Final report

1.1 Project details

Project title	Ammonia for enhancing biogas yield & reducing NOx
Project identification (program abbrev. and file)	Energinet.dk project no. 12069
Name of the programme which has funded the project	ForskEL
Project managing company/institution (name and address)	Technical University of Denmark(DTU) DTU Kemiteknik Søltofts Plads 229 2800 Kgs. Lyngby Danmark
Project partners	Danish Gas Technology Centre Nordic BioEnergy ApS EnviDan A/S
CVR (central business register)	29102384
Date for submission	

1.2 Short description of project objective and results

AMMONOX focused on developing a sustainable process for enhancing the productivity of biogas plants based on manure. Also, the developed technology (combined with existing technologies) can significantly contribute to minimizing NOx emissions from gas engines (use of excess ammonia produced) and increasing biogas supply to the gas grid. The concept is based on the separation of liquid and solid fraction of manure on site and subsequent transfer of the solid fraction to centralised biogas plants treating manure and/or the use of lignocellulosic residues, i.e. straws, to be codigested with manure. The key and innovative technology developed is the Aqueous Ammonia Soaking (AAS) pretreatment of lignocellulosic fibers for increasing their methane yield and the subsequent removal and recycling of ammonia. AAS that has yielded impressive results (over 244% increase of the methane yield of manure fibers after only 17 days of digestion) has been optimised in lab-scale. A process design for a future scalling up of the developed technology has been performed. Implementation of AMMONOX technology will boost biogas production from lignocellulosic biomasses in general with positive impacts not only on biogas plants' economy but also on National energy balance.

1.3 Executive summary

Liquid manure is one of the most important sources of environmental pollution, contributing significantly to the anthropogenic Greenhouse Gas (GHG) emissions. The anaerobic digestion process of liquid manure is a mature technology that allows capturing emissions in the form of biogas, while simultaneously improving the characteristics of manure for soil application. Nevertheless, the anaerobic digestion process in biogas plants treating solely swine manure, is usually economically non-feasible due to the low conversion rate of the solid lignocellulosic fraction (manure fibers), and due to the high water and ammonia content. The pretreatment of manure fibers, or of other lignocellulosic biomasses, with Aqueous Ammonia Soaking

(AAS) coupled to an ammonia recovery step, could potentially overcome these limitations when added to manure. However, the efficiency of AAS on increasing the methane yield of lignocellulosic biomasses may vary significantly depending on the conditions of the pretreatment applied.

The main objective of this project was to evaluate the efficiency of AAS on improving the methane yield of swine manure fibers when applied under different conditions. The importance of different AAS parameters was tested and the most influencing factors identified were the NH_3 concentration of the reagent, the duration of AAS and the solid-to-liquid (S:L) ratio. Heating up to 50°C during AAS did not produce any significant effect on the methane yield of pretreated fibers, allowing thus for a less energy intensive pretreatment process at ambient temperature (20°C). The AAS of swine manure fibers, depending on the conditions applied resulted in a variation of the methane yield from 90 to 214 ml/g TS after 17 days of batch anaerobic digestion. The optimal conditions for maximizing the methane yield corresponded to 7% w/w NH_3, 4 days of AAS and 0.16 kg fibers/l reagent, resulting in average to a 244% increase of the methane yield after only 17 days of digestion. Nevertheless, a strong interaction effect among the NH_3 concentration and the duration of AAS on the resulting methane yield was found, providing some flexibility to the process configuration. Empirical models were constructed for predicting the methane yield of manure fibers as a function of the levels of the AAS parameters. Based on these models, 5-11% w/w NH_3 and 3.8-6 days of AAS duration can be applied in order to obtain 95% of the maximum increase of methane yield.

The influence of the same AAS parameters as for manure fibers were also investigated on the methane yield of wheat straw, as this is an abundant lignocellulosic residue that could be considered for boosting the methane production of manure-based anaerobic digestion. The AAS of wheat straw at ambient temperature (20°C) resulted in a variation of the methane yield between 223 to 325 ml/g TS after 17 days of batch digestion, depending on the conditions of AAS applied. The NH_3 concentration was found to be the most influencing factor for the efficiency of the AAS pretreatment of wheat straw, and the optimal conditions corresponded to 18% w/w NH_3, 7 days of duration and 50 g/l reagent, resulting in a 43% increase of the short-term methane yield (after 17 days of digestion). Strong interactions were identified among the NH_3 concentration and the duration of AAS, permitting a higher flexibility on the process configuration for increasing the short-term methane yield of pretreated wheat straw, as compared to swine manure fibers. According to the results obtained, a 95% of the maximum increase of methane yield can be obtained by pretreating wheat straw with 7.3-29% w/w NH_3 concentration for 3.5-7 days.

In an attempt to better understand how the biomasses investigated in this project were affected by AAS under optimal conditions, an evaluation of the compositional changes that occurred due to the pretreatment was carried out. The results obtained, showed that no lignin removal took place on swine manure fibers, in contrast to wheat straw where limited removal was observed (9%). The hemicellulose fraction of both biomasses was significantly solubilized (37% for swine manure fibers and 62% for wheat straw), an effect that is hypothesized to promote a better access of enzymes to carbohydrates improving thus the hydrolysis rate of the biomasses and their conversion to methane.

The performance of the optimally AAS-treated manure fibers on continuous manure-based anaerobic digestion was evaluated (in laboratory scale), as compared to the digestion of manure enriched with untreated manure fibers. A significantly improved performance of the digester running on manure enriched with optimally AAS-treated fibers was observed in all aspects. Based on the experiments run, an 18% and 38% increase of the biogas productivity and methane yield respectively could be achieved by pretreating manure fibers under optimal conditions. Additionally, a higher reduction of all organic components (carbohydrates, lipids, proteins, and lignin) could be achieved as compared to untreated fibers, being cellulose the fraction most significantly affected (42% increased reduction efficiency).

A preliminary economic evaluation of the AMMONOX process has clearly revealed that it may have a significant and positive effect on the economy of a biogas plant. Furthermore, the process will result to an excess of ammonia production which is more than it is needed to cover the needs for the SCR treatment of the flue gas from a gas engine, hereby reducing the NOx emissions from the plant. A conceptual design of a future test unit for the

AMMONOX process has also been performed. It included flowdiagrams and complete mass and energy balances using the simulation tool HYSYS.

Overall, the experimental results obtained in this project, contributed to a better understanding of the potential and flexibility of the AAS pretreatment for ensuring high methane yields of the lignocellulosic biomasses tested. A systematic experimental procedure was followed for evaluating the effects of different AAS parameters on the methane yield of manure fibers, including the exploration, screening and finally optimization of the most influencing AAS parameters for ensuring high methane yields through anaerobic digestion. Wheat straw was considered as an alternative biomass for improving manure-based anaerobic digestion, and the effects of the AAS parameters on the methane yield of wheat straw were also extensively studied. Empirical models were produced for facilitating a techno-economic analysis of the AAS process of swine manure fibers as well as of wheat straw and for providing valuable information on the process flexibility and limitations prior to scaling up. Additionally, the compositional analyses of the optimally pretreated biomasses contributed to a better understanding of the mechanism of AAS under optimal conditions. Finally, the continuous anaerobic digestion experiments demonstrated that a higher reduction efficiency of the organic compounds is possible when swine manure is enriched with optimally AAS-treated manure fibers as compared to untreated manure fibers. The results produced within the AMMONOX project can be used for the design and construction of a pilot scale biogas plant where the AAS pretreatment will be combined with the recovering and recycling of ammonia.

1.4 Project objectives

The purpose of AMMONOX project was to optimise AAS as a moderate and sustainable chemical pretreatment for enhanced methane production from manure fibres and lignocellulosic biomasses and to apply innovative ammonia recovery technology. Given that the ammonia can be used as the reducing agent for the catalytic removal of NOx from flue gas-ses, the purpose of the project was also to study the possibility to combine the pretreatment of biomass and the production of excess ammonia with the elimination of NOx emissions when the biogas is used for subsequent electricity generation with gas engines. Expected findings included i) the optimal conditions (temperature and duration) for the AAS of different biomasses, ii) preliminary design considerations for test unit layout and economic evaluation of the process, iii) the feasibility for recovering and reusing ammonia at a treatment plant and iv) the potential for production of excess ammonia and its use for the reduction of NOx emissions from biogas engines.

1.5 Project results and dissemination of results

The research work was broken down to 2 workpackages:

Workpackage 1: Optimization of AAS pretreatment

The determination of the optimal conditions for the AAS of the different biomasses took place using statistical optimization tools. The objective of the optimization procedure was the increase of the methane efficiency during the anaerobic digestion of the biomass. The work started with an analysis of the effects of Aqueous Ammonia Soaking on manure fibers using experimental results obtained in a previous research project. Based on this analysis, preliminary experiments were carried out in order to decide which parameters to include in the statistical analysis. Key parameters such as ammonia concentration, AAS treatment duration and temperature were screened. The screening identified the variables with a significant effect on the response. A second-order polynomial function was fitted to correlate relationship between variables and response (methane production). Predictable mathematical models for the optimum conditions for enhanced methane production have been generated. Biomasses examined were manure fibers and straw. The optimized conditions were obtained in a batch mode, which was necessary for statistical purposes (to have "statistically independent" experiments). The optimization results were confirmed in laboratory scale (3 L) continuous digesters for manure fibers.

Workpackage 2: Preliminary design considerations for test plant layout and economic evaluation of the process.

Based on the background experimental results (already obtained during RETROGAS project) from AAU laboratory scale tests the project consortium made a preliminary design for a test-unit layout. The design considerations included the estimation of minimum technical requirements and cost for combining the ammonia recovery system with the SCR catalysts for NOx reduction and the evaluation of the influence of AAS on the cost of biogas production. This preliminary design was finalized by taking into consideration the results from WP1.

The main results obtained during this project are summarised below. More details can be found in the scientific manuscripts/publications which come as appendix to this report.

1.5.1 Analysis of effects of aqueous ammonia soaking on manure fibers

All the experimental data used in this analysis originate from research at Aalborg University and are published in Jurado et al. and Mirtsou-Xanthopoulou et al. The data consist of CH_4 yields of digested swine manure fibers pretreated with AAS under two different temperatures (22°C and 55°C), three different pretreatment durations (1, 3 and 5 days) and six different NH_3 concentrations of the reagent (5%, 10%, 15%, 20%, 25% and 32% w/w). All pretreatment mixtures were further used for experiments after a distillation step where the NH_3 concentration was reduced to below-inhibition levels. Two data sets were formed for the data exploration analysis, both originating from the same experiments. The first data set, presented in Table 1.5.1.1, concerned ultimate CH_4 yields (CH_4 yield when no further gas production was detected, usually more than 30 days) of Biochemical Methane Potential (BMP) tests; and the second data set concerned the CH_4 yields after approximately 18 days from the same experiments. The purpose of analyzing the two different data sets was to assess the effect of the AAS parameters on the short term CH_4 yield and on the ultimate CH_4 yield. Both data matrixes were constructed by 54 rows, corresponding to the total amount of experiments (including triplicates), and 4 columns, corresponding to the pretreatment variables (temperature, duration and NH_3 concentration of the reagent) and to the CH_4 yield obtained under these conditions.

Principal Component Analysis (PCA) was used for data exploration purposes and for identifying tendencies of the CH_4 yield based on the different levels of the pretreatment variables. The software used for this purpose was The Unscrambler®X 10.3 (CAMO, Norway). Standardization of the data matrixes was performed by first subtracting the mean from the values and then dividing them by the standard deviation of the corresponding variable. This way, the variables that initially have a very different range of variance become more comparable as the variance becomes even. PCA revealed that within the ranges tested, temperature and NH_3 concentration of the pretreatment have more influence on CH_4 yield, while the duration of AAS is less important (Figure 1.5.1.1). Optimization of AAS of manure fibers must be conducted for guaranteeing maximum performance, and the effect of lower values of NH_3 concentration and duration should be included in the investigation. The most important factors of AAS that seem to affect the performance of the pretreatment and should be optimized are temperature, NH_3 concentration, duration and S:L ratio. It will be necessary to establish an experimental design that will allow a full impact also from interactions between these four factors, i.e. a so-called random design.

Table 1.5.1.1. Data matrix of ultimate CH_4 yields of digested manure fibers treated with AAS under different conditions used for PCA.*

N° of Experiment	Temperature of AAS (°C)	Duration of AAS (days)	NH_3 concentration of AAS (%w/w)	CH_4 yield (ml CH4 / g TS)
1a	22	1	32	106,2243
1b	22	1	32	111,5652
1c	22	1	32	107,0878
2a	22	3	32	143,8944
2b	22	3	32	128,7069
2c	22	3	32	141,5351

3a	22	5	32	139,7697
3b	22	5	32	126,7412
3c	22	5	32	128,7438
4a	55	1	32	110,8356
4b	55	1	32	119,3204
4c	55	1	32	110,6114
5a	55	3	32	125,8958
5b	55	3	32	134,3595
5c	55	3	32	132,4131
6a	55	5	32	119,7610
6b	55	5	32	124,3537
6c	55	5	32	124,6628
7a	22	3	32	144,0650
7b	22	3	32	127,2090
7c	22	3	32	163,6780
8a	22	3	25	163,3950
8b	22	3	25	153,7280
8c	22	3	25	187,3500
9a	22	3	20	181,0820
9b	22	3	20	180,0060
9c	22	3	20	144,2920
10a	22	3	15	145,1680
10b	22	3	15	177,6820
10c	22	3	15	167,3930
11a	22	3	10	146,3340
11b	22	3	10	171,3740
11c	22	3	10	177,0590
12a	22	3	5	166,8230
12b	22	3	5	165,6650
12c	22	3	5	156,4660
13a	22	1	25	218,9580
13b	22	1	25	202,4960
13c	22	1	25	217,1620
14a	22	3	25	205,0210
14b	22	3	25	227,4380
14c	22	3	25	222,6920
15a	22	5	25	158,9800
15b	22	5	25	178,3310
15c	22	5	25	162,6690
16a	22	1	5	169,4050
16b	22	1	5	201,0910
16c	22	1	5	240,9190
17a	22	3	5	197,9670
17b	22	3	5	191,9950
17c	22	3	5	209,1050
18a	22	5	5	205,2330
18b	22	5	5	185,5600
18c	22	5	5	196,9940

*Data graphically presented in Jurado et al. and Mirtsou-Xanthopoulou et al.

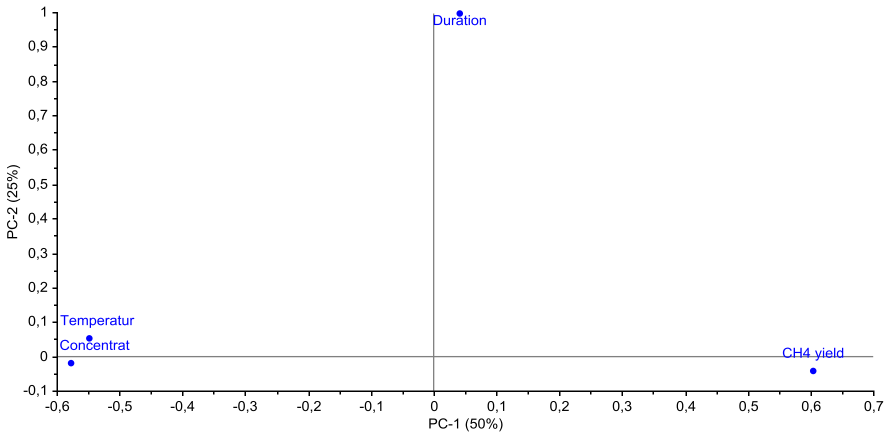

Figure 1.5.1.1. Loadings plot of the PCA showing the correlation of the three AAS parameters tested (temperature, NH_3 concentration and duration of AAS) with the ultimate CH_4 yield

For more detailed results relevant to section 1.5.1, see attached publication:
Lymperatou, A., Gavala, H.N. Esbensen, K.H., Skiadas, I.V. "AMMONOX: Ammonia for Enhancing Biogas Yield and Reducing NOx—Analysis of Effects of Aqueous Ammonia Soaking on Manure Fibers", Waste and Biomass Valorization 2015 6: 449-457

1.5.2 Statistical Optimization of parameters affecting the CH4 yield of Aqueous-Ammonia-soaked raw swine manure fibers [Optimal conditions for the treatment of manure fibers (Milestone 1.1)]

The screening experiments for identifying the most influential parameters of Aqueous Ammonia Soaking (AAS) of raw manure fibers on the resulted CH_4 yield have shown that the temperature can be considered as the least important. Therefore, by keeping the temperature constant (at 20 ± 1°C) experiments were carried out in order to obtain a model that describes how the important parameters of AAS (ammonia concentration A, duration D and solid-to-liquid ratio SL) affect the CH_4 yield of treated raw swine manure fibers. The experimental design chosen for this purpose was the Central Composite Design, and the software used was The Unscrambler®.
The AAS pretreatment was applied on raw manure fibers under 15 different conditions by varying the values of A, D and SL. According to the Central Composite design, the number of experiments for optimizing 3 parameters is 15 comprising of 8 cube points, 6 axial points and 1 center point covering the experimental region as shown in Figure 1.5.2.1. Each parameter is tested in total at 5 levels. For statistical reasons, one of these experiments, the center point (all parameters set at middle values) is repeated 3 times. Based on this experimental design, in total 17 AAS pretreatments of raw manure fibers were performed and after their completion, an ammonia removal step took place (by vacuum distillation). The different combinations of AAS parameters tested are shown in Table 1.5.2.1. Biochemical Methane Potential (BMPs) tests of the AAS-treated fibers were set up for monitoring the CH_4 production during anaerobic digestion. In order to compare the CH_4 yield of the pretreated to the raw fibers, BMP tests were set up with non-pretreated (NP) raw swine manure fibers. All BMP tests were set up in triplicate. The inoculum used for the tests originated from an industrial biogas plant processing animal manures (pig and cow) and organic residues.

Table 1.5.2.1 Experiments under different conditions of Aqueous Ammonia Soaking on raw swine manure fibers

N° of Experiment	Central Composite Design point (Fig.1)	A - Ammonia concentration (%w/w)	D - Duration (hours)	SL - Solid to Liquid ratio (100g fibers/ml reagent)
1	cube	7	28	16
2	cube	25	28	16
3	cube	7	96	16
4	cube	25	96	16
5	cube	7	28	28
6	cube	25	28	28
7	cube	7	96	28
8	cube	25	96	28
9	axial	0,9	62	22
10	axial	31,1	62	22
11	axial	16	4,8	22
12	axial	16	119,2	22
13	axial	16	62	12
14	axial	16	62	32
15	center	16	62	22
16	center	16	62	22
17	center	16	62	22

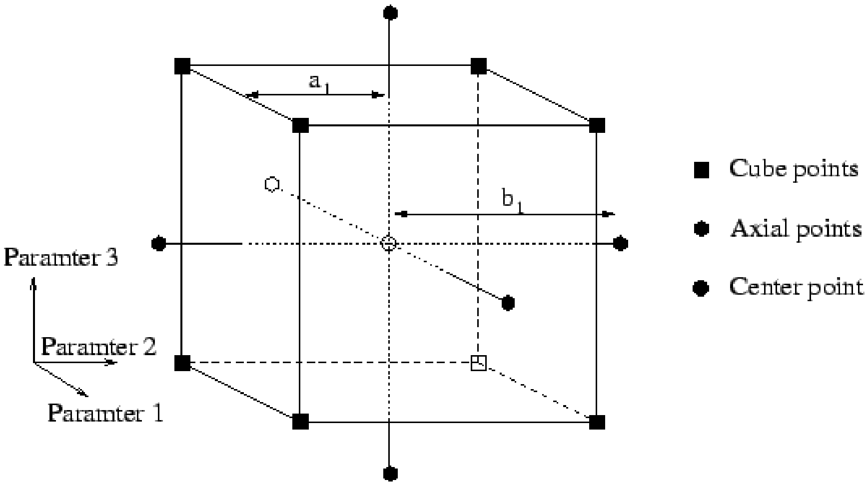

Figure 1.5.2.1 Central composite design straucture

The recorded cumulative CH_4 yield of the 17 experiments (18 including the NP fibers) expressed in ml of CH_4 per gram of Total Solids (TS) are shown in Figure 1.5.2.2. As it can be seen in Fig. 1.5.2.2, all BMP tests of AAS-pretreated manure fibers performed better than NP fibers by producing more CH_4. The experiments lasted 38 days, duration after which no further CH_4 production was detected. The cumulative CH_4 yield after 38 days of NP fibers was 91ml/g TS while the AAS-treated fibers yielded from 152 – 230 ml/g TS corresponding to an increase of 59% up to 176% compared to NP fibers. The AAS-treatment that produced the least increase of CH_4 yield is experiment 9, an axial point of the experimental region, corresponding to the lowest NH_3 concentration (0,9% w/w) and the middle values of duration and solid-to-liquid ratio (62 hours and 0,22 g/ml respectively). The AAS-treatment that performed better was experiment 3, a cube point, where the fibers were treated with 7% w/w NH_3 (aq.), for 4 days (96 hours) at a solid-to-liquid ratio of 0,16 g/ml.

In Fig. 1.5.2.2 it can be viewed that except experiment 3 that performed clearly better than any other experiment and except the NP fibers, two groups of experiments have been formed after 17 days of digestion. The group that performed poorer contains experiments 1, 5, 9 and 11 and the rest of experiments form another group that performed better. Regarding the first group, experiments 1 and 5 have been performed at the lowest cube-point NH_3 concentration (7% w/w) and for the lowest cube-point duration (28 hours). Experiment 9 seems to have been affected by the very low NH_3 concentration regardless the duration as it corresponds to an axial point. On the other hand, in experiment 11 the fibers were treated with the middle value of NH_3 (16% w/w) although for a very short time (4,8 h) as it corresponds to the low axial point of the design for duration. Based on these observations it appears that a strong correlation between NH_3 concentration and duration exists, in a way that a low NH_3 concentration requires a large duration (as also indicated by experiment 3) and vice versa.

The above experimental data were further analyzed with the use of statistical software (The Unscrambler) scoping to build a model that could predict the CH_4 yield of AAS-treated fibers depending on the conditions under which the pretreatment takes place. Response Surface methodology (RSM) was used for this purpose and for plotting the effects of the three parameters on CH_4 yield. The generic form of the modeled response y (CH_4) for the chosen experimental design is:

$$y = b_0 + \sum b_i x_i + \sum b_{ij} x_i x_j + \sum b_{ii} x_i^2 \qquad (1)$$

Where b_0, b_i, b_{ij}, b_{ii} are the regression coefficients for the intercept, linear, interaction and quadratic effects respectively and x_i, x_j are the independent variables (A, D and SL).

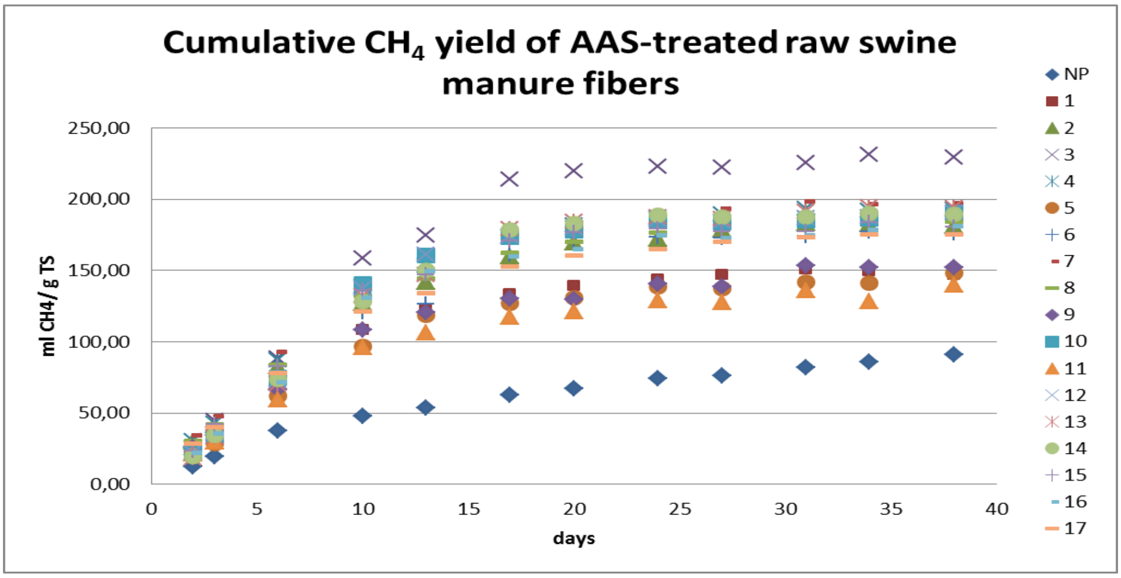

Figure 1.5.2.2 Cumulative CH4 yield resulted from BMP tests of raw manure fibers treated under different conditions of Aqueous Ammonia Soaking pretreatment. The numbers of experiments are explained in Table 1.5.2.1.

In figures 1.5.2.3, 1.5.2.4 and 1.5.2.5 the response surface of A-D, A-SL and D-SL are shown respectively for CH_4 yield at 17 days of digestion. According to the Response Surface plot (Fig. 1.5.2.3), the optimal conditions of AAS-treated raw manure fibers for maximizing the CH_4 yield after 17 days of digestion are located in the following ranges of parameters: 7-16% w/w NH_3 (aq.), 88-96 hours of duration of the pretreatment and 0,16 – 0,17 g of fibers to ml of NH_3 (aq.) solution. By defining one of the three parameters constant, then the ranges of the two parameters left become narrower. It is clear though that based on the performed experiments the maximum response corresponds to 7% w/w NH_3 concentration, 96 hours of duration and at a solid-to-liquid ratio of 0,16 g/ml. The predicted CH_4 yield under these conditions corresponds to 201ml CH_4 /g TS, which is lower than the actual value of 214ml CH_4/g TS produced after 17 days of digestion. This is expected as in RSM the effects are smoothened as the experimental results are expected to slightly vary when repeated.

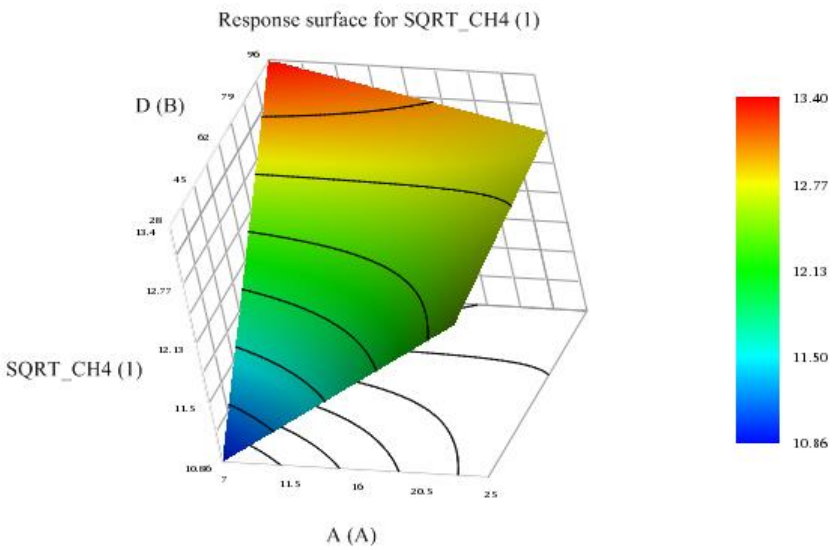

Figure 1.5.2.3 Response surface of parameters A (% w/w ammonia concentration) and D (days of duration of the pretreatment) with response $\sqrt{CH_4}$. The SL parameter (solid-to-liquid ratio) is set as constant at 0,22g of fibers per ml of NH_3 (aq.) solution. The red region corresponds to the maximum response, corresponding to the optimal ranges of the parameters.

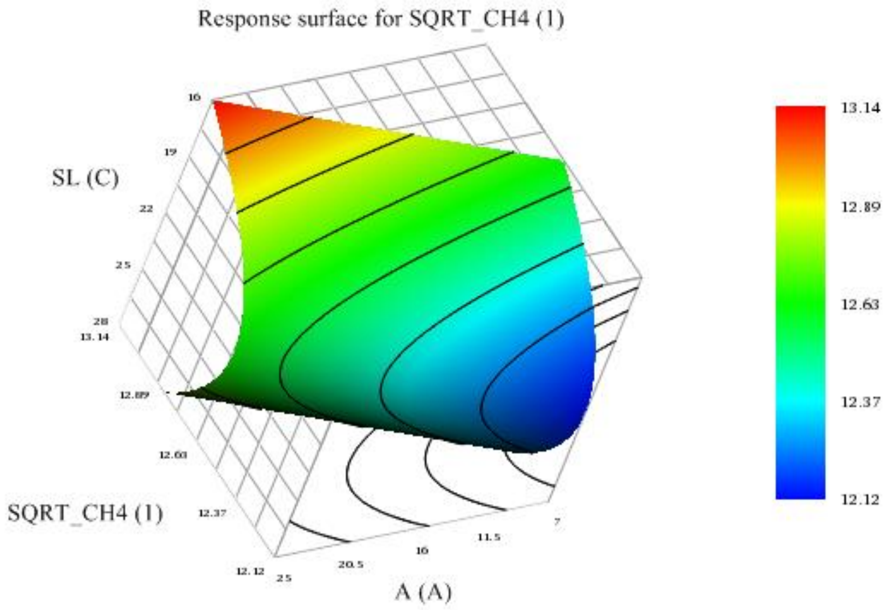

Figure 1.5.2.4 Response surface of parameters A (% w/w ammonia concentration) and SL (solid-to-liquid ratio) with response $\sqrt{CH_4}$. The D parameter (duration of pretreatment) is set constant at 62 hours. The red region corresponds to the maximum response, corresponding to the optimal ranges of the parameters.

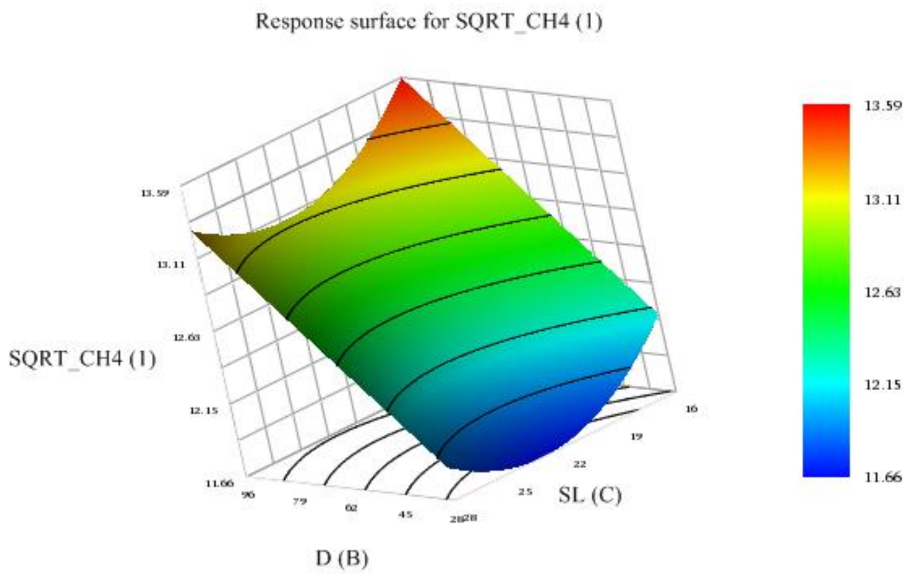

Figure 1.5.2.5 Response surface of parameters D (hours of duration of AAS) and SL (solid-to-liquid ratio) with response $\sqrt{CH_4}$. The A parameter (ammonia concentration) is set constant at 16% w/w. The red region corresponds to the maximum response, corresponding to the optimal ranges of the parameters.

After transformation of the response from ml CH_4/g TS to $\sqrt{CH_4}$ in order to better fit the data to the model, the quadratic equation obtained for predicting the response at 17 days of digestion of AAS-treated raw manure fibers is:

$$\sqrt{CH_4} = 12{,}3876 + 0{,}256x_1 + 0{,}7085\, x_2 - 0{,}5636\, x_1\, x_2 + 0{,}3495\, x_3^2 \quad (2)$$

Where:
x_1: coded value of A, the NH3 concentration of the reagent
x_2: coded value of D, the duration of the pretreatment
x_3: coded value of SL, the solid-to-liquid ratio at which the pretreatment takes place
In equation (2) only the effects that resulted to be significant to the response (p-value ≤ 1) are included, namely the linear effect of A (p-value = 0,0649), the linear effect of D (p-value

= 0,0005), the interaction effect between A and D (p-value = 0,0078) and the quadratic effect of SL (p-value = 0,0647). The model is significant for a p-value of 0,0004 and in combination with the p-value of lack-of-fit (p-value = 0,40) it is indicated that the model can be trusted for prediction. The fit of the experimental data to the model is R^2 = 0,84, while of the prediction is R^2 = 0,63.
The above quadratic equation is the result of the preliminary analysis of the experimental data. Further investigation of the nature of the relation of the response will be conducted in order to improve the R^2 of the prediction. This will be achieved by testing different transformations of the response and/or the independent parameters. After conclusion of the model describing satisfactorily the response, validation will take place.
The present results indicate that there is some flexibility on choosing operational conditions for the AAS pretreatment, as the ranges of the parameters found to be optimal are relatively wide. In conclusion, for maximizing the CH_4 yield of raw swine manure fibers focus should be given in low NH_3 concentrations and solid-to-liquid ratios and high durations. The low solid-to-liquid ratio might result to larger reactor volumes, although it facilitates the NH_3 distillation and thus the NH_3 recycling. After the final quadratic model of CH_4 yield of AAS-treated raw manure fibers is concluded, it will be used as a useful tool for assisting the further design of the process.

1.5.3 Statistical Optimization of parameters affecting the CH4 yield of Aqueous-Ammonia-soaked raw swine manure fibers [Further investigation of the possible empirical models]

Following the successful implementation of the statistical optimization of the parameters of Aqueous Ammonia Soaking (AAS) of swine manure fibers on the CH_4 yield (reported in the section 1.5.2 above), further investigation of the possible empirical models was conducted. Based on the results obtained it was decided to proceed with a second step of optimization experiments. In the following, both the final model of the 1st series of experiments is presented, as well as a detailed presentation of the results of the 2nd step of optimization. As a result of this two-step optimization process, the optimum conditions of AAS of swine manure fibers are concluded.
<u>First step of Optimization of AAS of swine manure fibers</u>
In order to conclude on the most significant model of the 1st Central Composite Design conducted (section 1.5.2), the statistical software Design Expert 9 was used that is specialized on optimization designs. Based on the significance of the statistical tests performed on the modelled data, the final model that predicts the CH_4 yield of the swine manure fibers treated with AAS under different conditions satisfactorily is:

$$\boldsymbol{CH_4\ 17d} = 195{,}499 + 3{,}774 * \boldsymbol{A} + 1{,}328 * \boldsymbol{D} - 1176{,}160 * \boldsymbol{SL} - 0{,}050 * \boldsymbol{A} * \boldsymbol{D} + 2540{,}255 * \boldsymbol{SL}^2 \quad (\textbf{\textit{eq.1}})$$

Where:
$\boldsymbol{CH_4\ 17d}$, corresponds to the CH_4 yield of AAS-treated fibers after 17 days of digestion, expressed in ml /g Total Solids (TS)
$\boldsymbol{A}$, corresponds to the level of NH_3 concentration of the reagent used for AAS, expressed in % w/w in water
$\boldsymbol{D}$, corresponds to the duration of the AAS pretreatment, expressed in hours
$\boldsymbol{SL}$, corresponds to the solid-to-liquid ratio at which the pretreatment takes place, expressed in g fibers / ml reagent

In table 1.5.3.1, the results from the ANOVA test of the model are presented, where the *p values* of the significant terms included in the model can be seen. According to the table, the model constructed (*eq.1*) is statistically highly significant (*p = 0,0001*), while the fit of the data to the model is satisfactory ($R^2 = 0{,}84$) and the lack of fit of the data to the model was found to be insignificant (*p = 0,4177*). The adjusted R^2 is 0,77, which is close to the R^2 of the data, indicating that the terms included in the final model are sufficient. The effects that were found to influence mostly the CH_4 yield of the treated fibers are, the duration of AAS ($p < 0{,}0001$), the interaction effect of A and D ($p = 0{,}0020$) and the quadratic effect of SL (*p* =

0,0086). Although the main effects of A and SL on the CH_4 yield do not contribute much on the prediction of CH_4 yield, these were left in the model for respecting the hierarchy of the quadratic model. The values of the CH_4 yield of the experiments as predicted by the model are shown in Table 1.5.3.2, where they can be compared to the actual values obtained from the experiments.

Table 1.5.3.2 ANOVA table of the 1st model as resulted from the 1st Central Composite Design followed for the optimization of AAS of swine manure fibers

ANOVA for Response Surface Reduced Quadratic model						
Analysis of variance table [Partial sum of squares – Type III]						
Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	8230.59	5	1646.12	13.26	0.0001	significant
A-A	*537.38*	*1*	*537.38*	*4.33*	*0.0578*	
B-D	*4494.06*	*1*	*4494.06*	*36.20*	*< 0.0001*	
C-SL	*167.95*	*1*	*167.95*	*1.35*	*0.2657*	
AB	*1845.02*	*1*	*1845.02*	*14.86*	*0.0020*	
C^2	*1186.18*	*1*	*1186.18*	*9.56*	*0.0086*	
Residual	1613.70	13	124.13			
Lack of Fit	*1210.30*	*9*	*134.48*	*1.33*	*0.4177*	*not significant*
Pure Error	*403.40*	*4*	*100.85*			
Cor Total	9844.29	18				

In Figure 1.5.3.1, the Response Surface graph of the modelled system is presented, where the surface represents the predicted value of the CH_4 yield as a function of the duration of AAS (D) and the NH_3 concentration of the reagent (A). The solid-to-liquid ratio (SL) is set constant to its optimum value (0,16 g/ml) as it was found not to interact with the rest of AAS parameters (interaction terms between A and SL, and D and SL gave a *p value> 0,0500*).

Table 1.5.3.3 Actual values of CH_4 yield of AAS-treated fibers as compared to the predicted values by the 1st model

Nº of experiment	**A (% w/w)**	**D (hours)**	**SL (g fibers/ ml reagent)**	**Actual Value – ml CH_4/g TS**	**Predicted Value – ml CH_4/g TS**
5	7	28	0,28	126,84	119,19
11	16	4,8	0,22	117,38	122,65
1	7	28	0,16	126,63	126,21
9	0,9	62	0,22	130,06	142,61
19	16	62	0,22	155,48	153,15
16	16	62	0,22	159,66	153,15
15	16	62	0,22	170,74	153,15
18	16	62	0,22	143,15	153,15
17	16	62	0,22	153,11	153,15
6	25	28	0,28	160,87	162,11
10	31,1	62	0,22	173,60	163,70
8	25	96	0,28	162,47	168,02
2	25	28	0,16	159,56	169,13
14	16	62	0,32	178,48	173,12
4	25	96	0,16	173,23	175,03
12	16	119,2	0,22	174,29	183,66
13	16	62	0,12	179,05	184,92
7	7	96	0,28	176,27	185,85
3	7	96	0,16	213,96	192,86

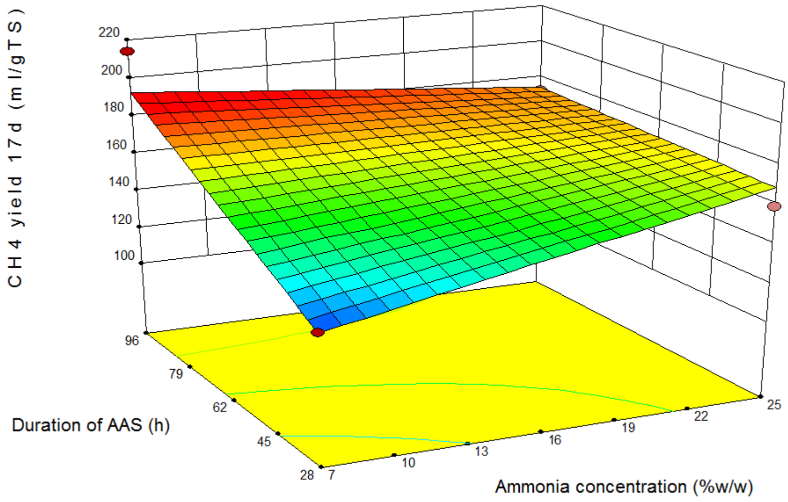

Figure 1.5.3.1 Response Surface graph of 1st optimization model predicting the CH_4 yield of AAS-treated fibers as a function of the duration of AAS and of the NH_3 concentration of the reagent. The solid-to-liquid ratio is set constant at 0,16 g/ml of reagent.

According to equation 1, the optimum conditions of AAS that result in maximum CH_4 yield of swine manure fibers after 17 days of digestion correspond to 7 % w/w of NH_3 (aq.) in the reagent, 96 hours of pretreatment and 0,16 g fibers / ml of reagent. This can also be observed from the Response Surface graph (Fig. 1.5.3.1) where the red color corresponds to the highest CH_4 yield predicted. Given that these conditions correspond to the limits of the experimental region, it was decided to continue with a second set of optimization experiments towards lower NH_3 concentrations and higher durations, in order to investigate if any further increase of CH_4 yield could be obtained at such conditions.

Second step of Optimization of AAS of swine manure fibers

A second CCD was followed where A and D levels were further investigated, while the SL ratio was kept constant at its optimum value (0,16 g /ml reagent). The levels of the parameters are shown in Table 1.5.3.3. According to this design, swine manure fibers were treated by AAS under 9 different combinations of NH_3 concentration and duration of AAS, comprising of 4 cube points, 4 axial points and 1 center point, replicated 4 times (12 experiments in total). After the finalization of the AAS pretreatment, the NH_3 concentration of each batch was reduced to less than 1 g/l by vacuum distillation. Subsequently the different batches were used for setting Biochemical Methane Potential (BMPs) tests, during which the CH_4 production was monitored through Gas Chromatography. The inoculum used for the BMPs originated from the same industrial-scale digester (Hashøj biogas) as the one used at the first series of optimization experiments. The main composition of the manure fibers used was 32,51 % TS and 22,43 % Volatile Solids (VS).

Table 1.5.3.4 Experimental levels of AAS parameters of 2nd Central Composite Design

Parameter of AAS	Low level	Center level	High level
	-1	**0**	**1**
A -NH_3 concentration (% w/w)	1	4	7
D – Duration of AAS (hours)	96	120	144

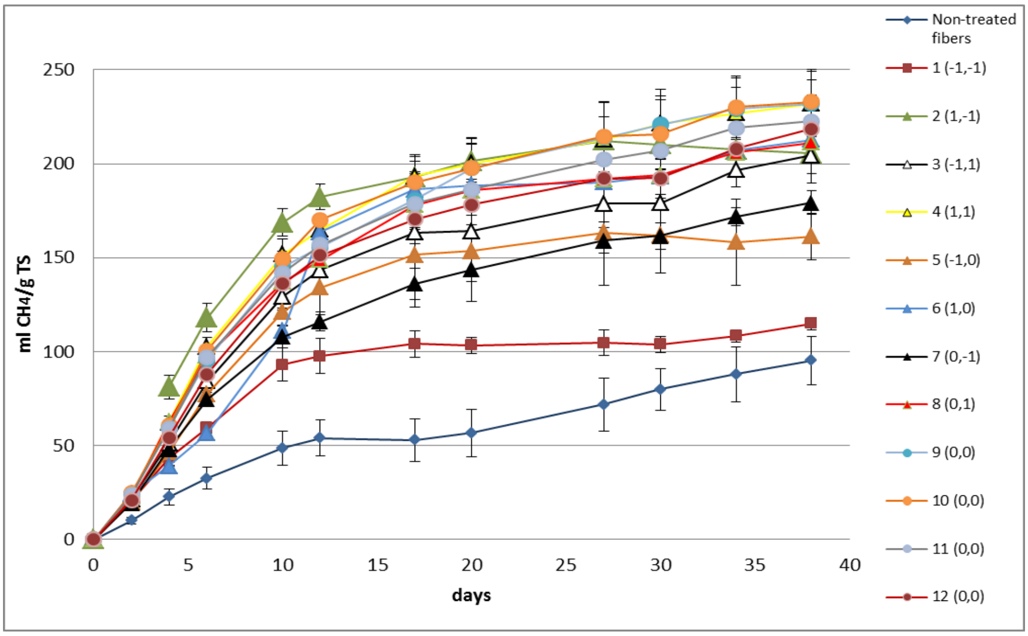

Figure 1.5.3.2 Cumulative CH_4 yields of experiments run according to the 2nd Central Composite Design. Each number corresponds to a different AAS pretreatment of manure fibers, while in parentheses the levels of (A,D) are given based on the design of Table 3.

The cumulative CH_4 yields obtained from the 2nd CCD are presented in Figure 1.5.3.2. As observed in the figure, all pretreated manure fibers resulted in a higher CH_4 yield during the digestion experiments as compared to the non-treated fibers, regardless the conditions of AAS. The CH_4 yields obtained after 17 days of digestion were inserted to the Design Expert software for constructing a model able to predict the CH_4 yield of the treated fibers in the range of the 2nd step of optimization.

The 2nd empirical model constructed from the second step of optimization experiments is:

$$\boldsymbol{CH_4\,17d} = -52{,}409 + 33{,}809 * \boldsymbol{A} + 1{,}519 * \boldsymbol{D} - 0{,}203 * \boldsymbol{A} * \boldsymbol{D} \qquad \textbf{(eq.2)}$$

Where:

$\boldsymbol{CH_4\,17d}$, corresponds to the CH_4 yield of AAS-treated fibers after 17 days of digestion, expressed in ml /g TS

$\boldsymbol{A}$, corresponds to the level of NH_3 concentration of the reagent used for AAS, expressed in % w/w in water

$\boldsymbol{D}$, corresponds to the duration of the AAS pretreatment, expressed in hours

$\boldsymbol{SL}$, corresponds to the solid-to-liquid ratio at which the pretreatment takes place, expressed in g fibers/ml reagent

According to the ANOVA test run for the construction of this model (Table 1.5.3.4), the empirical model is statistically significant ($p = 0{,}0011$), while the effects found to be more influencing on the response (CH_4 yield after 17 days of digestion) are the main effect of A ($p = 0{,}0006$), the main effect of the D ($p = 0{,}0110$) and the interaction effect of A and D ($p = 0{,}0485$). The quadratic effects of A and D were found not to have a significant effect on the CH_4 yield of treated fibers ($p > 0{,}0500$). This was expected based on the observations from the first step of optimization, were these terms were found to be insignificant. The fit of the data on the 2nd model was very satisfactory, $R^2 = 0{,}85$, and in good agreement with the *adjusted* $R^2 = 0{,}80$. Thus, the model can be trusted for prediction. A comparison of the predicted values of CH_4 yields of the experimental points and the real values obtained is given at Table 1.5.3.5.

Table 1.5.3.5 ANOVA table of the 2nd model as resulted from the 2nd Central Composite Design followed for the optimization of AAS of swine manure fibers

ANOVA for Response Surface 2FI model						
Analysis of variance table [Partial sum of squares - Type III]						
Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	7352.74	3	2450.91	15.45	0.0011	significant
A-A	*4773.74*	*1*	*4773.74*	*30.09*	*0.0006*	
B-D	*1721.25*	*1*	*1721.25*	*10.85*	*0.0110*	
AB	*857.76*	*1*	*857.76*	*5.41*	*0.0485*	
Residual	1269.06	8	158.63			
Lack of Fit	*1074.10*	*5*	*214.82*	*3.31*	*0.1770*	*not significant*
Pure Error	*194.97*	*3*	*64.99*			
Cor Total	8621.81	11				

The Response Surface graph of the 2nd empirical model is shown in Figure 1.5.3.3. As it can be seen from this graph, reducing the NH_3 concentration of the reagent down to 1 % w/w, affects highly the CH_4 yield transforming this factor to a critical one. The optimum NH_3 concentration corresponds to 7 % w/w, where the maximum CH_4 yield is predicted (red color indication). Regarding the duration of AAS, it is still a critical factor only when the NH_3 concentration is under 5 % w/w. At optimum concentration of NH_3 (7 % w/w), no significant difference of the CH_4 yield is predicted between 96-144 hours (5 ml/g TS based on the prediction of the model and 1 ml/g TS obtained experimentally). Consequently, 96 hours (4 days) could be concluded to be the optimum value for the duration of AAS.

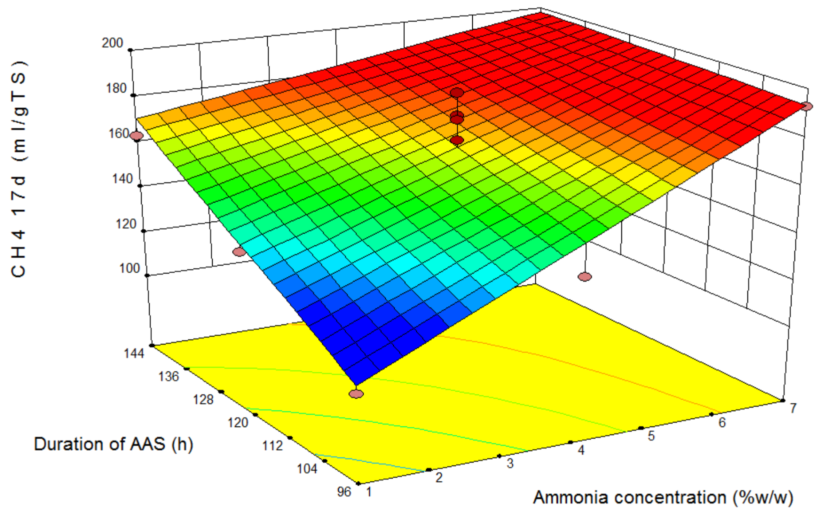

Figure 1.5.3.3 Response Surface graph of the 2nd optimization model predicting the CH_4 yield of AAS-treated fibers as a function of the duration of AAS and of the NH_3 concentration of the reagent.

Table 1.5.3.6 Actual values of CH_4 yield of AAS-treated values as compared to the predicted values by the 2nd model

N° of experiment	**A (% w/w)**	**D (hours)**	**Actual Value ml CH_4/g TS**	**Predicted Value – ml CH_4 / g TS**
1	1	96	104,17	107,72
5	1	120	135,75	139,31
7	4	96	136,14	150,57
10	4	120	190,09	167,51

9	4	120	180,85	167,51
12	4	120	170,45	167,51
11	4	120	178,86	167,51
3	1	144	163,30	170,89
8	4	144	178,07	184,45
2	7	96	192,85	193,43
6	7	120	186,19	195,72
4	7	144	193,41	198,01

Conclusions on Optimization of AAS of swine manure fibers

Two experimental designs were followed for optimizing AAS of swine manure fibers (CCDs), with the purpose to find the optimum conditions of the most influencing parameters of AAS that result to maximum CH_4 yield of treated manure fibers. The most influencing effects of AAS on the CH_4 yield were found to be the NH_3 concentration of the reagent (A), the duration of the pretreatment (D), the interaction between these two factors (A*D), and the quadratic effect of the solid-to-liquid ratio (SL^2). The conditions of operation of AAS found to be optimum for the performance of the pretreatment of swine manure fibers were found to be: 7 % w/w NH_3 (aq.), 4 days of AAS duration (96 hours) and 0,16 g fibers / ml reagent. Two empirical models were constructed (eq.1 and eq.2) able to predict the CH_4 yield of AAS-treated manure fibers after 17 days of digestion as a function of the levels of A, D and SL of AAS applied. These models can be used for a thorough techno-economic analysis, for comparing the performance of the system and concluding on the conditions of AAS to be applied prior to scaling up the process. According to the models the prediction of the CH_4 yield under optimum conditions corresponds to 192,86 ± 11,14 ml/g TS (eq.1) and 193,43 ± 12,59 ml/g TS. In order to validate the models, experiments under optimum conditions were repeated and the results were in line with the predictions, 190,05 ± 6,70 ml/g TS. Taking into account all the experiments run under optimum conditions (1st CCD, experiment 3, 2nd CCD experiment 2 and Validation experiments) the average CH_4 yield observed was 198,95 ± 9,49 ml/g TS, corresponding to an impressive 240 % increase of the CH_4 yield as compared to the non-treated manure fibers in only 17 days of digestion.

For more detailed results relevant to sections 1.5.2 and 1.5.3, see attached publications:

- ✓ Lymperatou, A., Gavala, H.N. Esbensen, K.H., Skiadas, I.V. "Screening for the important variables of aqueous ammonia soaking as a pretreatment method for enhancing the methane production from swine manure fibers" Extended Abstract in Proceedings of 14th World Congress on Anaerobic Digestion, 2015
- ✓ Lymperatou, A., Gavala, H.N., Skiadas, I.V."Optimization of Aqueous Ammonia Soaking of manure fibers by Response Surface Methodology for unlocking the methane potential of swine manure" Bioresource Technology, 244, p.509-516, 2017.

1.5.4 Optimization of Aqueous Ammonia Soaking of Wheat Straw [Optimal conditions for the treatment of straw (Milestone 1.2)]

Similarly to the strategy for optimizing the AAS pretreatment of swine manure fibers, a Central Composite Design was followed for optimizing AAS of wheat straw. In total 15 different combinations of AAS were applied to wheat straw, according to the levels of the parameters of AAS as resulted from the CCD shown in Table 1.5.4.1. The center point of the design was replicated 6 times in order to have an estimation of the standard deviation of the whole process. Prior to the pretreatment the wheat straw was cut with a cut mill Retsch 2000 and sieved to pass through a 6 mm sieve. Subsequently it was used for performing the different combinations of AAS at ambient temperature. After the duration of each pretreatment has finalized, each mixture of wheat straw and aqueous ammonia solution passed through a vacuum distillation process for reducing the NH_3 concentration to below inhibitory levels. Finally, the differently pretreated batches were used for setting up BMP tests at mesophilic conditions (37°C) and the CH_4 production was monitored through Gas Chromatography. The inoculum used for the BMP tests originated from a 3l laboratory digester fed with swine manure. All BMP tests were performed in triplicates and non-treated wheat straw was used as control. The main composition of the wheat straw used was 93,60 % TS and 89,60 % VS.

Table 1.5.4.1 *Central Composite Design followed for optimization of AAS of Wheat Straw*

Parameter of AAS	Low level	Center level	High level
	-1	**0**	**1**
A -NH_3 concentration (% w/w)	1	16,5	32
D - Duration of AAS (days)	1	4	7
SL - solid-to-liquid ratio in g wheat straw/l reagent	50	75	100

The cumulative CH_4 yields of the optimization experiments are shown at Figure 1.5.4.1. The BMP tests lasted 66 days, although approximately after 42 days of digestion the further CH_4 production of the majority of experiments was minor. Interestingly, not all pretreated straws yielded more CH_4 than the non-treated. As observed in Fig. 1.5.4.1, experiment N° 13 yielded significantly less than RWS1 and RWS2. Nevertheless, the rate of CH_4 production during the first days of digestion has been positively affected by all pretreatment conditions. As wheat straw is proposed for AAS pretreatment for co-digestion with livestock manure, and as an alternative to AAS-treated manure fibers in order to provide some flexibility to biogas plant operation, the same duration of digestion was chosen to be modelled (17 days) as in the case of manure fibers.

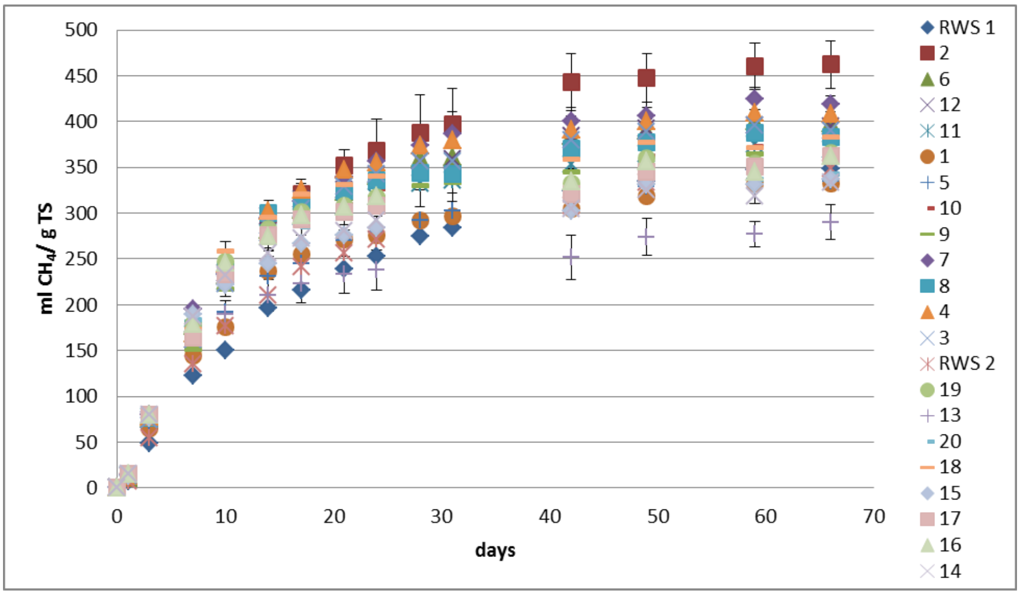

Figure 1.5.4.*1 Cumulative CH_4 yields of AAS-treated wheat straw; the numbers correspond to the different conditions of AAS applied as presented in Table* 1.5.4.3*, and RWS stands for Raw Wheat Straw (non-treated straw)*

The CH_4 yields of AAS-treated wheat straws were inserted to the statistical software Design Expert 9, in order to produce an empirical model. The ANOVA test of the model constructed is shown in Table 1.5.4.2 and was found to be highly significant ($p < 0,0001$). The effects that were found to be most influencing on the CH_4 yield of the treated wheat straw were the main effect of A ($p =0,0001$), the main effect of D ($p =0,0006$), the interaction effect between these two factors ($p =0,0075$), the quadratic effect of A ($p = 0,0003$) and the quadratic effect of SL ($p = 0,0010$). The fit of the experimental data to the model was very satisfactory with $R^2 = 0,89$ and in good agreement with the adjusted $R^2 = 0,83$. The predicted CH_4 yields of the experimental points in comparison to the actual values obtained from the experiments can be viewed in Table 1.5.4.3.

The empirical model constructed that can be used for prediction of the CH_4 yield of AAS-treated wheat straw after 17 days of digestion is:

$$\boldsymbol{CH_4\ yield\ 17d} = 442{,}795 + 6{,}781 * \boldsymbol{A} + 9{,}939 * \boldsymbol{D} - 6{,}583 * \boldsymbol{SL} - 0{,}272 * \boldsymbol{A} * \boldsymbol{D} - 0{,}134 * \boldsymbol{A}^2 + 0{,}044 * \boldsymbol{SL}^2$$

(**eq.3**)

Where:

$\boldsymbol{CH_4\ 17d}$, corresponds to the CH_4 yield of AAS-treated fibers after 17 days of digestion, expressed in ml /g TS

$\boldsymbol{A}$, corresponds to the level of NH_3 concentration of the reagent used for AAS, expressed in % w/w in water

$\boldsymbol{D}$, corresponds to the duration of the AAS pretreatment, expressed in days

$\boldsymbol{SL}$, corresponds to the solid-to-liquid ratio at which the pretreatment takes place, expressed in g fibers/l of reagent

Table 1.5.4.2 *ANOVA table of the empirical model constructed (eq. 3) for the prediction of CH_4 yield of AAS-treated wheat straw*

ANOVA for Response Surface Reduced Quadratic model						
Analysis of variance table [Partial sum of squares - Type III]						
Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Block	1159.33	1	1159.33			
Model	11404.79	6	1900.80	15.38	< 0.0001	significant
A-Ammonia	*3809.40*	*1*	*3809.40*	*30.81*	*0.0001*	
B-Duration	*2681.79*	*1*	*2681.79*	*21.69*	*0.0006*	
C-S:L ratio	*0.78*	*1*	*0.78*	*6.342E-003*	*0.9378*	
AB	*1275.59*	*1*	*1275.59*	*10.32*	*0.0075*	
A^2	*3169.86*	*1*	*3169.86*	*25.64*	*0.0003*	
C^2	*2279.36*	*1*	*2279.36*	*18.44*	*0.0010*	
Residual	1483.47	12	123.62			
Lack of Fit	*1010.37*	*8*	*126.30*	*1.07*	*0.5103*	*not significant*
Pure Error	*473.10*	*4*	*118.27*			
Cor Total	14047.59	19				

The Response Surface graph of the model (eq.3) is shown in Figure 1.5.4.2, where the surface represents the CH_4 yield of the treated straw as predicted from the model and as a function of the duration of AAS (D) and of the NH_3 concentration of the reagent (A). The SL ratio is set to its optimum value (50 g/l reagent), as it was found not to interact with A and D.

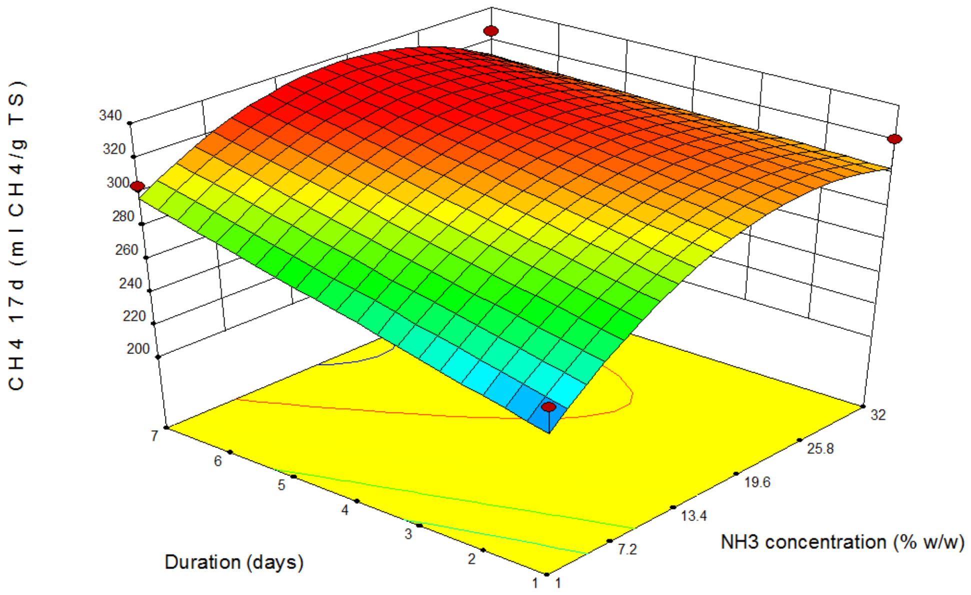

Figure 1.5.4.2 *Response Surface graph of the model (eq.3) of CH_4 yield as a function of NH_3 concentration and duration of AAS*

Based on the Response Surface, it can be seen that middle levels of A are more favorable for high CH_4 yield (red color indication) in combination to high D and according to the model, the optimum conditions for operation of AAS of wheat straw are approximately 18 % w/w NH3 (aq.), 7 days of pretreatment duration and 50 g wheat straw / l of reagent. The prediction of the model of the CH_4 yield under these conditions corresponds to 337,04 ± 11,12 ml / g TS, while validation experiments under these conditions that were run three times, yielded an average of 325,87 ± 16,74 ml CH_4/ g TS, corresponding to an increase of 48% of the CH_4 yield as compared to non-treated wheat straw.

Table 1.5.4.3 *Comparison of Actual values of CH_4 yield of experimental points of AAS-treated wheat straw and predicted values by the model (eq.3)*

N° of experiment	**A (% w/w)**	**D (days)**	**SL (g wheat straw/ l reagent)**	**Actual Value – ml CH_4/g TS**	**Predicted Value – ml CH_4/g TS**
13	1	4	75	223,40	232,04
5	1	1	100	245,29	247,72
1	1	1	50	254,67	248,28
15	16,5	1	75	266,41	267,47
14	32	4	75	271,96	271,07
19	16,5	4	75	301,25	292,64
20	16,5	4	75	285,51	292,64
16	16,5	7	75	297,71	300,22
12	16,5	4	75	315,29	292,64
9	16,5	4	75	291,00	292,64
10	16,5	4	75	296,56	292,64
11	16,5	4	75	295,14	292,64
7	1	7	100	312,25	305,73
3	1	7	50	304,45	306,29
18	16,5	4	100	321,28	310,95
17	16,5	4	50	293,42	311,51
6	32	1	100	303,18	312,01
2	32	1	50	320,60	312,57
8	32	7	100	313,92	319,51
4	32	7	50	325,59	320,07

Conclusions on Optimization of AAS of wheat straw

The important parameters of AAS were optimized for application on wheat straw in order to maximize the CH_4 yield under mesophilic conditions. The effects that were found to be most influencing on the performance of AAS on wheat straw were found to be the same with the ones observed for manure fibers, namely the NH_3 concentration of the reagent (A), the duration of the pretreatment (D), the interaction between these two factors (A*D), and the quadratic effect of the solid-to-liquid ratio (SL^2), accompanied by a strong quadratic effect of the NH_3 concentration (A^2). This distinction explains why the optimum NH_3 concentration was found to be ca. 18 % w/w, significantly higher than 7 %w/w that was found to be the optimum for manure fibers. The optimum duration of AAS on wheat straw was found to be 7 days and the solid-to-liquid ratio at 50 g wheat straw / l of reagent. An empirical model was constructed (eq. 3) able to predict the CH_4 yield of AAS-treated wheat straw after 17 days of digestion. The maximum predicted CH4 yield of AAS-treated wheat straw at the above-mentioned conditions is 337,04 ± 11,12 ml / g TS and was found to be in good agreement with the validation experiments. The maximum increase of CH_4 yield obtained from AAS treatment on wheat straw corresponded to 48 % as compared to non-treated wheat straw. This increase is significantly lower than the one achieved on manure fibers (240%) as expected, given that AAS appears to be more suitable on more recalcitrant to digestion biomasses. Nevertheless, wheat straw is a residual biomass that is available in large quantities in agricultural systems, consisting of a high biogas potential and thus presents a good candidate for the AMMONOX process.

For more detailed results relevant to sections 1.5.4, see attached publication:
Lymperatou, A., Gavala, H.N., Skiadas, I.V. "Optimization of Aqueous Ammonia Soaking at ambient temperature for Enhancing the Methane Yield of Wheat Straw", Submitted for publication.

1.5.5 Estimation of the effects of AAS on the composition of treated biomasses

In previous experiments, Aqueous Ammonia Soaking (AAS) was optimized regarding the most important parameters affecting the CH_4 yield of the pretreated biomasses, namely raw manure fibers and wheat straw. As a continuation of this work, the raw (non-treated) biomasses and the optimally AAS-treated biomasses were analyzed for estimating the effects of AAS on their composition and for assisting further configuration of the AMMONOX process.

The preparation and compositional analyses of the biomasses was performed following the Protocols of NREL. A brief description of the procedure followed for all biomasses is presented in continuation.

Pretreatment and Sample preparation.
Both biomasses were pretreated with AAS under the conditions found to be optimum for maximizing the CH_4 yield. The manure fibers were pretreated with 7 % w/w NH_3 for 4 days at a solid-to-liquid ratio of 0,16 g/ml reagent, and wheat straw was pretreated with 18 % w/w NH_3 for 7 days at a solid-to-liquid ratio of 0,05 g/ml reagent. Raw manure fibers as well as AAS-pretreated manure fibers and AAS-pretreated wheat straw were dried at 45°C, while raw wheat straw was not subjected to drying due to the already high dry matter content. Once the biomasses fulfilled the minimum dry matter requirements (90%) for the compositional analysis, they were grounded to 1mm by means of an IKA micro-grinder (IKA, MF 10.1; IKA®-Werke GmbH).

Determination of Extractives.
In order to quantify the total carbohydrate and lignin content in the biomasses with minimum bias, the biomasses were subjected to a two-step extraction process; initially an extraction for 6 hours with water took place and subsequently an exhaustive extraction for 24-hours with 96% v/v ethanol. A Soxhlet apparatus (Gerhardt, Germany) was used for this purpose. Determination of total extractives and volatiles was based on the loss of mass of the initial sample during the two-step extraction process according to the Protocol "Determi-

nation of extractives in biomass" (NREL/TP-510-42619). All analyses were performed at least in duplicates.

Determination of Carbohydrates and Lignin.

Once the biomasses were extracted, a two-step acid hydrolysis took place, according to the Protocol "Determination of structural carbohydrates and lignin in biomass" (NREL/TP-510-42618). Briefly, each extracted and dried sample was hydrolyzed at 30°C with 72% w/w sulfuric acid for 60 min. followed by a second hydrolysis step with weak acid (4% w/w sulfuric acid) at 121°C for 60 min. After the hydrolysis has finalized, the sample was vacuum-filtered through a filter crucible. The liquid fraction was used for structural carbohydrate quantification, while the solids remaining on the crucible were used for the Klason lignin determination.

Soluble carbohydrates were also determined in both raw and pretreated biomasses. The liquid fraction of the pretreated biomasses was centrifuged at 10,000 rpm for 10 min and filtered to pass through 0,45 μm. Subsequently, a weak acid hydrolysis took place (4%w/w sulfuric acid) at 121°C for 20 min. In order to quantify the soluble carbohydrates of the raw biomasses, water was added and the biomasses were left to soak for 24 hours. Afterwards, the same procedure as with the pretreated biomasses took place, as described above.

Free sugars in the liquid fraction of the pretreated biomasses and in the water fraction of the raw biomasses were quantified as well, after centrifugation of samples (10,000 rpm for 10 min.) and filtration through 0,22 μm. Samples were acidified with 0,1M H_2SO_4. Quantification of carbohydrates in the hydrolysates and of free sugars in the samples was done through High Performance Liquid Chromatography (BioRad AMINEX HPX-87H column, 12mM H_2SO_4 eluent).

The dry matter content of samples was determined as the mass of the sample remaining after drying at 105°C for 24 hours, and the remaining mass after igniting at 550°C for 3 hours was considered as ash.

Compositional Analysis of optimally AAS-treated swine manure fibers.

In Table 1.5.5.1 the results from the compositional analysis of raw manure fibers (RMF) and optimally AAS-treated manure fibers (AAS RMF) are shown. The total structural carbohydrate content of the AAS RMF was found to be less than the content of RMF. This reduction of structural sugars in AAS RMF is associated to the hemicellulosic fraction of the biomass, as only xylan and arabinan contents are reduced. Thus, it appears that AAS under optimum conditions produced partial solubilization of hemicellulose. This is also evident from the higher concentration of xylose and arabinose in the liquid fraction of the pretreated biomass (0,59 and 0,36 %DM respectively) as compared to the raw biomass (0,03%DM and no arabinose detected). Nevertheless, as the total content of sugars of AAS RMF is less than the content of RMF, further degradation of sugars might have occurred. The acid-insoluble lignin appears not to have been affected by the pretreatment, as the values of the two biomasses are equal. Reduction of the ash content is also observed as a result of the pretreatments, which is mainly associated to sand that is prawn to settling in the pretreatment vessel and is difficult to transfer.

Taking into account the amount of extractives of AAS RMF (13,06 ± 2,24 %DM) that is much higher than the extractives of RMF (9,10 ± 0,14 %DM), it can be concluded that no mass loss occurred. The extractives and volatiles include all degradation products from the pretreatment (oligosaccharides, free sugars, solubilized lignin if any, lipids, solubilized proteins) as well as inorganic components of the biomass (e.g. ammonium, sand, etc.).

Table 1.5.5.1 Composition of swine manure fibers – raw biomass and optimally AAS-treated

	Raw manure fibers	AAS-treated manure fibers
Dry matter (% wet mass)	**35,13 ± 1,76**	**3,14 ± 0,08**
Glucan (% DM)	27,20 ± 0,14	28,26 ± 1,04
Xylan (% DM)	16,04 ± 0,28	10,73 ± 0,46
Arabinan (% DM)	5,71 ± 0,20	3,14 ± 0,22

Total structural carbohydrates (% DM)	**48,95 ± 0,62**	**42,14 ± 1,71**
Klason lignin (% DM)	**16,30 ± 0,68**	**16,57 ± 0,82**
Extractives & volatiles* (% DM)	**9,10 ± 0,14**	**13,06 ± 2,24**
Free sugars (% DM)	**0,09 ± 0,00**	**0,09 ± 0,03**
Glucose (% DM)	0,09 ± 0,00	0,07 ± 0,02
Xylose (% DM)	n.d.	0,01 ± 0,00
Arabinose (% DM)	n.d.	0,01 ± 0,00
Soluble sugars (% DM)	**0,08 ± 0,00**	**1,14 ± 0,01**
Glucose (% DM)	0,14	0,28 ± 0,02
Xylose (% DM)	0,03	0,59 ± 0,04
Arabinose (% DM)	n.d.	0,36 ± 0,03
NH_4^+-N content (% DM)	0,37 ± 0,00	0,99 ± 0,00
Ash (% DM)	**32,62 ± 1,34**	**30,22 ± 1,54**

*n.d. stands for not detected

Compositional Analysis of optimally AAS-treated wheat straw.

Similarly as in the case of RMF, wheat straw was analyzed for determining the compositional changes due to the pretreatment. In table 1.5.5.2 the detailed composition of raw wheat straw (RWS) and optimally AAS-treated wheat straw (AAS WS) are shown. The pretreatment appears to have produced mainly the same effect on wheat straw as on manure fibers, i.e. the partial solubilization of hemicellulose. The xylan and arabinan content of AAS WS are significantly reduced (9,51 ± 0,44 %DM xylan and 1,08 ± 0,04 %DM arabinan) as compared to RWS (23,77 ± 1,18 %DM xylan and 3,26 ± 0,10 %DM arabinan) , and a large fraction of the difference is found in the form of soluble carbohydrates (oligosaccharides) in the liquid fraction of AAS WS (4,51 ± 0,02 % DM xylose and 1,14 ± 0,00 % DM arabinose). In the case of wheat straw a slight solubilization of lignin occurred, though considering the magnitude of the standard deviation it was not that significant (16,24 ± 0,73 %DM for RWS and 15,08 ± 0,95 %DM for AAS WS). The amount of extractives and volatiles, was found to be very high for both RWS and AAS WS, and the difference among them (14,58 ± 0,04 %DM for RWS and 20,73 ± 0,38 %DM for AAS WS) equals the amount of total soluble sugars found in the liquid fraction of AAS WS (6,36 ± 0,04 %DM). This indicates that no solubilization of other compounds occurred during the pretreatment of wheat straw.

Table 1.5.5.2 Composition of wheat straw – raw biomass and optimally AAS-treated

	Raw wheat straw	AAS-treated wheat straw
Dry matter (% wet mass)	**93,99 ± 0,14**	**3,70 ± 0,10**
Glucan (% DM)	41,07 ± 2,94	44,31 ± 1,29
Xylan (% DM)	23,77 ± 1,18	9,51 ± 0,44
Arabinan (% DM)	3,26 ± 0,10	1,08 ± 0,04
Total structural carbohydrates (% DM)	**68,10 ± 4,23**	**54,90 ± 1,69**
Klason lignin (% DM)	**16,24 ± 0,73**	**15,08 ± 0,95**
Extractives & volatiles* (% DM)	**14,58 ± 0,04**	**20,73 ± 0,38**
Free sugars (% DM)	**0,33 ± 0,01**	**0,10 ± 0,02**
Glucose (% DM)	0,14 ± 0,01	0,09 ± 0,00
Xylose (% DM)	0,19 ± 0,01	n.d.
Arabinose (% DM)	n.d.	0,01 ± 0,01
Soluble sugars (% DM)	**0,69 ± 0,12**	**6,36 ± 0,04**
Glucose (% DM)	0,31 ± 0,03	0,80 ± 0,00
Xylose (% DM)	0,55 ± 0,06	4,51 ± 0,02
Arabinose (% DM)	0,16 ± 0,02	1,14 ± 0,00
NH_4^+-N content (%DM)	**0,01 ± 0,00**	**0,06 ± 0,00**
Ash (% DM)	**5,32 ± 0,91**	**5,32 ± 0,01**

General conclusions for compositional analysis.

The compositional analyses of the biomasses have shown that the main mechanism of AAS on lignocellulosic biomasses under the experimental procedure followed has been the solubilization of hemicellulose. Hemicellulose is mainly composed by xylan and arabinan (in the studied biomasses) that resides between lignin and cellulose. Thus solubilization of hemicellulose, facilitates the access of the cellulolytic enzymes to cellulose for the conversion of glucose to methane. Further analyses are still to be carried out, where the protein content of the biomasses will be determined. The reduction of the total hemicellulose of the biomasses could be explained if degradation of xylose and arabinose to furfurals has occurred. This will be further examined from analysis on the liquid fraction of the AAS-treated biomasses. Furfurals can produce inhibition to biological conversions, nevertheless no inhibition was observed during the anaerobic batch tests run, and methanogens are known to be capable of adapting to low concentrations.

For more detailed results relevant to sections 1.5.5 (compositional analysis), see attached publications:

- ✓ Lymperatou, A., Gavala, H.N., Skiadas, I.V. "Effect of optimized Aqueous Ammonia Soaking of manure fibers on the continuous anaerobic digestion of swine manure", Submitted for publication.
- ✓ Lymperatou, A., Gavala, H.N., Skiadas, I.V. "Optimization of Aqueous Ammonia Soaking at ambient temperature for Enhancing the Methane Yield of Wheat Straw", Submitted for publication.

1.5.6 Assessment of Performance of optimally AAS-treated raw swine manure fibers in continuous swine manure mono-digestion.

Following the promising results obtained by AAS of raw swine manure fibers from batch experiments, the performance of optimally AAS-treated fibers when enriched to swine manure was evaluated in continuous anaerobic digestion. In comparison to batch experiments, continuous mode anaerobic digestion can provide valuable information on the performance of the process in terms of biogas and CH_4 productivity and stability since these processes are closer to real applications. The main objectives of this study were to assess the biogas productivity and CH_4 yield of manure enriched with pretreated fibers, as well as the reduction efficiency of the major organic components, i.e. cellulose, hemicellulose, lignin, proteins and lipids, as compared to manure enriched with untreated manure fibers.

In order to assess the performance of optimally AAS-treated fibers when enriched to swine manure, three CSTR-type digesters (3 l active volume) were operated for 120-125 days. All processes were run at mesophilic conditions (37°C) with an HRT of 17-18 days and with organic loading rate of ca. 1g VS/l/d. The first digester was fed on swine manure alone in order to obtain an estimation of background productivity and yield of manure without fiber enrichment. In the sequel, the digested manure was used for inoculating two new digesters, one fed with swine manure enriched with optimally AAS-treated manure fibers (7% w/w, 4 days, 0.16 kg/l, AAS digester) and the other fed with swine manure enriched with non-pretreated fibers (NP digester). The feed of the mixture-based digesters was prepared based on a 2:1 ratio of swine manure to manure fibers (TS basis). NP fibers were diluted with tap water in order to obtain the same TS concentration of the influent as for the AAS digester. The comparison of the conversion efficiency of the major organic components was carried out through compositional analyses of the influents and effluents of the two mixture-based digesters. During the experiments the pH, soluble COD, TS, VS, total ammonia N (TAN) concentration, biogas and CH_4 production were monitored.

The addition of manure fibers (both NP and AAS-treated) to liquid manure resulted in an increase of the carbohydrate fraction in the mixture-based digesters. In both processes where manure fibers were added to swine manure (NP and AAS digester) the initially moderate TAN concentration of manure (2.73 g/l) was further reduced (1.82 g/l and 2.04 g/l for the NP and AAS digester respectively), reducing thus the risk for NH_3 inhibition. Generally though, no inhibition was observed in all three processes, confirmed by the low VFA concentrations in the digesters (0.19-0.26 g/l).

The AAS digester presented an increased biogas and CH_4 productivity in comparison to the control digester fed only with raw manure (12% and 7% respectively). The NP digester, besides having the lowest TAN and free NH_3 concentration among all processes, presented a lower productivity than the control digester (-5% and -11% biogas and CH_4 productivity in comparison to the control digester). Thus, the low biodegradability of the added fibers did not improve manure mono-digestion regardless the improved TAN concentration. The resulting productivity was higher in the high solids digester while the CH_4 yield proved to be less than in the low solids digester. This was partly attributed to the higher NH_3 concentration in the high solids digester as a result of the higher TAN content of fibers in comparison to manure, producing inhibition of the process. However, our study showed that even when the added manure fibers present a lower TAN concentration than manure, the biogas production may not be improved as the degradability of the fibers is a more decisive factor for improving manure mono-digestion.

The efficiency of the pretreatment on increasing the energy recovery of manure fibers could be evaluated by comparing the performance of the mixture-based digesters. Overall, the AAS digester presented an improved performance, increasing the biogas and CH_4 productivities by 17% and 20% respectively when compared to the NP digester. By assuming that the CH_4 yield of swine manure contributed equally to the mixture-based digesters (204ml/g TS_{fed}), and taking into account the manure-to-fibers TS feed ratio, it was calculated that the CH_4 yield of the AAS manure fibers corresponded to 235.7 ml/g TS_{fed} while the CH_4 yield of the NP fibers to 59.7 ml/g TS_{fed}. This corresponds to a 295% increase of the CH_4 yield obtained by AAS on manure fibers at continuous digestion with an HRT of 18 days, which is higher than found at batch experiments (see previous sections).

The improved bioconversion of pretreated manure fibers was also evidenced by the increased reduction of the major organic groups of the influents (Table 1.5.6.1). The main difference among the digesters was observed in the carbohydrate content of the feeds, and especially in the reduction efficiency of cellulose. A 60.3% reduction of cellulose was achieved from the AAS digester in comparison to only 42.6% from the NP digester (Table 1.5.6.1), corresponding to a 42% improved reduction efficiency of cellulose. Interestingly, the rest of components, including proteins, lipids and lignin were also reduced in a greater degree in the AAS digester, indicating that AAS affected to a certain extent also the reduction of these fractions (Table 1.5.6.1). As a result of the significantly reduced cellulose content in the effluent of the AAS digester, the cellulose/lignin ratio, which has been suggested as an indicator of maturity of digestates, was significantly reduced from 0.98 to 0.78 in the AAS digester in comparison to a reduction from 0.97 to 0.90 in the NP digester, (Fig. 1.5.6.1).

Table 1.5.6.1 Removal of major components in continuous anaerobic digestion of manure enriched with non-pretreated fibers (NP digester) and with optimally AAS-treated manure fibers (AAS digester)

	NP digester			AAS digester		
Component	Influent (g/kg)	Effluent (g/kg)	% reduction	Influent (g/kg)	Effluent (g/kg)	% reduction
VS	21.87 ± 0.53	11.85 ± 1.93	45.8	20.32 ± 1.96	10.02 ± 2.16	50.7
Cellulose	4.76 ± 0.00[a]	2.74 ± 0.02	42.6	4.53 ± 0.11[a]	1.80 ± 0.11	60.3
Hemicellulose	3.83 ± 0.01[a]	1.76 ± 0.02	54.1	2.81 ± 0.01 [a]	0.98 ± 0.06	65.3
Proteins	6.21 ± 0.79[a]	3.70 ± 0.03	40.5	6.25 ± 1.20[a]	3.27 ± 0.03	47.7
Lipids	2.37 ± 0.18[a]	1.52 ± 0.13	35.6	2.01 ± 0.01	1. 11 ± 0.19	44.6
Lignin	4.92 ± 0.36[a]	3.03 ± 0.00	38.5	4.61 ± 0.35[a]	2.39 ± 0.10	48.2

[a] Estimated through mass balance

Overall, the efficiency of optimal AAS on improving the biogas and CH_4 production of swine manure fibers when added to swine manure was confirmed on continuous anaerobic digestion tests. Additionally, AAS significantly increased the reduction of all organic components, observing an especially significant reduction of the cellulosic fraction. The necessity to investigate an increasing share of pretreated fibers in the feed was highlighted in order to evaluate the stability of a high solids process, which could lead to a significant increase of the amounts of manure treated anaerobically.

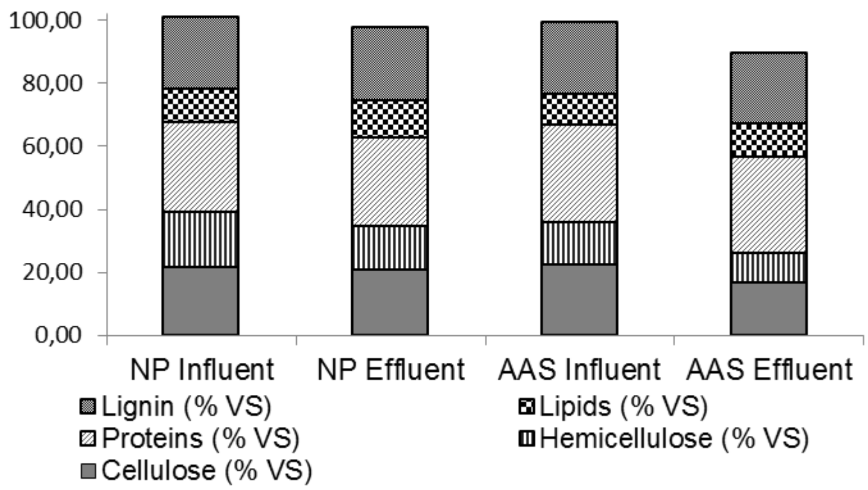

Figure 1.5.6.1 Composition of influents and effluents of NP and AAS digesters expressed in % of VS.

For more detailed results relevant to sections 1.5.6 (compositional analysis), see attached publications:

- ✓ Lymperatou, A., Gavala, H.N., Skiadas, I.V. “Effect of optimized Aqueous Ammonia Soaking of manure fibers on the continuous anaerobic digestion of swine manure”, Submitted for publication.

1.5.7 Preliminary economic evaluation of the AMMONOX process (Milestone 2.1)

The Morsø Bioenergy biogas plant has been used as the basis for all of the following assessments, since Morsø Bioenergy is thought to be the site for the pilot project. Production data and more technical data have been taken from /1/.

Table 7.5.7.1 Production data for Morsø /1/

Biogas production	m^3/year	4,300,000
Feed	ton/year	375,000
Annual power production	MWh/year	10,000
Annual heat production	MWh/year	8,500

Determination of maximum cost of AAS-system.

The work has focused on three scenarios, in the following named A, B and C. Scenario A is status quo, meaning no pre-treatment of manure; scenario B is for the 50/50 mixture of manure and AAS-treated raw fibres; and scenario C is for the 50/50 mixture of manure and AAS-treated digested fibres. The scenarios correspond to previous lab-scale CSTR-experiments performed by AAU during project RETROGAS, and results from these experiments have been used for the assessment of methane production.

To simplify the calculations the ASS-system including NH_3-recycling has been viewed as a "black box", and it is the total cost of the box that is estimated.

Table 1.5.7.8 Results from the CSTR-experiments

Scenario	**Feed**	**Biogas production**	**Methane production**	
		L/L/day	L/L/day	L/g TS
A	manure	0.86	0.52	0.116
B	manure + AAS (raw)	1.05	0.64	0.230
C	manure + AAS (digest)	0.94	0.62	0.238

At Morsø the normal TS content of the feed is 15 %.

For scenario A the production data in Table 7 have been applied, and the expected amount of biogas produced has been calculated based on the results in Table 1.5.7.8. It is assumed that the engine will have the same efficiency for all scenarios, and so the amount of biogas produced is directly proportional to the power generated. The possible change in gas composition, and thus calorific value, has not been included.

In order to estimate the added value of the AAS, the maximum subsidy for power produced from biomass has been applied (total power price of 1.153 DKK/kWh)/2/, for comparisons the added value has also been calculated at a power price of 0.3 DKK/kWh, see Table 1.5.7.9.

Table 1.5.7.9 Power production and added value

Scenario	**Power production [MWh/year]**	**Added value (1.153 DKK/kWh) [DKK/year]**	**Added value (0.3 DKK/kWh) [DKK/year]**
A	10,000	-	-
B	12,209	2,547,325	662,790
C	10,930	1,072,558	279,069

It has been checked that the expected power production does not exceed what the engine can deliver, though for scenario B the engine is expected to run 98 % of the year to meet the power production.

There is clearly an added value by adding AAS-treatment to the plant and as long as the government gives subsidies the value is significant. The possible added value of the additional heat production is not included.

Based on these simplified calculations, the cost (operation and depreciation) of the AAS-system should not exceed the incomes listed in Table 1.5.7.9. In the actual implementation it would be sensible to take in to account that the subsidies will most likely change, and possibly a mixture of B and C will be used.

NH_3 requirements for addition of SCR[1] to the gas engine.

When the AAS-treatment is implemented, an excess of ammonia will be generated. This ammonia could be utilized for SCR treatment of the flue gas from the gas engine, hereby reducing the NO_x emissions from the plant.
Based on the Morsø biogas plant, the amount of ammonia needed to supply an SCR-unit has been estimated. In the calculation is has been assumed that the NO_x primarily consists of NO_2 or NO. Since the emission data from Morsø is unknown, the standard emission factor for biogas fired engines has been used /3/. For SCR the amount of NH_3 added should be close to stoichiometric/4/.
For the SCR the ammonia can either be used as pure ammonia or in an aqueous solution. It is important that the ammonia does not introduce poisonous compounds that can deactivate the catalyst, such as alkali and alkali earth metals. It is, therefore, important that if an aqueous solution is used, the water is demineralised. The average Danish water has a high content of calcium and magnesium, and the average manure also has a high content of calcium (~ 1.2 kg/ton, TS 5 %/5/). However, if the ammonia is to be recovered from the biogas production by distillation or a similar procedure, this would not pose a problem.
For the calculation, a biogas composition of 60 % methane and 40 % CO_2 has been assumed, giving a gas-to-flue gas ratio of 5.5. Based on the expected amount of flue gas and the NO_x emission factor the annual amount of NO_x has been calculated. Assuming that all the NO_x is NO_2 or NO the stoichiometric amount of NH_3 can be calculated as seen in Table 1.5.7.10.

Table 1.5.7.*10* *Expected annual demand for ammonia*

	NO_x emission [ton/year]	**NH_3 demand [ton/year]**	**32 % NH_3 [ton/year]**
NO_2	16.02	5.93	18.53
NO	16.02	9.09	28.41

It is therefore necessary to extract 6-9 tons of ammonia per year in order for the SCR to be solely supplied with ammonia from the plant. It has not been possible to find the expected ammonia production of the Morsø plant.

Processes for recovering ammonia.
One of the most common procedures for removing ammonia is stripping. The stripping can either be facilitated by air or steam, but in both cases the slurry needs to be made alkaline (pH >10) to obtain a good removal of ammonia. For utilisation of NH_3 in SCR, the steam stripping would be most interesting since the product will be an approximately 20 % solution of ammonia/6/.
A non-pH-dependent solution is a thermally-driven stripper /7/; in order for this to be economically feasible, heat should be readily available from the process.
Flash distillation is also an option, but this also requires energy and preferably alkalisation to get the best ammonia extraction. Flash distillation, however, does not require as much space as the stripping process /8/.
Since ammonia is also utilised in the AAS step a full removal is not necessary, and so the alkalisation is not necessary either. It is, therefore, necessary to assess the available space and the surplus heat available for the ammonia recovery. When this is clarified, the optimal recovery process can be chosen.

Added value from NH_3.
Under the assumption that 2 g ammonia are produced per 25 l biogas, the overall ammonia production exceeds the amount of ammonia needed for the SCR by many orders of magnitude. If it is assumed that 70 % of the excess ammonia can be extracted and sold as fertilizer, there could be an added value of 1,200,000 DKK. This, however, does not take into ac-

[1] SCR – selective catalytic reduction

count that ammonia, when used as fertilizer, is used in its pure liquid form. This will give added expenses in order for the ammonia extracted from the process to be usable for agriculture purpose. It should, however, be possible to get a significant added value from the ammonia, which will increase the financing for the ASS and ammonia recovery.
It should not be a problem to sell the ammonia; in 2012/13 the annual amount of liquid ammonia used in agriculture in Denmark was 8,200 ton /9/, and the plant would produce 245 ton/year.
The overall financing available from extra power production and sale of ammonia as fertilizer would amount to around 3 million DKK a year. At an interest rate of 10 % this will mean that the acquisition cost of the AAS system and ammonia recovery can amount to 30 million DKK.

References

/1/ *Assessment of economic feasibility and environmental performance of manure processing technologies*, Technical Report No. IV to the European Commission, Directorate-General Environment, Manure Processing Activities in Europe - Project reference: ENV.B.1 / ETU / 2010 / 0007

/2/ Danish national law regarding subsidies for renewable energy. *Act amending the Act on the Promotion of Renewable Energy, the Electricity Supply Act, the Natural Gas Supply Act and the Act on Energinet.dk,* LOV nr. 576 of 18/06/2012. In Danish.

/3/ Danish national emission factors for 2012, http://envs.au.dk/videnudveksling/luft/emissioner/emission_factors/

/4/ *Selective Catalytic Reduction of NO_x emissions from gas turbines with minimal impact on plant performance*, H. Jensen-Holm and P. Lindenhoff, Haldor Topsøe A/S

/5/ Danish Agricultural Consultancy, *Optimal Utilisation of Pig Manure*, Dyrkningsvejledning 2007. In Danish

/6/http://www.sswm.info/sites/default/files/reference_attachments/RVT%202010%20Ammonia%20Recovery_%20Ammonia%20Removal%20from%20Liquids%20and%20Gases.pdf

/7/ http://www.organics.com/DataSheets/ODSP09%20Thermally-driven%20ammonia%20stripping.pdf

/8/ *Overview of nitrogen removal technologies and application/use of associated end products*, M. Ohrentlicher, Proceedings, Enhancing Environmental and Economic Sustainability Conference, Liverpool, New York, March 2012.

/9/ Denmark's sale of fertilizer 2012/2013, http://naturerhverv.dk/fileadmin/user_upload/NaturErhverv/Filer/Landbrug/Handelsgoedning/Danmarks_salg_af_handelsgoedning_2012_2013.pdf. In Danish

1.5.8 Preliminary design of a test unit (Milestone 2.2)

Initial calculations/estimations for a future AMMONOX test plant have been made using the software package HYSYS. The calculations concerned the ammonia separation process, which was assumed that will be done by heating and vacuum boiling/distillation. The energy consumption for heating if all of the ammonia should be extracted after the AAS-treatment would be in the order of 400% of the gained extra energy (CH_4 yield). The energy consumption for the compressor for the vacuum distillation would be in the order of 80% of the extra CH_4 yield. So obviously this method would be prohibitive.
From these calculations it is obvious that:

- The energy consumption of vacuum distillation/boiling of the full amount of manure would be prohibitive.
- A mechanical separation is necessary after the AAS treatment unit for recirculating ammonia rich liquid to the pretreatment process.
- The vacuum distillation should be done in batch mode (not continuous) for highest efficiency/lowest energy consumption.

It is necessary that only the solid part of the manure should be AAS treated. The liquid part should be brought directly to the digestion unit.
The additional separation after the AAS treatment unit will be made for recirculating the liquid part to the AAS process. The liquid part containing the major part of the ammonia

(aquous ammonia solution) should be recirculated to the AAS treatment where it will be combined with the solid part of manure from the previous separation step, while the solid part after AAS treatment should be brought to the digester after extracting the ammonia by vacuum distillation. The extracted ammonia should be used for adding to the AAS process and for other purposes (NOx reduction or production of fertilizer).

Based on the above findings, a new strategy was developed covering two different scenarios: one with co-digestion of manure fibers and liquid manure and a second with co-digestion of liquid manure and wheat straw.

The new strategy accounts for three different streams available for the biogas plant. That is:

- A stream of fresh manure from farmers relatively close to the biogas plant (around 5-10% total solids (TS))
- A stream of separated manure from farmers relatively far from the biogas plant (around 30% TS)
- A stream of straw from farmers to increase the solids in the biogas plant (around 90% TS)

The thinking behind this is that the stream of fresh manure secures the necessary liquid for the biogas plant. When only farms close to the biogas plant deliver fresh manure, the cost of transport can be minimized. This liquid manure is not separated at the biogas plant but is added directly to the digester without pretreatment. On the other hand, farmers far from the biogas plant could deliver separated manure with high TS. This will minimize the transport cost. This separated manure is pretreated with AAS in the biogas plant to increase the conversion efficiency. The third possible input stream is straw with low moisture content from farmers at close or far distances. This straw is cut or chopped and mixed with recirculated manure for possible pumping at the biogas plant. This will ease the handling of straw. The straw is pretreated with AAS at the plant for maximizing the methane yield.

Two examples have been modelled by the Aspen HYSYS code. The first (example 1) is an example with 1 kg of straw combined with 10 kg of fresh manure. The second example (example 2) includes 3 kg of separated manure combined with 10 kg fresh manure (see table 1.5.8.1). The size of these figures is only arbitrarily chosen and they could be multiplied by the same factor to relate to any size of biogas plant.

Table 1.5.8.1. The conditions for the two modelled examples.

Input and other conditions for modelling		**Example 1**	**Example 2**
Input material		Wheat Straw + fresh manure	Manure solids + fresh manure
Straw/solids input	(kg)	1	3
Total solids (TS) in straw/solids	(% mass)	90	30
Ammonia (NH_3) in straw/solids	(% mass)	0	0.2
Fresh manure input	(kg)	10	10
Total solids (TS) in fresh manure	(% mass)	6	6
Ammonia (NH_3) in fresh manure	(% mass)	0.7 (0.4)	0.7 (0.4)
Ammonia in AAS treatment	(% mass)	Around 7	Around 7
TS in AAS treatment	(% mass)	Around 5	Around 5
TS in mixture for NH_3 extraction	(% mass)	< 12	< 12
NH_3 in mixture after NH_3 extraction	(% mass)	< 0.5	< 0.5
Vacuum distillation pressure	(bar abs)	0.13	0.13
Internal heat exchange	(MJ)	2.4	2.7
Energy for compressor	(kJ)	432	434
NH_3 extraction temperature	(°C)	49	49
AAS pretreatment temperature	(°C)	32	14
Biogas output energy (estimated)	(MJ)	22.6	21.1

The flow diagrams below have been extracted from the HYSYS modelling.

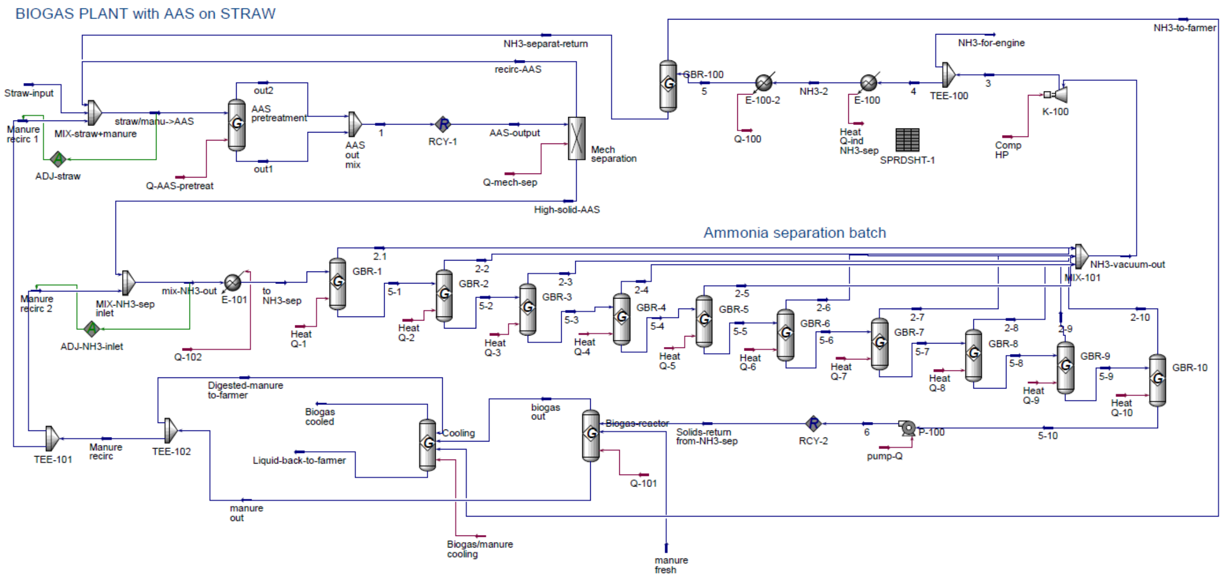

Figure 1.5.8.1 *HYSYS diagram of example 1 with straw input and fresh manure to digester.*

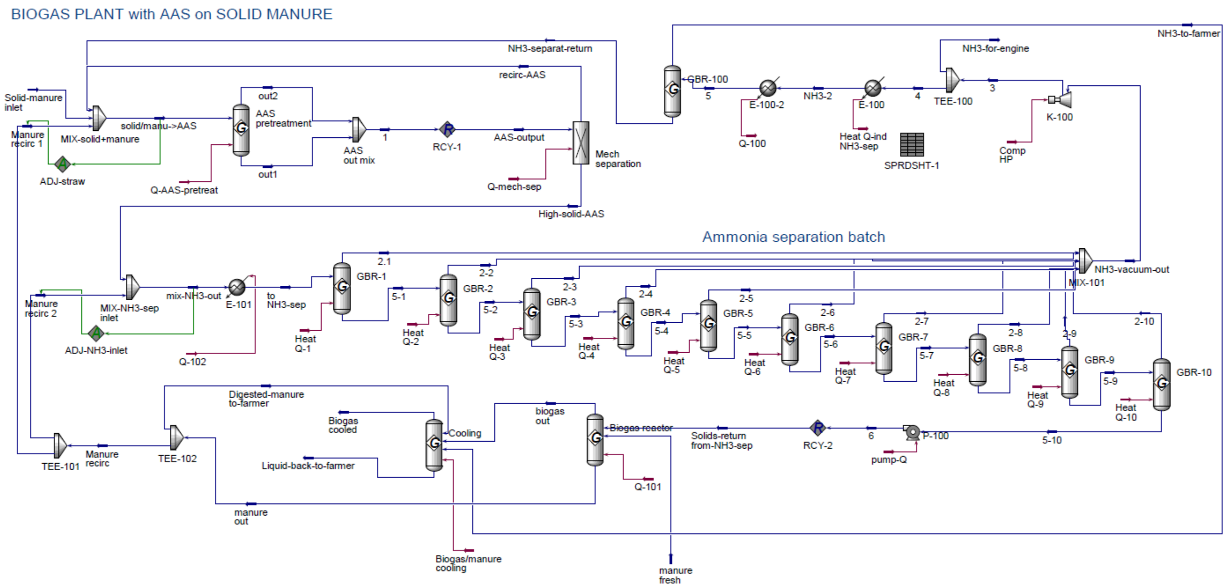

Figure 1.5.8.2 *HYSYS diagram of example 2 with solid manure input and fresh manure to digester.*

<u>*Test unit design*</u>

Based on the HYSYS modelling work above, a test plant was designed. Initially batch separation, as well as true plug-flow AAS-pre-treatment, where discussed as design conditions. However, to enable commercial upscaling of the technology, the test plant should to a high degree be scalable to a full industrial scale plant. All though batch separation would yield the highest efficiency, as per previous work, the batch approach was found to be unsuited in a full scale industrial plant. In addition to this true plug-flow would require several kilometres of piping in a full-scale setting which makes the approach neither practical nor economical feasible. The mass flow from the HYSYS simulation was scaled and fitted to two designs, one of a test and one of a full-scale plant. The design and dimensioning of components for both the test and full scale plants were made to supply a reasonably sized digester for its purpose. Applied digester dimensions are shown in table *1.5.8.2.*

		Test plant		Full scale plant	
Digester volume	**V**	2400	l	9000	m³
Retentiontime	t_R	25	days	25	days
Mass flow	$Q_{m,dim}$	90	kg/day	360	ton/day
Flow	$Q_{V,dim}$	90	l/day	360	m³/day
Density	**ρ**	1	kg/l	1000	kg/m³
Scale factor		4,36		17,44	

Table 1.5.8.2. Applied digester dimensions for the test and the full scale designed plants.

As part of the design work, a preliminary piping and instrumenting diagram (P&I-diagram) of the plant was created. In addition to the P&I-diagram a list of all mass flows regarding the design as well as pipe dimensions for both test-scale and full-scale plant have been calculated (table 1.5.8.3 and 1.5.8.4).

After the initial design, a market survey was conducted, to determine the availability of off-the-shelf products suitable for the design in both scales. The vacuum stripper was found to be the most challenging aspect of the design, as no standard commercial product seemed available to fit the specification of the design.

Table 1.5.8.3. Flow dimensioning

		HYSYS	Test plant					Full scale														
Name	Flow ID	Mass flow	Mass flow	Volume flow	Run time	Volume flow	Solid	Mass flow	Volume flow	Run time	Volume flow	Solid	Phase	Substance	Density	Enthalpy	Ammonia	Carrbon dioxide	Methane	Water	Pressure (Gas)	Temperature
	Symbol:	qm	qm	qv	t	qv	TS%	qm	qv	t	qv	TS%	-	-	ρ	H	NH_3	CO_2	CH_4	H_2O	Pabs	Temperature
	Unit:	kg/day	kg/day	l/day	h	l/h	TS%	ton/day	m^3/day	h	m^3/h	TS%	-	-	kg/m^3	kJ/kg	m% NH_3	m% CO_2	m% CH_4	m% H_2O	Bar	°C
Input	**Q1**	1,00	4,36	97	24	4,0	90,00%	17,4	387,6	24	16	90,00%	Solid	Straw	45		0,0%	-	-		-	10
	Q2	18,69	81,50	82	24	3,4	5,22%	326,0	329,3	24	14	5,22%	Liquid	Straw/Manure	990		7,0%	-	-		-	30
	Q3	19,51	85,07	86	24	3,6	5,00%	340,3	343,7	24	14	5,00%	Liquid	Straw/Manure	990		7,0%	-	-		-	30
	Q4	19,51	85,07	86	24	3,6	5,00%	340,3	343,7	24	14	5,00%	Liquid	Straw/Manure	990		7,0%	-	-	0	-	30
	Q5	3,76	16,40	17	24	0,7	25,95%	65,6	66,2	24	3	25,95%	Liquid/Solid	Straw/Manure	990		5,50%	-	-		-	30
	Q6	10,22	44,56	45	4,50	10,0	12,01%	178,3	180,1	24	8	12,01%	Liquid	Straw/Manure	990		2,16%	-	-		-	30
	Q7	10,19	44,43	45	24	1,9	11,98%	177,73	179,5	24	7	11,98%	Liquid	Straw/Manure	990		0,49%	-	-		-	49
Output	**Q8**	10,45	45,57	46	24	1,9	**3,90%**	182,3	184,1	24	8	**3,90%**	Liquid	Digested manure	990		0,62%	-	-		-	15
Input	**Q9**	10,00	43,60	44	24	1,8	6,00%	174,4	176,2	24	7	6,00%	Liquid	Fresh Manure	990		0,7%	-	-		-	10

Q10	8,40	36,63	37	24	1,5	3,90 %	146,5	148,0	24	6	3,90 %	Liquid	Recirc. Manu-re	990		0,58%	-	-		-	37
Q11	6,46	28,17	28	24	1,2	3,90 %	112,7	113,8	24	5	3,90 %	Liquid	Recirc. Manu-re	990		0,58%	-	-	0	-	37
Q12	1,94	8,46	9	24	0,4	3,90 %	33,8	34,2	24	1	3,90 %	Liquid	Recirc. Manu-re	990		0,58%	-	-	0	-	37
Q13	15,75	68,68	72	24	3,0	-	274,7	286,2	24	12	-	Liquid	Am-monia	960		7,40%	-	-		-	30
Q14	0,83	3,62	54.033	24	2251,4	-	14,5	216.132,6	24	9006	-	Gas	Am-monia	0,067		23,5%	**0,50 %**	**0%**	**76 %**	0,1	46
Q15	0,82	3,58	4	24	0,2	-	14,3	15,1	24	1	-	Liquid	Am-monia	950		**23,40 %**	-	-	**76,60%**	-	20
Output **Q16**	1,35	5,89	5.016	24	209,0	-	23,5	20.065,5	24	836	-	Gas	Biogas	1,17		**0,30 %**	**66,20%**	**32,40%**	**1,10 %**	1	15
Q17	0,01	0,04	38	24	1,6	-	0,2	150,4	24	6	-	Gas	CO2	1,16		**43,70 %**	**55,30%**	**0,00 %**	**1,10 %**	1	20
Q18	0,83	3,62	9.771	24	407,1	-	14,5	39.085,4	24	1629	-	Gas	Am-monia	0,370		23,5%	**0,50 %**	**0%**	**76 %**	1	304
Q19	0,80	3,49	3	24	0,1	-	14,0	14,0	24	1	-	Liquid	Water	999,7	45	-	-	-			10
Input **Q20**	**0,80**	**3,49**	42.113	24	1754,7	-	**13,95**	168.450,4	24	7019	-	Gas	Steam	0,083	2975	-	-	-	100 %	0,2	250

Table 1.5.8.4. Piping

✓ **Full scale**

Name	Flow ID	Phase	Substance	Mass flow	Volume flow	Pipe diameter	Pipe diameter	Pipe cross section	Velocity
	Symbol:	-	-	qm	qv	O.D	I.D		
	Unit:	-	-	ton/day	m³/h	mm	mm	m²	m/s
	Q1	Solid	Straw	17,4	16,1	90	79,2	0,0049	0,9
	Q2	Liquid	Straw/Manure	326,0	13,7	90	79,2	0,0049	0,8
	Q3	Liquid	Straw/Manure	340,3	14,3	90	79,2	0,0049	0,8
	Q4	Liquid	Straw/Manure	340,3	14,3	90	79,2	0,0049	0,8
	Q5	Liquid/Solid	Straw/Manure	65,6	2,8	90	79,2	0,0049	0,2
	Q6	Liquid	Straw/Manure	178,3	7,5	90	79,2	0,0049	0,4
	Q7	Liquid	Straw/Manure	177,7	7,5	90	79,2	0,0049	0,4
	Q8	Liquid	Digested manure	182,3	7,7	90	79,2	0,0049	0,4
	Q9	Liquid	Fresh Manure	174,4	7,3	90	79,2	0,0049	0,4
	Q10	Liquid	Recirc. Manure	146,5	6,2	90	79,2	0,0049	0,3
	Q11	Liquid	Recirc. Manure	112,7	4,7	90	79,2	0,0049	0,3
	Q12	Liquid	Recirc. Manure	33,8	1,4	90	79,2	0,0049	0,1
	Q13	Liquid	Ammonia	274,7	11,9	90	79,2	0,0049	0,7
	Q14	Gas	Ammonia	14,5	9005,5	450	396,6	0,1235	20,2
	Q15	Liquid	Ammonia	14,3	0,6	90	79,2	0,0049	0,0
	Q16	Gas	Biogas	23,5	836,1	180	158,5	0,0197	11,8
	Q17	Gas	CO2	0,2	6,3	90	79,2	0,0049	0,4
	Q18	Gas	Ammonia	14,5	1628,6	450	396,6	0,1235	3,7
	Q19	Liquid	Water	14,0	0,6	90	79,2	0,0049	0,0
	Q20	Gas	Steam	14,0	7018,8	450	396,6	0,1235	15,8

✓ **Test plant**

Name	Flow ID	Phase	Substance	Mass flow	Volume flow	Pipe diameter	Pipe diameter	Pipe cross section	Velocity
	Symbol:	**-**	**-**	**qm**	**qv**	**O.D**	**I.D**		
	Unit:	**-**	**-**	**kg/day**	**l/h**	**mm**	**mm**	**m²**	**m/s**
Input	**Q1**	Solid	Straw	4,36	4,0	50	44,0	0,0015	0,0007
0	**Q2**	Liquid	Straw/Manure	81,50	3,4	50	44,0	0,0015	0,0006
0	**Q3**	Liquid	Straw/Manure	85,07	3,6	50	44,0	0,0015	0,0007
0	**Q4**	Liquid	Straw/Manure	85,07	3,6	50	44,0	0,0015	0,0007
0	**Q5**	Liquid/Solid	Straw/Manure	16,40	0,7	50	44,0	0,0015	0,0001
0	**Q6**	Liquid	Straw/Manure	44,56	10,0	50	44,0	0,0015	0,0018
0	**Q7**	Liquid	Straw/Manure	44,43	1,9	50	44,0	0,0015	0,0003
Output	**Q8**	Liquid	Digested manure	45,57	1,9	50	44,0	0,0015	0,0004
Input	**Q9**	Liquid	Fresh Manure	43,60	1,8	50	44,0	0,0015	0,0003
0	**Q10**	Liquid	Recirc. Manure	36,63	1,5	50	44,0	0,0015	0,0003
0	**Q11**	Liquid	Recirc. Manure	28,17	1,2	50	44,0	0,0015	0,0002
0	**Q12**	Liquid	Recirc. Manure	8,46	0,4	50	16,0	0,0002	0,0005
0	**Q13**	Liquid	Ammonia	68,68	3,0	20	16,0	0,0002	0,0041
0	**Q14**	Gas	Ammonia	3,62	2251	40	35,2	0,0010	0,6426
0	**Q15**	Liquid	Ammonia	3,58	0,2	20	16,0	0,0002	0,0002
Output	**Q16**	Gas	Biogas	5,89	209,0	40	35,2	0,0010	0,0597
0	**Q17**	Gas	CO2	0,04	1,6	20	16,0	0,0002	0,0022
0	**Q18**	Gas	Ammonia	3,62	407	40	35,2	0,0010	0,1162
0	**Q19**	Liquid	Water	3,49	0,1	20	16,0	0,0002	0,0002
Input	**Q20**	Gas	Steam	3,49	1754,7	20	16,0	0,0002	2,42

1.5.9 Dissemination of results

The following presentations/publications have been made from the project start-up:

Presentations

- Conference oral presentation at the 13th World Congress on Anaerobic Digestion: Recovering (bio) Resources for the World, Santiago de Compostela, Spain, June 25-28. **AMMONOX-Ammonia for enhancing biogas yield & reducing NOx** by H.N. Gavala, P.G. Kristensen, N.B.K. Rasmussen, P. Thostrup and I.V. Skiadas.
- Conference oral presentation at the 5th International Conference on Engineering for Waste and Biomass Valorisation, Rio de Janeiro, Brazil, August 25-28, 2014. "**AMMONOX-Ammonia for enhancing biogas yield & reducing NOx: Optimization of Aqueous Ammonia Treatment**" by Lymperatou Anna, Gavala Hariklia and Skiadas Ioannis.
- Conference oral presentation at the ATHENS 2014 International Conference on Sustainable Solid Waste Management, Athens, Greece, 12-14 June 2014. "**AMMONOX research project: Use of ammonia for enhancing biogas production from waste lignocellulosic biomass & reducing NOx emissions from biogas engines**" by I.V. Skiadas and H.N. Gavala.
- A. Lymperatou, H.N. Gavala, K.H. Esbensen, I.V. Skiadas. **Screening of the important variables of aqueous ammonia soaking as pretreatment method for enhancing the methane production from swine manure fibers**. Presented at the *14th World Congress on Anaerobic Digestion, Viña del Mar, Chile, November 15-18, 2015*.
- A. Lymperatou, H.N. Gavala, I.V. Skiadas. **Increasing the Methane Yield of Swine Manure Fibers by means of Ammonia**, A poster presentation at the *14th World Congress on Anaerobic Digestion, Viña del Mar, Chile, November 15-18, 2015*.
- A. Lymperatou, H.N. Gavala, I.V. Skiadas. **An integrated approach for enhancing biogas yield of manure-based anaerobic digestion**. Poster presentation at the *Sustain DTU Conference "Creating Technology for a Sustainable Technology", Kgs. Lyngby, Denmark, December 17, 2015*.
- Oral presentation to the *6th International Conference on Engineering for Waste and Biomass Valorisation, Albi, France, May 23-26, 2016*. **Application of Response Surface Methodology for assessing the effects of Aqueous Ammonia Soaking parameters on the Methane Yield of swine Manure Fibers**, by A. Lymperatou, H.N. Gavala, I.V. Skiadas.
- Oral presentation at the Seminar series to the Center for Bioprocess Engineering (BioEng), Technical University of Denmark, Kgs. Lyngby, June 24, 2016. **Response Surface Methodology for assessing the effects of Aqueous Ammonia Soaking on the Methane Yield of Swine Manure Fibers,** by A. Lymperatou, H.N. Gavala, I.V. Skiadas.
- Poster presentation at the KT Research Day, Department of Chemical and Biochemical Engineering, Technical University of Denmark, Kgs. Lyngby, May 27th, 2016. **Increasing the Methane Yield of Swine Manure Fibers by means of Ammonia**, by A. Lymperatou, H.N. Gavala, I.V. Skiadas.
- Oral presentation to the Center for Experimental Process and Equipment Design (PILOT), Technical University of Denmark, Kgs. Lyngby, March 15th, 2016. **Optimization of ammonia pretreatment of lignocellulosic biomasses for maximizing the methane yield,** by A. Lymperatou, H.N. Gavala, I.V. Skiadas.

Scientific articles

- A. Lymperatou, H.N. Gavala, K. Esbensen and I.V. Skiadas. **AMMONOX-Ammonia for enhancing biogas yield & reducing NOx: Towards the optimization of Aqueous Ammonia Soaking**. *Waste and Biomass Valorization*, DOI 10.1007/s12649-015-9365-4.
- Lymperatou, A., Gavala, H. N. and Skiadas, I.V. (2017) **Optimization of Aqueous Ammonia Soaking of manure fibers by Response Surface Methodology for**

unlocking the methane potential of swine manure, *Bioresource Technology*, 244, p.509-516.

- Lymperatou, A., Gavala, H.N., Skiadas, I.V. **Optimization of Aqueous Ammonia Soaking at ambient temperature for Enhancing the Methane Yield of Wheat Straw**, Submitted .
- Lymperatou, A., Gavala, H.N., Skiadas, I.V. **Effect of optimized Aqueous Ammonia Soaking of manure fibers on the continuous anaerobic digestion of swine manure**, Submitted

1.6 Utilization of project results

The extensive laboratory scale tests performed in the frame of AMMONOX have clearly documented that ammonia is very effective for the pre-treatment of manure fibers and other lignocellulosic biomasses such as straw before anaerobic digestion. The optimum conditions for the AAS treatment of manure fibers (duration of 4 days and 7% w/w NH3 solution) and straw (duration of 7 days and 18 % w/w NH3 solution) have been defined during AMMONOX project using powerful statistical optimization tools.

However and due to the nature of the biomasses handled (high dry matter content) it was not possible to test the ammonia recovery and recycling system in the laboratory scale tests performed during AMMONOX project. It was possible to remove ammonia by vacuum evaporation before the biomasses were digested but the removed ammonia could not be recovered and reused in laboratory scale. Furthermore, the optimization of the conditions for the AAS treatment followed an empirical approach without providing a clear explanation on how these conditions were affected by the biomass composition.

The AMMONOX technology efficiency for increasing the methane yield of lignocellulosic biomasses is well documented in this research work but the practice of the designed process has not been demonstrated in a fully operational pilot scale. Therefore the AMMONOX project participants expect to utilize the project results in a future pilot scale operation which will be used to solve all possible technical issues before full scale demonstration and commercialization. Most of the individual process steps are considered of very low technical risk since they are well established and commercially available unit operations (such as tanks with or without mixing, mechanical solids separation, anaerobic digesters). The ammonia stripping is also a well-established technology and in a future pilot scale operation it will have to be adapted to the handling of a stream of relatively high solids content. The purpose of a future demonstration project will be:

a. To scale up to a pilot plant and demonstrate the efficiency of the above described technology.
b. To document the possibility of efficient ammonia extraction from the stream after the AAS treatment and the reuse of ammonia for the AAS treatment of fresh biomass in pilot scale.
c. To develop a simulation tool that will be able to predict the optimum conditions for the AAS treatment of different biomasses as a function of the biomass composition.

1.7 Project conclusion and perspective

The laboratory scale tests performed in the frame of AMMONOX clearly documented that ammonia is very effective for the pre-treatment of manure fibers and other lignocellulosic biomasses such as straw before anaerobic digestion. Specifically, aqueous ammonia soaking (AAS) at room temperature and pressure (thus, requiring no expensive equipment for maintaining high temperature and pressure as it is common with traditional biomass pretreatment methods) was able to increase the methane yield of manure fibers (the solid fraction of manure) more than 200% and the methane yield of wheat straw almost 50% in less than 20 days (17 days) digestion at 37°C which can significantly improve a biogas plant economics. The high efficiency of AAS in enhancing the methane productivity has been also verified in continuous, CSTR, experiments. In the technology developed in AMMONOX project, the ammonia used for the pretreatment is recovered (by stripping) and recycled to the pretreatment process. This brings two significant advantages: i) the biomass pumped in to the anaerobic digester is characterized by an ammonia concentration well below inhibitory levels and ii) no ammonia consumption is required for the AAS treatment of the biomass. In addition to this, ammonia can actually be produced in excess through the recycling of a portion of the digester effluent. As a result and on top of the above mentioned advantages, the AMMONOX technology is expected to offer the possibility to significantly reduce the ammonia concentration in the digesters handling manure (elimination of ammonia inhibition during anaerobic digestion of manure) and also it is expected to result in the production of an ammonia solution in water (around 20% w/w NH_3) which can be used as fertilizer by farmers. A small part of the produced ammonia solution may be used for the catalytic (SCR) reduction of NO_x emissions from biogas plants where the biogas is used as fuel to gas engines for electricity generation.

The optimum conditions for the AAS treatment of manure fibers (duration of 4 days and 7% w/w NH_3 solution) and straw (duration of 7 days and 18 % w/w NH_3 solution) have also been defined during AMMONOX project using powerful statistical optimization tools.

The AMMONOX technology efficiency for increasing the methane yield of lignocellulosic biomasses is well documented in laboratory scale but the practice of the designed process has not been demonstrated in a fully operational pilot scale. This is assumed a vital step before any effort to demonstrate the technology in full scale and attempt to commercialize it. Testing the suggested process in pilot scale will indicate all bottlenecks and malfunctions that usually arise when handling robust materials like manure fibers, straw and other lignocellulosic biomasses. Pilot scale operation can therefore be used to solve all possible technical issues before full scale demonstration and commercialization.

Among main energy policy objectives for Denmark (as specified in the DK Energy Agreement of March 22 2012) is that Denmark shall keep on being self-sufficient with energy (national security priority). In the long run (by 2050) Denmark's entire energy supply (electricity, heating, industry and transport) will be covered by renewable energy sources. Therefore, renewable energies share of gross energy shall further increase to a 35% by 2020 and more than half of this will be produced from biomass. The use of all types of biomass is expected to increase to a 166PJ in 2020 compared to a 132PJ in 2012. In the long term, an even larger share of the Danish energy system will be based on renewable energy, and a number of scenarios for the consumption of biomass in 2050 have been analysed, with the results showing that the consumption of biomass varies between roughly 200 and 700 PJ. In this frame, the production of biogas in Denmark is rapidly increasing. The total production is expected to reach a total annual production of 15 PJ, more than triple compared to 2012. However, biogas is currently promoted through public subsidies and it faces a number of serious challenges in the near future. That is, the current subsidies are being phased out and (depending on EU regulations and market status) they might disappear completely after 2023 and (with the existing limitations of energy crops in biogas production) it is being difficult to find suitable biomass to supplement slurry in order to achieve high enough biogas production.

The scalling up and commercialization of AMMONOX technology can increase significantly the methane potential of lignocellulosic biomasses (non energy crops) such as manure fibers and straw. The usual processes in a biogas plant only utilize about 50% of the theoretical maximum methane potential present in the feedstock. However, the AMMONOX technology has a potential of exploiting a large part of the wasted bioenergy and increase the yield considerably. It is expected that the technology will make it possible to increase the methane efficiency of biogas plants from about 50% to as high as 70-90%. This will allow the biogas sector to contribute to a higher percentage to the renewable energy supplies and thus becoming a more important player for the security of energy supplies.

Annex

Relevant links