Evaluation of technology structure based on energy yield from wheat straw for combined bioethanol and biomethane facility

Viktoria Leitner [a], [*], Johannes Lindorfer [b]

[a] University of Applied Sciences Upper Austria, Wels Campus, Stelzhamerstrasse 23, 4600 Wels, Austria
[b] The Energy Institute at the Johannes Kepler University Linz, Altenberger Straße 69, 4040 Linz, Austria

ARTICLE INFO

ABSTRACT

The objective of this paper is to evaluate a combined bioethanol and biomethane production from wheat straw applying process network synthesis for maximised energy yield per ton lignocellulosic biomass input. Experimental results in combination with literature data were implemented in process synthesis software for energy optimisation. Wheat straw was steam exploded at different pretreatment conditions on laboratory scale. Glucose and ethanol yields as well as specific biogas yields of different solid and liquid fractions were determined via batch-experiments. Preferable pretreatment conditions differ between biogas and bioethanol production. The optimal process configuration was found to consist of direct biogas production from steam explosion pretreated straw at 170 °C for 20 min combined with bioethanol production from straw pretreated at 200 °C for 20 min. This process results in a purified methane yield of 7892 MJ and a purified ethanol yield of 964 MJ per ton untreated straw input.

1. Introduction

The promotion of renewable energy production has multiple drivers: reduction of greenhouse gas emissions, rising energy demands while "peak-oil" might have already been reached, or desired independency from oil imports. Utilization of biomass is a possibility to provide renewable energy without dramatic changes in infrastructure and consumption technologies as it results in material energy carriers. For every fossil energy source, a bio-based alternative already exists.

Bioethanol and biogas are the sustainable alternatives to gasoline or natural gas. Both energy carriers have different fields of application. Especially an application as sustainable fuel alternative seems to be a suitable possibility due to the necessity of only minor changes in infrastructure and drive technology. Biogas (containing bio-methane as value defining component) can be produced from diverse input materials like animal manure, different energy crops and any type of organic waste and by-product. Biomethane yields are predominantly depending on the input material [1] and the costs of transportation and storage are especially influenced by the energy content of the selected raw-material. A large number of

biogas plants use energy crops like maize as their main input material [2] because of its high yield per hectare. However the proportion of arable land is limited and the rising demand on agricultural land for food and feed production caused by a rising world population and an exploding meat demand intensifies the competition for agricultural land [3]. One possibility to realise biogas production without energy crop cultivation is to develop concepts for the utilization of agricultural waste and by-products. For the production of bioethanol the situation is quite similar. Today bioethanol is primarily produced from sugar cane, maize or any type of grain. As a consequence this bio-based product is often criticised for the competition with the food market. Concepts for bioethanol production from agricultural by-products already exist in various demonstration activities [4,5]. Large scale market penetration is inhibited by the low economic competitiveness of the technology [6]. To guarantee the maximum economic output from the biomass used, biorefinery systems seem to be an attractive solution. The biorefinery concept is analogous to today's petroleum refinery, which produces multiple fuels and products from petroleum. Biomass energy and material recovery is maximized when a biorefinery approach is considered, in which many technological processes are jointly applied [7]. According to René and Bert [8], the current biorefinery classification system is in a developing stage, where categories have until now been differentiated based mainly on: raw material inputs, type of technology (e.g. biochemical or

thermo-chemical biorefinery), status of technology (conventional and advanced biorefinery, 1st and 2nd generation biorefinery) and main (intermediate) product produced [9]. Biorefinery is being holistically defined as "an integrated pattern of farming and conversion activities capable to provide bioenergy and biomaterials as alternative to fossil-based refineries, increasing job and income in rural areas" [10]. This approach of extracting diverse resources and energy services from biomass should be preferred over simply incinerating organic materials for thermal energy production. Prioritization of fuelled conversion technologies is thus imperative. Bioethanol producing biorefineries are one possible option especially for lignocellulosic residuals like straw. The proportion of cellulose, hemicellulose and lignin determine the conversion pathway and products to be delivered. The higher the cellulose to lignin ratio, the higher the biodegradability of the biomass. Biogas plants are commonly integrated in those biorefinery concepts as end of pipe treatment facilities for solid and liquid waste (ethanol stillage and wastewater streams) [11–16], and are not recognized as energy producing facilities in their own right.

Different strategies to increase the efficiency of lignocellulosic biorefinery plants are currently persued. The pretreatment technology is one of the key steps in the lignocellulosic biorefinery [17]. In general, pretreatment technologies are divided into four major groups i.e. physical, chemical, physic-chemical and biological [18]. The intention of the pretreatment is a maximised recovery of fermentable sugars with low energy input and inhibitory co-products. Although each method has some advantages, one method could not be the choice for all types of biomass. With reference to the investigated process of combined bioethanol and biogas production from straw steam explosion pretreatment was applied for partial hemicellulose hydrolysis and improved enzyme accessibility as steam explosion is reported among the limited number of cost-effective pretreatment technologies for pilot scale demonstration and commercial application [19]. Compared to chemical pretreatment with acid, alkaline, ionic liquids or organic solvents the cellulose decrystallization and lignin removal for steam explosion pretreatment is low [20]. Besides the pretreatment simultaneous saccharification and fermentation, improved enzymes for hydrolysis, different yeast strains or yeast and bacteria mixtures, cascading fermentation of different sugars and genetic modification of yeast and bacteria strains are some of the current research topics [21–26], to improve the efficiency of biomass conversion. Especially the additional conversion of pentoses to ethanol seems to be necessary in order to become economically competitive. Compared to single glucose conversion, an increase in ethanol yield of 38% is theoretically possible using pentoses.

The approach of a combined bioethanol and biogas refinery highlights another possible way to convert pentoses to energy without sophisticated process adaptions of ethanol fermentation (often realised with genetically modified yeast). The conversion of pentoses into biomethane in conventional biogas plants can easily be done without any changes of the design and operation method. Beside the advantage of converting pentoses to methane, a biorefinery with integrated biogas production also helps to minimize wastewater output.

The current paper evaluates a combined biogas and bioethanol plant to maximise energy output based on one ton untreated wheat straw as input material and investigates synergistic effects between both separated processes. Bioethanol production from steam exploded wheat straw was performed on laboratory scale, encompassing the processing steps pretreatment, enzymatic hydrolysis and ethanol fermentation. Beside ethanol production different process streams were analysed for their biological methane potential. All data for the energetic process evaluation study was collected via own laboratory experiments to enable complete mass balances and comparable basic conditions for bioethanol and biogas production. The mass balance data from experiments was extended with process energy demand data from literature. The collected data was input for multiway optimisation via process network synthesis described below to optain maximised energetic product output (from biomethane as well as bioethanol) from 1 ton straw input.

1.1. Energetic process optimisation via process network synthesis (PNS)

Process network synthesis (PNS) is a possibility for structural optimisation. The system is based on the p-graph framework and the use of combinatorial methods to find all feasible structures linking given inputs with required products using a certain set of technological options [27–29]. It is usually used for economic optimisation of networks but in this study PNS is used for energy output optimisation. PNS is an economic simulation tool and needs detailed input data for generating reliable simulation results. In this study data was generated by laboratory experiments and literature review and the results are of theoretical character.

With the help of PNS the optimal process pathways of a combined bioethanol and biogas plant was determined. The optimal solution was defined by maximum energy output (bioethanol and/or biogas) from one ton wheat straw. PNS calculations are based on energy and mass balances in combination with economic parameters (costs and prices) allocated to each process stream and technology step. The selected approach of excluding prices and profit for every process stream and technology and assigning heating values as "prices" to the product flows allows energy output optimisation. At the start of process optimisation a so-called maximum structure has to be generated. This network includes all feasible processes and sub-processes as well as their mass and energy balances. By using PNS, scenario definition is no longer necessary. As a solution of the p-graph framework an optimal structure is created representing the process chain or network with the highest economic benefit or in the case of this work with the highest energy output. Processes with smaller economic benefit are not integrated in the optimal structure.

1.2. Basic process description

The basic flow sheet of the process is presented in Fig. 1. Data on specific flows are provided in Table 1. The ethanol process is defined as 2nd generation ethanol production with wheat straw as input material. Wheat straw is pretreated with steam-explosion and then enzymatically hydrolysed to sugar monomers. Onsite enzyme production on a partial flow of pretreated straw is performed as part of the biorefinery concept. Enzymatic hydrolysis is followed by a solid/liquid separation where "waste" fibres are separated from the sugar solution. The glucose present in the liquid fraction is fermented to ethanol by genetically unmodified yeast. Finally the ethanol solution is purified to 960 mL L^{-1} ethanol by distillation. Further purification to anhydrous ethanol is not included in the study. The process network is completed with a biogas plant and a methane purification unit for biomethane upgrade. For process network synthesis all process flows are defined as possible input substrate for biogas production. Necessary process energy is provided by optional biomass (residual lignin fraction and untreated input straw) or biogas incineration with combined heat and power generation.
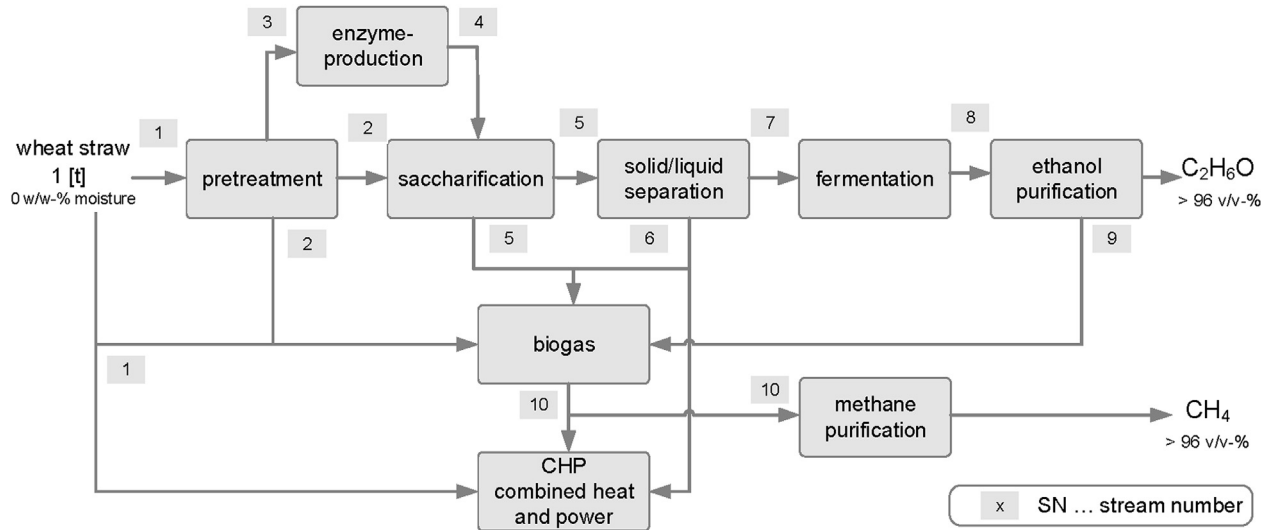
Fig. 1. Process flow sheet of the analysed process network options. Numbers represent the process streams and are defined below.

Table 1
Input data for process network synthesis.

Steam-explosion-pretreatment		
Temperature	[°C]	170–200
Duration	[min]	20
Mass loss	[g kg^{-1}]	0–180
Glucose recovery	[%]	95–100
Xylose recovery	[%]	40–100
Arabinose recovery	[%]	30–100
Steam demand	[g kg^{-1}]	Thermodynamic minimum
Enzyme production		
Temperature	[°C]	30
Enzyme yield	[FPU g$_{C6}^{-1}$]	175
Electricity demand	kJ FPU^{-1}]	0.029
Enzymatic hydrolysis		
Temperature	[°C]	50
Reaction time	[Days]	3.5
Enzyme loading	[FPU g$_{C6}^{-1}$]	15
Dry matter loading	[g kg^{-1}]	200
Electricity demand	[kJ kg$^{-1}_{DM}$]	72.0
Solid/liquid separation		
Separation performance	[%]	100
Electricity demand	[kJ L^{-1}]	4.68
Ethanol fermentation		
Temperature	[°C]	30
Reaction time	[d]	1.5
Glucose → ethanol yield	[g g^{-1}]	0.48
Ethanol distillation		
	[MJ kg$^{-1}_{C2H6O}$]	147.31 x$^{-1.761}$ x … concentration of ethanol in feed [wt-%]
Biogas production		
Temperature	[°C]	38
Electricity demand	[MJ m$^{-3}_{CH4}$]	0.93
Heat demand	[MJ m$^{-3}_{CH4}$]	8.86
Biogas purification		
Electricity demand	[MJ m$^{-3}_{CH4}$]	0.72
CHP (combined heat & power)		
Thermal efficiency	[%]	50
Electrical efficiency	[%]	40

2. Material and methods

2.1. Pretreatment

2.1.1. Raw material input

Wheat straw (*Triticum aestivum*) was provided by a local farmer in the region of Upper Austria. It was stored as bale (L × W × H = 800 × 500 × 350 mm) in a garage until further use.

Straw was chopped with a commercial garden shredder into a cardboard box prior to laboratory experiments. The chemical composition of the straw is presented in Table 2.

2.1.2. Steam explosion pretreatment

Pretreatment was performed in a 15 L batch steam-explosion reactor (VAM GmbH&Co) at the University of Applied sciences Upper Austria, campus Wels, Austria. 900 g chopped wheat straw

Table 2
Chemical composition of untreated and pretreated wheat straw.

SN	Pretreatment	log (R_0)[−]	DS w/w-%	Mass$_{DM}$ [g]	XA [g]	Glc [g]	Xyl [g]	Ara [g]	Lignin [g]
1	Untreated	0	90.7 ± 0.4	1000	44.1 ± 0.2	412.1 ± 15.2	253.1 ± 41.7	28.9 ± 7.8	225.9 ± 0.1
2	170 °C/20 min	3.36	23.8% ± 0.7	970	44.2 ± 0.1	417.1 ± 15.4	259.4 ± 20.5	32.9 ± 8.8	215.2 ± 3.2
	180 °C/20 min	3.66	22.6% ± 1.2	920	39.7 ± 0.1	418.6 ± 13.3	211.8 ± 10.1	19.4 ± 5.4	226.8 ± 2.6
	190 °C/20 min	3.95	21.2% ± 1.0	840	45.9 ± 0.8	394.8 ± 12.6	126.0 ± 8.1	8.3 ± 3.9	271.4 ± 2.1
	200 °C/20 min	4.25	20.0% ± 0.2	820	47.3 ± 0.7	393.6 ± 16.5	102.0 ± 11.8	9.4 ± 8.0	263.2 ± 4.5

log (R_0)-severity factor; DS-dry substance; XA-ash content; Glc-glucose; Xyl-xylose; Ara-arabinose; numbers represent process streams (see Fig. 1).

was mixed with 900 mL water and boiled under pressure with directly injected saturated steam for 20 min. Pretreatment temperature ranged from 170 to 200 °C or 3.07–4.25 in terms of severity factor (log R_0) [30,31]. Samples of wet pretreated straw were stored in plastic bags at 4 °C for a maximum period of 3 days and were frozen for permanent storage at −20 °C.

For process network synthesis thermal process energy demand was set close to optimal thermodynamic efficiency which is in opposition to laboratory scale results whereas two to three times higher demands could be observed (data not shown). Improved heat integration in the front end of the processes of steam explosion pretreatment however leads to a reduction in thermal energy demand. A steam-explosion design with two flash tanks for stepwise depressurising and utilisation of flash vapour for preheating incoming process water can be applied to recover exergy. Internal heat integration of the process allows preheating of the process water to 114 °C. Efficiency of the steam generator is assumed to be 50% based on the LHV. All assumptions are related to data from National Renewable Energy Laboratory publication [32].

2.1.3. Mass loss determination in pretreatment

Mass loss during steam explosion was determined by dry matter quantification of pretreated straw. The mass of wet pretreated straw (FM_{PS}) was determined with a platform balance immediately after steam explosion. A minimum of 1000 g wet pretreated straw was oven dried until constant mass at 40 °C directly after pretreatment. Dry substance content of the pretreated straw (DS_{PS}) was determined. Total dry matter (DM_{PS}) after steam explosion was calculated (Formula 1).

$$DM_{PS} = FM_{PS} \times DS_{PS} \qquad (1)$$

Dry matter recovery (w_{DM}) (Formula 2) and mass loss (ML) (Formula 3) were calculated based on the straw input of 818 g DM (cf. Section 2.2)

$$w_{DM} = DM_{PS}/818 \text{ g} \qquad (2)$$

$$ML = 1 - W_{DM} \qquad (3)$$

2.2. Analytical methods

Dry substance content (DS) and volatile solids (VS) were analysed according to the DIN Standard Methods (DIN 38414-S2, DIN 38414-S3) [33,34], and by means of a moisture balance.

Structural carbohydrates and lignin of the biomass were determined according to NREL method NREL/TP-510-42618 [35]. Monosaccharides in liquid solution were quantified by high performance liquid chromatography (HPLC) after two-stage exhaustive acid hydrolysis. The analysis were performed on an Agilent Technologies 1200 Series equipped with a Varian Metacarb 87H column at 65 °C with H_2SO_4 (c = 5 mmol L^{-1}) as eluent and a flow rate of 0.8 mL min^{-1} and UV 210 nm as well as RI detection.

Mannose, galactose and fructose could not be separated clearly from xylose − only a combined quantification of those sugars was possible. Hereinafter this fraction is referred to as xylose (Xyl). This was regarded admissible as xylose is the major fraction of hemicellulose [36,37].

The concentration of dissolved monosaccharides, acids and ethanol after hydrolysis and fermentation were quantified using the HPLC system defined before.

Cellulase activity was determined following the microplate-based filter paper assay described by Xiao et al. [38]. Filter paper disks were transferred into 96-well PCR-plates and incubated with the enzyme for 1 h. Glucose concentration was measured photometric after DNS-reagent reaction.

2.3. Enzymatic hydrolysis

Liquefaction of raw material was accomplished by enzymatic hydrolysis with the commercial enzyme mixture Accelerase 1500 from Genencor®. Hydrolysis was performed in a shaking incubator with a frequency of 150 min^{-1} at 50 °C and an incubation time of 72 h. Experiments were carried out in triplicates in 1000 mL glass bottles with 500 g reaction volume. Straw was neither washed nor dried nor autoclaved prior to enzymatic hydrolysis. 50 g (dry substance) wet biomass was mixed with citrate buffer (c = 0.1 Mol L^{-1}, pH 5) and 15 mL enzyme mixture to a total mass of 500 g. The determined enzyme activity was 47 FPU mL^{-1}. pH value was readjusted with NaOH (c = 4 mol L^{-1}) if necessary after 6 and 24 h. For process network synthesis onsite enzyme production was assumed. Enzyme yield was set to 175 FPU g^{-1} cellulose [39,40]. Enzyme loading for hydrolysis was assumed to be 15 FPU g^{-1} cellulose.

2.4. Solid/liquid separation

After hydrolysis the suspension was separated into a liquid (LF) and solid fraction (SF) via vacuum filtration (MN615 4–12 μm). SF was washed with distilled water, to extract adherent sugars. Therefore SF was mixed with three times of its mass with distilled water. The suspension was shaken overnight at a frequency of 100 min^{-1} at room temperature. Washed SF was separated again via vacuum filtration (MN615 4–12 μm) and oven dried at 40 °C for 48 h. For PNS calculations solid liquid separation was assumed to have a separation performance of 100%, respectively no mass loss in the separation was included.

2.5. Ethanol fermentation and purification

The fermentation of glucose to ethanol was done by commercial baker's yeast Saccharomyces cerevisiae from Ed. Haas Austria GmbH, Traun, Austria. 100 mL LF was mixed with 2 mL CaCl$_2$*2H$_2$O (γ = 150 g L^{-1}), 2 mL KH$_2$PO$_4$ (γ = 143 g L^{-1}), 2 mL MgSO$_4$*7H$_2$O (γ = 75 g L^{-1}) and 0.44 g (NH$_4$)2HPO$_4$. pH value was adjusted to 4.6 with H$_2$SO$_4$. For inoculation 7 g of the yeast was diluted with 100 mL distilled water and incubated for 30 min at 30 °C. 2 mL of

the yeast suspension was added to the fermentation mixture. The glucose concentration in the liquid faction after hydrolysis reached 5.8 w/w-%, the xylose concentration 2.3 w/w-%. Fermentation was performed in a shaking incubator with a frequency of 110 min^{-1} at 30 °C and an incubation time of 168 h. The long incubation time in the laboratory batch-experiments is in line with other published approaches to experience the kinetics of the sugar conversion [41—43].

For PNS calculation ethanol yield was assumed to be 95%. Ethanol is purified to 960 mL L^{-1} ethanol by distillation and further purification is not considered. Energy demand of distillation is considered as function of ethanol concentration based on property data from Ref. [44]. The energy demand as a power function of ethanol concentration is visualised in Fig. 2 and is in accordance to other studies [45].

The correlation underlines the requirement of maximized ethanol concentration in the fermentation broth for energy efficient biomass conversion and subsequent product recovery.

2.6. Biological methane potential

Biological methane potential (BMP) was determined by means of laboratory experiments and theoretical yield calculations.

2.6.1. Laboratory batch experiments
The BMP of untreated as well as pretreated wheat straw and SF was analysed by running laboratory batch tests according to VDI 4630 [46]. Experiments were performed in triplicates in 2 L glass bottles with volumetric biogas measurement with eudiometer tubes. 300 mL inoculum was mixed with 700 mL tap water and 3 g$_{VS}$ substrate. Temperature was set to 38 °C. Bottles were shaken by hand once a day. Biogas production was measured on a daily basis. Methane content was determined with a DRÄGER X-am 7000 mobile gas-analyser in week three. The liquid fraction of an agricultural biogas plant was used for inoculation. To evaluate the inoculum quality, maize silage was used as a reference substrate.

2.6.2. Theoretical methane calculations
The methane potential of the liquid phase after hydrolysis and fermentation was theoretically calculated with the Buswell equation [47].

$$C_aH_bO_c + (a - b/4 - c/2)\, H_2O \rightarrow (a/2 + b/8 - c/4)\, CH_4 + (a/2 - b/8 + c/4)\, CO_2 \qquad (4)$$
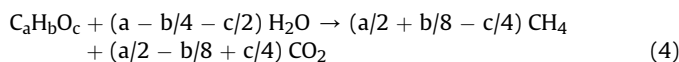
Glucose ($C_6H_{12}O_6$), xylose ($C_5H_{10}O_5$) and acetic acid ($C_2H_4O_2$) in the liquid fraction after hydrolysis and the liquid fraction after

fermentation were considered for theoretical methane calculations.

2.7. Process network synthesis

The process network was modelled in PNS studio (accessible from http://www.p-graph.com). The maximum structure was set according to the process flow sheet presented in Fig. 1. All tested pretreatment conditions are integrated in the maximum structure. Combined hexose and pentose conversion to ethanol was integrated as an alternative to straight hexose conversion. Energy and mass balances were made according to laboratory and literature data as described in chapter 2.1—2.6. An energy self-sufficient process was stipulated whereas process heat and power is provided by integrated combined heat and power (CHP) from untreated wheat straw, lignin or biogas. Selecting the optimal pathway for energy production is part of process network syntheisis. The energy efficiency of the CHP was set to 40% for power production and 50% for process heat based on lower heating value (LHV). The LHV of the carbohydrate streams was calculated according to Thomsen et al. [48]. Process heat requirements beside steam explosion and distillation is neglected when straw is pretreated − assuming that necessary process heat can be recovered from process exhaust steam through heat integration installations. All input data for PNS is summarised in Table 1.

3. Results and discussion

3.1. Chemical composition and mass loss steam explosion pretreatment

The chemical composition of untreated and pretreated wheat straw is summarised in Table 2. Results are presented as mass balance based on one kg untreated straw process input representing process stream one (untreated wheat straw) and two (pretreated wheat straw − various conditions) of the process flow sheet presented in Fig. 1.

As visualised in Fig. 4 accumulated mass of ash, lignin and glucose are relatively constant for different steam explosion pretreatment conditions representing 700 g (wheat straw process input 1 kg DM). Xylose and arabinose masses are declining with harsher pretreatment conditions and a linear correlation with the severity factor was found (see Fig. 3).

The calculation method of dry matter losses during steam explosion pretreatment is reported under paragraph 2.4. The mass loss in pretreatment is primarily caused by degradation of hemicellulose to volatile compounds that are vented off within the
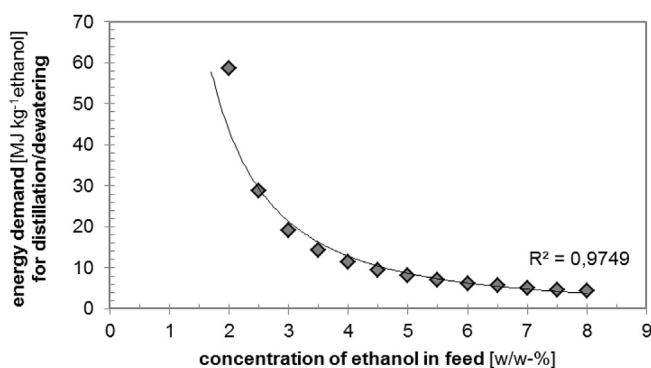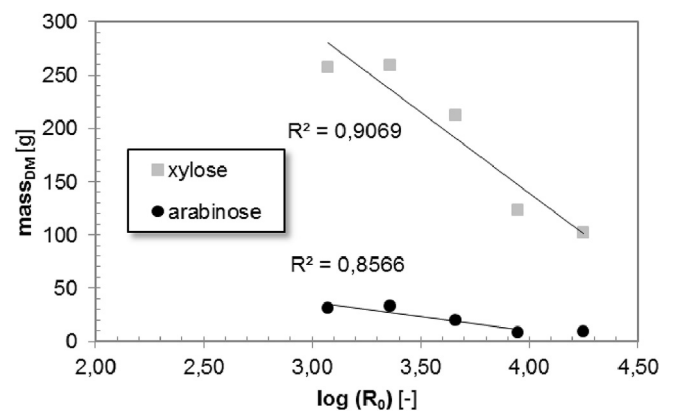

Fig. 2. Correlation between mass concentration of ethanol [w/w-%] and energy demand [MJ kg^{-1}ethanol] for distillation.

Fig. 3. Correlation of xylose and arabinose mass fractions [g] with the severity factor based on 1 kg untreated wheat straw.
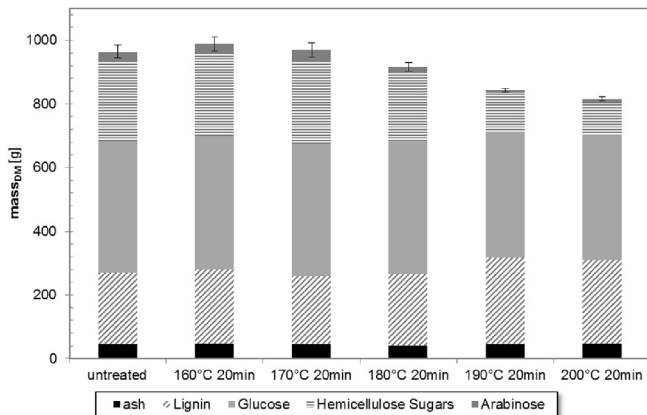
Fig. 4. Mass fractions [g] of pretreated straw for diverse pretreatment conditions based on 1 kg untreated wheat straw.

exhaust steam of the pretreatment section. The maximum dry matter loss was determined to be 18%. This result is in good accordance with literature data where mass losses between 15 and 25% for batch as well as continuous steam explosion facilities are reported [49—51]. Pyrolysis, oxidation and dehydrogenation reactions are responsible for the sugar-degrading, wherein the pyrolysis in the absence of oxygen takes place by thermal decomposition of the organic materials. Oxidation promotes the degradation of the organic substance to carbon dioxide and water, and also contributes to a partial conversion of pentoses to carboxylic acids and other degradation products. For longer residence times or increasing pretreatment temperatures, the production of furfural and HMF increases by dehydration of pentoses and hexoses to [52]. The thermal energy consumption in pretreatment is almost linearly proportional to the liquid/solid ratio based on thermodynamic calculations [53]. A minimal critical solids loading of 25 w/w-% is required to limit thermal energy input for pretreatment [54].

3.2. Enzymatic hydrolysis

During enzymatic hydrolysis polysaccharides are degraded into monosaccharide sugars and biomass is partially liquefied. Table 3 summarises the measured sugar contents in the solid and liquid phase after hydrolysis as well as the liquefaction yield of glucose (GL) and xylose (XL) (The liquefaction yield describes percentage of liquefied sugar monomers from cellulose and hemicelluloses

compared to the theoretical yield).

Enzymatic hydrolysis shows the highest efficiency at the harshest pretreatment conditions of 200 °C/20 min with a GL of 53% and a XL of 81% of the theoretical yield. Comparable values are reported by Dererie et al. [55] for oat straw and Vintila et al. for wheat straw [56]. Other literature sources report glucose yields up to 98% [57—59], for wheat straw but Wang et al. [60] found that the overall glucose yield is strongly dependent on the cellulose loading. They report a glucose yield of 50% for cellulose concentrations of 50 g L^{-1} in hydrolysis. Similar yields were published by other research groups [57,61,62]. Due to high cellulose contents in the straw used in this study, the cellulose loading in the liquefaction experiments was 47 g L^{-1}, which might explain the comparably low glucose yield.

With respect to possible process optimisations due to optimised enzyme mixtures or pretreatment an optimal ethanol process is considered in the maximum structure of PNS. For the optimised ethanol process a GL of 90% and a XL of 85% is assumed. The possibility of xylose conversion to ethanol is considered in the maximum structure as well.

3.3. Bioethanol fermentation

Laboratory fermentation experiments resulted in an 80% conversion of glucose to ethanol. An increase in conversion for optimal fermentation processes up to 97% has already been proven. Comparable low ethanol yield can be explained by the used batch system and aerobic conditions at the beginning of the fermentation experiments [63]. For PNS simulation a conversion rate of 95% was assumed. Ethanol amount in Table 3 is already calculated with a conversion rate of 0.48 g g^{-1} glucose.

3.4. Biogas and methane potential studies

Experimentally determined as well as calculated methane potentials were the basis for the evaluation of the energy output of the biogas plant implemented in the biorefinery concept. All results are summarised in Table 4.

Untreated wheat straw has a specific biogas yield of 490 $Nm^3 t^{-1}$ VS with a methane concentration of 55%. Literature data varies between 50 and 297 $Nm^3 t^{-1}$ VS methane [64—67]. These differences can be explained by different particle sizes and different incubation temperatures [64,67,68]. Positive effects of steam explosion pretreatment on anaerobic digestibility of lignocellulosic material have already been reported [64,67,69,70]. Reduced methane yields for more severe pretreatment conditions can be

Table 3
Sugar contents in the solid/liquid phase after hydrolysis and liquefaction rate of glucose (GL) and xylose (XL).

SN	6					7					8		
	Solid fraction after hydrolysis					Liquid fraction after hydrolysis					Liquid fraction after fermentation		
Pretreatment	Mass$_{DM}$ [g]	Glc [g]	Xyl [g]	Ara [g]	Lignin [g]	Mass [g]	Glc [g]	Xyl [g]	GL [w/w-%]	XL [w/w-%]	Mass [g]	Ethanol [g]	Xyl [g]
170 °C/20 min	825	478.0 ± 3.1	199.0 ± 16.2	23.1 ± 8.3	216.3 ± 2.3	4025	97.3 ± 24.5	33.2 ± 1.2	23	13	4025	47.1 ± 2.0	29.3 ± 0.0
180 °C/20 min	720	326.2 ± 9.5	100.4 ± 17.4	8.2 ± 6.9	252.0 ± 3.6	3880	109.5 ± 16.7	82.1 ± 1.7	26	39	3880	53.1 ± 6.0	64.3 ± 6.3
190 °C/20 min	510	191.3 ± 3.7	40.0 ± 3.2	3.2 ± 1.6	252.5 ± 1.9	3690	199.0 ± 9.7	80.4 ± 5.1	51	65	3690	96.4 ± 5.7	56.2 ± 8.1
200 °C/20 min	500	189.0 ± 4.4	36.5 ± 3.2	2.2 ± 0.4	248.0 ± 5.1	3600	210.4 ± 1.8	83.3 ± 1.6	53	81	3600	101.9 ± 5.7	83.3 ± 1.4
200 °C/20 min opt.	329	39.4*	15.3*	2.2*	248.0*	3771	354.2*	86.7*	90	85	3771	171.6*	86.7*
200 °C/20 min opt.+C$_5$	329	39.4*	15.3*	2.2*	248.0*	3771	254.2*	86.7*	90	85	3771	213.5*	0.0*

Glc-glucose; Xyl-xylose; Ara-arabinose; GL-glucose liquefaction rate; XL-xylose liquefaction rate; numbers represent process streams (see Fig. 1).
[a] ... Optimised ethanol process with increased glucose and xylose liquefaction − calculated data only.
[b] ... See footnote a as well as glucose and xylose conversion to ethanol − calculated data only.
*Standard deviation not specified − only calculated data not based on laboratory experiments.

Table 4
Results of biogas and methane potential studies.

SN	2		6		7				9			
Pretreatment	Pretreated straw		Solid fraction after hydrolysis		Liquid fraction after hydrolisis				Liquid fraction after fermentation			
	Biogas [L kg^{-1}$_{DM}$]	c CH$_4$ [v/v-%]	Biogas [L kg^{-1}$_{DM}$]	c CH$_4$ [v/v-%]	Biogas [L kg^{-1}$_{DM}$]		c CH$_4$ [v/v-%]		Biogas [L kg^{-1}$_{DM}$]		c CH$_4$ [v/v-%]	
Untreated straw	478 ± 6.3	55 ± 1.5	546 ± 10.9	51 ± 0.0	n.s.		n.s.		n.s.		n.s.	
170 °C/20 min	549 ± 14.8	54 ± 1.5	548 ± 21.9	50 ± 0.7	24.7	*	50	*	6.7	*	50	*
180 °C/20 min	508 ± 7.0	55 ± 1.2	413 ± 6.9	53 ± 1.0	40.0	*	50	*	19.0	*	50	*
190 °C/20 min	517 ± 18.5	53 ± 1.2	288 ± 11.5	50 ± 0.5	60.5	*	50	*	20.2	*	50	*
200 °C/20 min	521 ± 12.0	55 ± 1.3	292 ± 8.8	50 ± 1.0	65.1	*	50	*	21.5	*	50	*
200 °C/20 min opt.					91.3	*	50	*	21.1	*	50	*
200 °C/20 min opt.+C$_5$**					91.2	*	50	*	4.0	*	50	*

*Standard deviation not specified − calculated data not based on laboratory experiments.
**90 w/w-% sugar yield in hydrolysis; hemicellulose sugar conversion to ethanol.

explained by degradable sugar losses during steam explosion. Severe pretreatment show reduced methane yield despite higher energy consumption for steam explosion but significantly increases degradation speed of lignocellulosic sugars by a factor of 2−2.6 (data not shown). Degradation speed was not included in the optimisation study.

A linear correlation was found (y = 1062.8 x − 205.49) for the methane yield of the solid fibre fraction after hydrolysis related to the undissolved sugar content (see Fig. 5).

The correlation of sugar content and biogas yield indicates that higher glucose liquefaction rate in the hydrolysis would lead to reduced methane yield of the fibre fraction. Kaparaju et al. [64] reported high methane yields of wheat straw stillage even though cellulose conversion rate was 90% and remaining sugars in the fraction was quite low. In difference to this study Kaparaju et al. [64] used fermentation stillage as a mixture of solid and liquid fraction containing liquid carbon sources not related to the biomass input like acetate, yeast or enzyme.

Biogas yield of liquid fractions were calculated as described in paragraph 2.6.2, results are presented in Table 4.

3.5. Process network synthesis

Originating from the maximum structure including all investigated operation conditions the optimal structure, which is the process pathway resulting in maximum energy output from 1 ton straw input, was determined as follows: Steam explosion of straw (817 kg) at 170 °C for 20 min and direct biogas production of the pretreated material as well as bioethanol production of straw (183 kg) pretreated at 200 °C for 20 min. This process results in a purified methane yield of 7892 MJ and a purified ethanol yield of 964 MJ per ton untreated straw input. Only 40 MJ produced process

heat is wasted. The waste process heat is a result of the stipulated internal electricity production for self-sufficient supply. The determined optimal structure is presented in Fig. 6.

The presented process structure was the result of simulation work and is defined as combined bioethanol and biogas facility with the highest energy output (methane and ethanol) of one ton wheat straw. 81.7% of the input material is used for biogas production and only 18.3% for ethanol production. Lignin combustion is preferred to biogas and untreated wheat straw incineration for process energy production. As expected the system selected optimised enzymatic hydrolysis (GL 90%) for cellulose liquefaction in combination with simultaneous hexose and pentose fermentation in order to minimize the energy consumption of the distillation unit. The advantage of anaerobic digestion of pretreated straw compared to biogas production of untreated straw is significant due the higher biogas and net energy production.

The robustness of this optimal structure was tested by varying the amount of ethanol produced. This evaluation was done for the "standard" ethanol process (GL 53%) and the optimised process (GL 90%). A brief summary of the resulting energy output is presented in Tables 5 and 6.

For all evaluated scenarios the results of the optimal process network structure is comparable. A higher proportion of the solid fraction is transferred to the biogas plant due to the missing valuation of electricity in the standard ethanol process. Due to the lower sugar content in the solid fraction of the optimised ethanol process (see Table 3 and Fig. 5) the whole fraction is transferred to the CHP resulting in high electricity production. For high liquefaction rates the total energy yield is relatively stable. The amount of straw pretreated with 170 °C is decreasing at an increasing amount of ethanol produced. The methodology proposed provides an assessment of the lignocellulosic biomass-to-ethanol and biomass-to-biomethane conversion technology systems with maximum energy output. However the choice of a technology concept will depend on various impact factors such as economic returns, socio-economic issues, national/regional policies or environmental impacts.

4. Conclusions

4.1. Performance of laboratory batch experiments on unit processes of the biorefinery concept

Fig. 5. Correlation of the undissolved sugar content with biogas yield of solid fraction after hydrolysis.

Xylose and arabinose masses are declining in linear correlation with harsher steam explosion pretreatment conditions. This mass loss of up to 18% is primarily associated with the degradation of hemicellulose to volatile compounds that are vented off within the
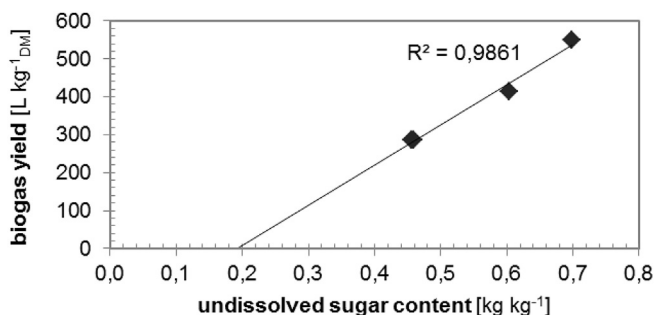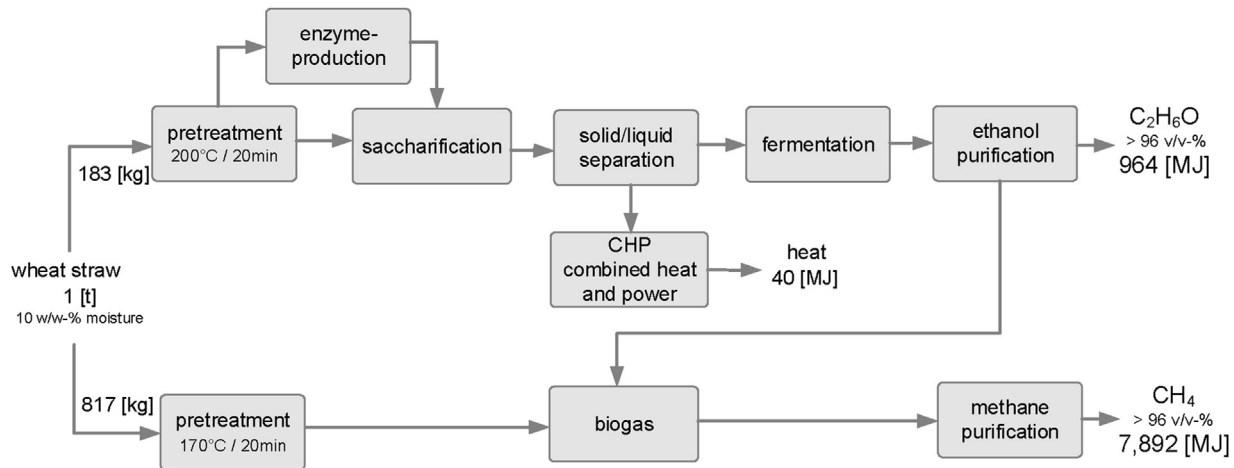
Fig. 6. Process flow sheet of the analysed optimal structure of process network.

Table 5
Results of scenario evaluation of process network synthesis for the standard ethanol process (GL 53%).

Postulated ethanol output	Standard ethanol process (GL 53%)			
	Biomethaneoutput	Biomethane + bioethanol output	Excess electricity output	Waste heat output
[MJ]	[MJ]	[MJ]	[MJ]	[MJ]
0	8838	8838	0	318
500	7897	8397	250	174
1000	6279	7279	1093	26
1500	4616	6116	1956	310
2000	2955	4955	2819	496
2500	1292	3792	3682	731

Table 6
Results of scenario evaluation of process network synthesis for the optimised ethanol process (GL 90%).

Postulated ethanol output	Optimised ethanol process (GL 90%)			
	Biomethane output	Biomethane + bioethanol output	Excess electricity output	Waste heat output
[MJ]	[MJ]	[MJ]	[MJ]	[MJ]
0	8838	8838	0	318
500	8346	8846	0	174
1000	7830	8830	23	58
1500	6941	8441	351	310
2000	6053	8053	679	562
2500	4708	7208	1385	2492
3000	3729	6729	1789	3079
3500	2750	6250	2191	3666
4000	2504	6504	1991	1568
4500	1616	6116	2319	1819
5000	729	5729	2646	2071
5270	251	5251	2933	3407

exhaust steam of the pretreatment section and strongly influences process performance of the biorefinery concept. Linked to harshest pretreatment conditions of 200 °C/20 min enzymatic hydrolysis showed highest efficiency with a GL of 53% and XL of 81%. Follow-up laboratory scale fermentation showed a conversion of 80% from glucose to ethanol. In contrast to the bioethanol route, severe pretreatment resulted in reduced biomethane yield despite higher energy consumption for steam explosion pretreatement. However degradation speed increases by a factor of 2—2.6 significantly for pretreatment conditions of 200 °C/20 min compared to 170 °C/20 min and the correlation of sugar content and biogas yield indicates that higher glucose liquefaction rate in hydrolysis would lead to reduced methane yield of the solid fibre fraction.

4.2. Energetic process output optimization via process network synthesis

Biorefinery systems are a high ranked option to guarantee the maximum economic output from available biomass sources. Bioethanol based biorefineries are one possible option especially for lignocellulosic residuals like straw. To reach competitive ethanol production costs in 2nd generation production facilities the factors raw material, logistics, amount of required auxiliary chemicals and location-specific plant size will have high influence.

From the conducted process network synthesis the necessity of process-integrated heat management as well as minimized conversion losses for an increase in the energy output/input ratio was

identified. Especially the valorisation of pentoses seems to be necessary in order to become competitive. The investigated approach of a combined bioethanol and biogas helps to minimise wastewater output and the achievement of closed nutrient cycles.

It was shown that biogas as well as combined bioethanol and biogas production can be realised with a considerable net energy surplus. The optimised process results in a purified methane yield of 7892 MJ and a purified ethanol yield of 964 MJ per ton untreated straw input which corresponds to a share of approximately 55% of the lower heating value.

As already mentioned the optimization goal was to identify a process configuration to biotechnologically convert one ton of wheat straw to a maximum output of transport- and storable final energy carriers. Also other investigations in biorefinery frameworks concluded that it is more energetically efficient to produce a range of biofuels from straw including biogas than producing bioethanol only [71]. The findings emphasise the examination how waste streams can be optimal capitalized in maximum energy conversion concepts. However the chosen approach is neglecting economic framework whereas a maximised ethanol output will trend to higher product revenues since the energy specific market price for ethanol is approximately five times higher than for methane/natural gas and consequently favour the return on the high investment for ethanol production capacities. A next step would be the examination of the economic attractiveness of the investigated process scenarios and the extent to material processing to provide valuable biobased products. If beside energy values also economic parameters (prices, costs or support schemes) would be considered in this evaluation a strong shift in the conclusions is possible. The results of the paper can therefore be regarded as reference concerning how much utilizable energy can be yielded from agricultural residues like wheat straw.

Acknowledgement

References

[1] M. Eder, S. Kirchweger, Aufbereitung & Analyse von Daten aus dem Arbeitskreis Biogas zu Kosten bestehender Biogasanlagen, Amt der Niederösterreichischen, June 2012. LR 2011, http://www.energieklima.at/fileadmin/user_upload/pdf/Zahlen_Daten/Studie_Biogas_NOE__2201___3_01.pdf.

[2] http://www.bioenergie-portal.info/fileadmin/bioenergie-beratung/bayern/dateien/biogasertraegedivers.pdf, June 2012.

[3] K. Fazeni, H. Steinmüller, Impact of changes in diet on the availability of land, energy demand, and greenhouse gas emissions of agriculture, Energy Sustain. Soc. 1 (2011) 6, http://dx.doi.org/10.1186/2192-0567-1-6.

[4] D. Bacovsky, N. Ludwiczek, M. Ognissanto, M. Wörgetter, Status of Advanced Biofuels Demonstration Facilities in 2012, 2013. IEA Bioenergy Task 39, Liquid Biofuels.

[5] J. Larsen, M.Ø. Haven, L. Thirup, Inbicon makes lignocellulosic ethanol a commercial reality, Biomass Bioenergy 46 (2012) 36–45.

[6] Anna Ekma, Ola Wallberg, Elisabeth Joelsson, Pål Börjesson, Possibilities for sustainable biorefineries based on agricultural residues – a case study of potential straw-based ethanol production in Sweden, Appl. Energy 102 (2013) (2013) 299–308.

[7] F. Cherubini, S. Ulgiati, Crop residues as raw materials for biorefinery systems – a LCA case study, Appl. Energy 87 (2010) 47–57.

[8] vR. René, A. Bert, Status Report Biorefinery 2007, NL-6700 AA, Agrotechnology and Food Sciences Group, Wageningen, 2007.

[9] F. Cherubini, The biorefinery concept: using biomass instead of oil for producing energy and chemicals, Energy Convers. Manag. 51 (2010) 1412–1421.

[10] S. Fahd, G. Fiorentino, S. Mellino, S. Ulgiati, Cropping bioenergy and biomaterials in marginal land: the added value of the biorefinery concept, Energy (2011), http://dx.doi.org/10.1016/j.energy.2011.08.023.

[11] K. Kemppainen, L. Ranta, E. Sipilä, A. Östman, J. Vehmaanperä, T. Puranen, et al., Ethanol and biogas production from waste fibre and fibre sludge – the fibre EtOH concept, Biomass Bioenergy (2012), http://dx.doi.org/10.1016/j.biombioe.2012.03.027.

[12] P. Oleskowicz-Popiel, Z. Kádár, S. Heiske, D. Klein-Marcuschamer, B.A. Simmons, H.W. Blanch, J. Schmidt, Co-production of ethanol, biogas, protein fodder and natural fertilizer in organic farming – evaluation of a concept for a farm-scale biorefinery, Bioresour. Technol. 104 (2012) 440–446, http://dx.doi.org/10.1016/j.biortech.2011.11.060.

[13] F. De Paoli, A. Bauer, C. Leonhartsberger, B. Amon, T. Amon, Utilization of by-products from ethanol production as substrate for biogas production, Bioresour. Technol. 102 (2011) 6621–6624, http://dx.doi.org/10.1016/j.biortech.2011.03.045.

[14] M. Shafiei, K. Karimi, M.J. Taherzadeh, Techno-economical study of ethanol and biogas from spruce wood by NMMO-pretreatment and rapid fermentation and digestion, Bioresour. Technol. 102 (2011) 7879–7886, http://dx.doi.org/10.1016/j.biortech.2011.05.071.

[15] P. Kaparaju, M. Serrano, I. Angelidaki, Optimization of biogas production from wheat straw stillage in UASB reactor, Appl. Energy 87 (2010) 3779–3783, http://dx.doi.org/10.1016/j.apenergy.2010.06.005.

[16] M.J. Taherzadeh, K. Karimi, Acid-based hydrolysis processes for ethanol from lignocellulosic materials: a review, BioResources 2 (3) (2007) 472–499. ncsu.edu/bioresources.

[17] L. da Costa Sousa, S.P. Chundawat, V. Balan, B.E. Dale, 'Cradle-to-grave' assessment of existing lignocellulose pretreatment technologies, Curr. Opin. Biotechnol. 20 (2009) 339–347.

[18] P. Kumar, D.M. Barrett, M.J. Delwiche, P. Stroeve, Methods for pretreatment of lignocellulosic biomass for efficient hydrolysis and biofuel production, Ind. Eng. Chem. Res. 48 (2009) 3713–3729.

[19] E. Tomas-Pejo, J.M. Olive, M. Ballesteros, Realistic approach for full-scale bioethanol production from lignocellulose: a review, J. Sci. Ind. Res. 67 (2008) 874–884.

[20] Sohrab Haghighi Mood, Amir Hossein Golfeshan, Meisam Tabatabaei, Gholamreza Salehi Jouzani, Gholam Hassan Najafi, Mehdi Gholami, Mehdi Ardjmand, Lignocellulosic biomass to bioethanol, a comprehensive review with a focus on pretreatment, Renew. Sustain. Energy Rev. 27 (2013) 77–93.

[21] R. Mutreja, D. Das, D. Goyal, A. Goyal, Bioconversion of agricultural waste to ethanol by SSF using recombinant cellulase from Clostridium thermocellum, Res. Pap. Enzyme Res. (2011), http://dx.doi.org/10.4061/2011/340279.

[22] http://www.ifr.ac.uk/esegp5/talks/Michinson%202.pdf, June 2012.

[23] F.K. Agbogbo, G. Coward-Kelly, M. Torry-Smith, K.S. Wenger, Fermentation of glucose/xylose mixtures using Pichia stipitis, Process Biochem. 41 (11) (2006) 2333–2336, http://dx.doi.org/10.1016/j.procbio.2006.05.004.

[24] Y. Kim, L.O. Ingram, K.T. Shanmugam, Construction of an Escherichia coli K-12 mutant for homoethanologenic fermentation of glucose or xylose without foreign genes, Appl. Environ. Microbiol. 73 (6) (2007) 1766, http://dx.doi.org/10.1128/AEM.02456–06.

[25] M. Ballesteros, J.M. Oliva, M.J. Negro, P. Manzanares, Ethanol from lignocellulosic materials by a simultaneous saccharification and fermentation process (SFS) with Kluyveromyces marxianus CECT 10875, Process Biochem. 39 (12) (2004) 1843–1848, http://dx.doi.org/10.1016/j.procbio.2003.09.011.

[26] K. Öhgrena, O. Bengtssonb, M.F. Gorwa-Grauslundb, M. Galbea, B. Hahn-Hägerdalb, G. Zacchi, Simultaneous saccharification and co-fermentation of glucose and xylose in steam-pretreated corn stover at high fiber content with Saccharomyces cerevisiae TMB3400, J. Biotechnol. 126 (2006) 488–498, http://dx.doi.org/10.1016/j.jbiotec.2006.05.001.

[27] F. Friedler, L.T. Fan, B. Imreh, Process network synthesis: problem definition, Networks 31 (2) (1998) 119–124 (doi: 10.1002/(SICI)1097-0037(199803)31:2<119::AID-NET6>3.0.CO;2-K).

[28] J.C. Garcia-Ojeda, B. Bertok, F. Friedler, Planning evacuation routes with the P-graph framework, Chem. Eng. Trans. 29 (2012) 1531–1536, http://dx.doi.org/10.3303/CET1229256.

[29] L. Vance, H. Cabezas, I. Heckl, B. Bertok, F. Friedler, Synthesis of sustainable energy supply chain by the P-graph framework, Ind. Eng. Chem. Res. 52 (1) (2013) 266–274.

[30] R.P. Overend, E. Chornet, Fractionation of lignocellulosics by steam-aqueous pretreatments, Philos. Trans. R. Soc. Lond. A 321 (1987) 523–536.

[31] F. Carvalheiro, T. Silva-Fernandes, L. Duarte, F. Gírio, Wheat straw autohydrolysis: process optimization and products characterization, Appl. Biochem. Biotechnol. 153 (2009) 84–93.

[32] National Renewable Energy Laboratory (NREL) NREL/TP-5100-47764 2011.

[33] DIN 38414-S2, Bestimmung des Wassergehaltes und des Trockenrückstandes bzw. der Trockensubstanz, DEV, vol. 84, 2012 (Lieferung).

[34] DIN 38414-S3, Bestimmung des Wassergehaltes und des Trockenrückstandes bzw. der Trockensubstanz, DEV, vol. 84, 2012 (Lieferung).

[35] NREL/TP-510–42618 http://www.nrel.gov/biomass/pdfs/42618.pdf.

[36] X.F. Sun, F. Xu, R.C. Sun, P. Fowlerc, M.S. Baird, Characteristics of degraded cellulose obtained from steam-exploded wheat straw, Carbohydr. Res. 340 (2005) 97–106, http://dx.doi.org/10.1016/j.carres.2004.10.022.

[37] A. Bercier, R. Plantier-Royon, C. Portella, Convenient conversion of wheat hemicelluloses pentoses (D-xylose and L-arabinose) into a common intermediate, Carbohydr. Res. 342 (2007) 2450–2455, http://dx.doi.org/10.1016/j.carres.2007.07.010.

[38] Z. Xiao, R. Storms, A. Tsang, Microplate-based filter paper assay to measure total cellulase activity, Biotechnol. Bioeng. 88 (2004) 832–837, http://dx.doi.org/10.1002/bit.20286.

[39] H. Esterbauer, W. Steiner, I. Labudova, A. Hermann, M. Hayn, Production of Trichoderma cellulase in laboratory and pilot scale, Bioresour. Technol. 36 (1) (1991) 51–65.

[40] Z. Barta, K. Kovacs, K. Reczey, G. Zacchi, Process design and economics of on-site cellulase production on various carbon sources in a softwood-based ethanol plant, Enzyme Res. 8 (2010), http://dx.doi.org/10.4061/2010/734182. Article ID 734182.

[41] Chizuru Yamaoka, Osamu Kurita, Tomoko Kubo, Improved ethanol tolerance of Saccharomyces cerevisiae in mixed cultures with Kluyveromyces lactis on high-sugar fermentation, Microbiol. Res. 169 (12) (2014) 907–914.

[42] J.N. Jackowetz, S. Dierschke, R. Mira de Orduña, Multifactorial analysis of acetaldehyde kinetics during alcoholic fermentation by Saccharomyces cerevisiae, Food Res. Int. 44 (2011) (2011) 310–316.

[43] Francisco B. Pereira, Aloia Romaní, Héctor A. Ruiz, José A. Teixeira, Lucília Domingues, Industrial robust yeast isolates with great potential for fermentation of lignocellulosic biomass, Bioresour. Technol. 161 (2014) 192–199.

[44] VDI-Wärmeatlas, Berechnungsblätter für den Wärmeübergang, vol. 6, VDI-Verlag, Düsseldorf, 1991.

[45] P.L. Coté, C. Roy, N. Bernier, M. Schwartz, M. Kazmir, R. Shamash, Field Demonstration of the Siftek[TM] membrane for ethanol production, in: 2007 Fuel Workshop, St. Louis, June 26-29, 2007.

[46] VDI 4630 Vergärung Organischer Stoffe Substratcharakterisierung, Probenahme, Stoffdatenerhebung, Gärversuche.

[47] H. Roediger, M. Roediger, H. Kapp, Anaerobe Alkalische Schlammfaulung, fourth ed., Oldenbourg, München, Wien, 1999, ISBN 3-486-26103-7, p. 68.

[48] M.H. Thomsen, A. Thygesen, A.B. Thomsen, Hydrothermal treatment of wheat straw at pilot plant scale using a three-step reactor system aiming at high hemicellulose recovery, high cellulose digestibility and low lignin hydrolysis, Bioresour. Technol. 99 (2008) 4221–4228, http://dx.doi.org/10.1016/j.biortech.2007.08.054.

[49] E. Viola, F. Zimbardi, M. Cardinale, G. Cardinale, G. Braccio, E. Gambacorta, Processing cereal straws by steam explosion in a pilot plant to enhance digestibility in ruminants, Bioresour. Technol. 99 (2008) 681–689, http://dx.doi.org/10.1016/j.biortech.2007.02.001.

[50] M. Ibrahim, W.G. Glasser, Steam-assisted biomass fractionation. Part III: a quantitative evaluation of the clean fractionation' concept, Bioresour. Technol. 70 (1999) 181–192.

[51] A.B. Bjerre, A.S. Schmidt, Development of Chemical and Biological Processes for Production of Bioethanol, Risø National Laboratory, 1997. Risø-R-967(EN), http://www.risoe.dtu.dk/rispubl/BIO/BIOpdf/ris-r-967.pdf.

[52] L.P. Ramos, The chemistry involved in the steam treatment of lignocellulosic materials, Quim. Nova 26 (6) (2003) 863–871, http://dx.doi.org/10.1590/S0100-40422003000600015.

[53] J.Y. Zhu, X.J. Pan, R.S. Zalesny Jr., Pretreatment of woody biomass for biofuel production: energy efficiency, technologies and recalcitrance, Appl. Microbiol. Biotechnol. 87 (2010) 847e57.

[54] J.Y. Zhu, X.S. Zhuang, Conceptual net energy output for biofuel production from lignocellulosic biomass through biorefining, Prog. Energy Combust. Sci.

[55] 38 (2012) (2012) 583–598.

[55] D.Y. Dererie, S. Trobro, M.H. Momeni, H. Hansson, J. Blomqvist, V. Passoth, et al., Improved bio-energy yields via sequential ethanol fermentation and biogas digestion of steam exploded oat straw, Bioresour. Technol. 102 (2011) 4449–4455, http://dx.doi.org/10.1016/j.biortech.2010.12.096.

[56] T. Vintila, M. Dradomirescu, V. Croitoriu, C. Vintila, H. Barbu, C. Sand, Saccharification of lignocellulose – with reference to Miscanthus – using different cellulases, Romanian Biotechnol. Lett. 15 (4) (2010) 5498–5504.

[57] P.D. Anantharam, S. Varanasi, C.A. Schall, Enhancement of Cellulose Saccharification Kinetics Using an Ionic Liquid Pretreatment Step, 2006 doi:10.1002/bit.21047, www.interscience.wiley.com.

[58] B.C. Saha, M.A. Cotta, Ethanol production from alkaline peroxide pretreated enzymatically saccharified wheat straw, Biotechnol. Prog. 22 (2006) 449–453, http://dx.doi.org/10.1021/bp050310r.

[59] E. Jakobsson, Optimization of the pretreatment of wheat straw for production of bioethanol. http://www.chemeng.lth.se/exjobb/025.pdf.

[60] W. Wang, L. Kang, H. Wie, A. Rajeev, Y.Y. Lee, Study on the decreased sugar yield in enzymatic hydrolysis of cellulosic substrate at high solid loading, Appl. Biochem. Biotechnol. 164 (2011) 1139–1149, http://dx.doi.org/10.1007/s12010-011-9200-8.

[61] P. Luo, Z. Liu, Conversion of Wheat Straw to Ethanol by Simultaneous Saccharification and Fermentation, IEEE, 2009, 978-1-4244-4713-8/10, http://ieeexplore.ieee.org/stamp/stamp.jsp?arnumber=05518007.

[62] A. Petersson, M.H. Thomsen, H. Hauggaard-Nielsen, A. Thomsen, Potential bioethanol and biogas production using lignocellulosic biomass from winter rye, oilseed rape and faba bean, Biomass Bioenergy 31 (2007) 812–819, http://dx.doi.org/10.1016/j.biombioe.2007.06.001.

[63] L. Laopaiboon, P. Thanonkeo, P. Jaisil, P. Laopaiboon, Ethanol production from sweet sorghum juice in batch and fed-batch fermentations by Saccharomyces cerevisiae, World J. Microbiol. Biotechnol. 23 (2007) 1497–1501, http://dx.doi.org/10.1007/s11274-007-9383-x.

[64] P. Kaparaju, M. Serrano, A.B. Thomsen, P. Kongjan, I. Angelidaki, Bioethanol, biohydrogen and biogas production from wheat straw in a biorefinery concept, Bioresour. Technol. 100 (2009) 2562–2568, http://dx.doi.org/10.1016/j.biortech.2008.11.011.

[65] KTBL Wirtschaftlichkeitsrechner Biogas, June 2012. http://daten.ktbl.de/biogas/startseite.do.

[66] W. Zhong, Z. Zhang, Y. Luo, S. Sun, W. Qiao, M. Xiao, Effect of biological pretreatments in enhancing corn straw biogas production, Bioresour. Technol. 102 (2011) 11177–11182, http://dx.doi.org/10.1016/j.biortech.2011.09.077.

[67] A. Bauer, P. Bösch, A. Friedl, T. Amon, Analysis of methane potentials of steam-exploded wheat straw and estimation of energy yields of combined ethanol and methane production, J. Biotechnol. 142 (2009) 50–55, http://dx.doi.org/10.1016/j.jbiotec.2009.01.017.

[68] A. Mshandetea, L. Bjoörnssonb, A.K. Kivaisia, M.S.T. Rubindamayugia, B. Mattiasson, Effect of particle size on biogas yield from sisal fibre waste, Renew. Energy 31 (2006) 2385–2392, http://dx.doi.org/10.1016/j.renene.2005.10.015.

[69] A.T.W.M. Hendriks, G. Zeeman, Pretreatments to enhance the digestibility of lignocellulosic biomass, Bioresour. Technol. 100 (2009) 10–18, http://dx.doi.org/10.1016/j.biortech.2008.05.027.

[70] R. Chandra, H. Takeuchi, T. Hasegawa, R. Kumar, Improving biodegradability and biogas production of wheat straw substrates using sodium hydroxide and hydrothermal pretreatments, Energy (2012), http://dx.doi.org/10.1016/j.energy.2012.04.029.

[71] P. Kaparaju, M. Serrano, A.B. Thomsen, P. Kongjan, Bioethanol Angelidaki I. biohydrogen and biogas production from wheat straw in a biorefinery concept, Bioresour. Technol. 100 (2009) 2562–2568.