer fra biogas taskforce, 12 maj 2015, Konference, Gastekniske dage, Billund**