

Fuels and plastics from lignocellulosic biomass *via* the furan pathway; a technical analysis†

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Biorefineries convert biomass into bio-based products, which have the potential to replace typical products produced by petroleum refineries. They provide a technology platform to reduce anthropogenic greenhouse gas emissions, increase security of supply and reduce the dependency on crude oil. The biorefinery concept presented in this paper focuses on a combination of (1) organosolv fractionation to produce carbohydrates from lignocellulosic biomass and (2) the furan technology to convert carbohydrates into polyethylene furanoate (PEF), a bio-based alternative to polyethylene terephthalate (PET), and furfuryl ethyl ether (FEE), a bio-based transportation fuel component. The goal of this paper is to determine the mass and energy balances of the production of PEF and FEE from lignocellulosic biomass and indicate the benefits, as well as potential bottlenecks in the coupling of organosolv and furan chemistry as a biorefinery concept. Three cases are defined, modeled and analyzed, each focusing on a different approach to combine the organosolv and furan conversion technologies and determine the possibility and degree of integration. Modeling results based on experimental data and expert judgments show that wheat straw, as an example of lignocellulosic biomass, can be converted into PEF and FEE at yields between 20 and 40 w/w%, based on total input, while energetic efficiencies are between 30 and 40%. This is comparable or even better compared to other upcoming bio-based processes, e.g. 15–35% yield for second generation bio-ethanol production and 25–50% energy efficiency. The conclusion is that in each of the three cases presented bio-based fuels and plastics can be produced *via* the furan pathway at efficiencies that constitute a viable option from a technological point of view.

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1. Introduction

Biorefineries are envisioned to produce a wide variety of products, much like today's petroleum refineries.¹ Furan derivatives, one of the envisioned bio-based product groups, may replace petrochemicals. Herein, 5-hydroxymethylfurfural (HMF) was identified as a key intermediate for the transition from fossil-based to bio-based industrial chemistry.² Recently, a comprehensive review on the occurrence, properties, formation and application of HMF was published.³ An overview of the most important furan derivatives is presented in Fig. 1.

The first methods of HMF synthesis were published independently by Düll⁴ and Kiermayer⁶ in 1895. In 1944, Haworth and

Jones published a method of HMF production *via* the dehydration of C6 sugars.⁷ In 1990, Antal *et al.*⁸ showed that HMF from hexoses (either fructose or glucose) is formed *via* a transformation of cyclic intermediates and that fructose is converted more readily than glucose. They ascribed the differences in reactivity to the higher stability of the glucopyranoside ring and furan-resembling part in the closed structure of fructose. The difference in reactivity was confirmed by others;³ at similar conditions, dehydration of glucose led to lower HMF yields than when starting from fructose.

Fig. 2 shows an overview of the relevant reactions for the production of furans from lignocellulosic biomass in alcohol-rich solvents (based on ref. 7–15).

Despite the potential HMF holds for a transition from fossil based industrial chemistry to bio-based industrial chemistry, HMF is not produced on a commercial scale today. The main problem is that HMF is a relatively unstable intermediate at the acidic conditions required for its formation; HMF is readily hydrolyzed in presence of (acidified) water to form levulinic acid (LA) and formic acid (FA).^{3,16} Avantium Chemicals B.V. (Avantium) reported that the use of an alcohol or organic acid as the solvent significantly reduced the production of LA and FA by the *in situ* formation of more stable HMF-ethers or -esters.^{9,10}

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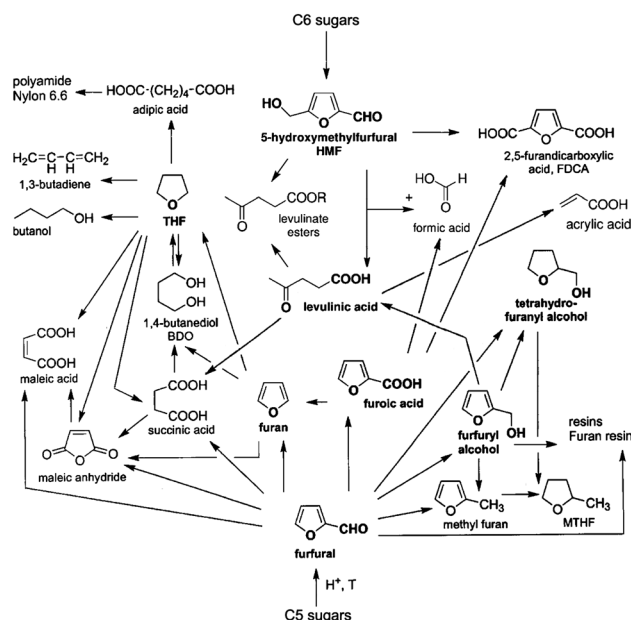


Fig. 1 Overview of the HMF and furfural family trees (adapted from Kamm *et al.*⁴)

The main HMF derivatives under investigation today are levulinic acid (LA) and 2,5-furandicarboxylic acid (FDCA). FDCA can be co-polymerized with ethylene glycol to produce polyethylene furanoate (PEF), a bio-based alternative to fossil-based polyethylene terephthalate (PET). In a previous study, it was shown that greenhouse gas (GHG) emissions and non-renewable energy use (NREU) can be reduced by 50–60% when PET is replaced by PEF, starting from corn-based fructose (first generation biorefinery) and using bio-based ethylene glycol.¹⁷

Even though the highest yields in HMF are obtained using fructose as the starting sugar,³ lignocellulosic biomass is eventually the preferred feedstock due to its economic, environmental and social advantages. One of the main challenges for the successful commercialization of second generation biorefineries is the development of a cost-effective pretreatment technology for lignocellulosic biomass. Unlike in traditional sources of sugar, such as starch, sugar beets and sugarcane, the sugar-precursors in lignocellulosic biomass, such as cellulose and hemicellulose, are protected, among others, by a surrounding matrix of lignin, which complicates hydrolysis and recovery of sugar. Several studies provide an overview of different pretreatment and fractionation technologies available for lignocellulosic biomass.^{18–21} None of these pretreatment technologies can be heralded as the best option, for factors, such as the type of biomass used and the targeted product(s), will vary from case to case.²¹

Following the philosophy of a biorefinery according to Bio-energy Task 42 of the International Energy Agency (IEA),²² the ideal pretreatment technology for second generation biorefineries will be one where all three major components of the biomass are obtained at high yields and purities. One of the most promising technologies that can achieve this goal is organosolv fractionation, a pretreatment technology using an organic solvent for delignification.^{23–26}

As early as 1893, organic solvents were used to remove lignin from woody biomass,^{27,28} but it took until 1931 before the full potential of organic solvents for fractionating biomass into its three main components was realized.²⁹ The main developments of the organosolv technology took place between 1970 and 1990 (ref. 30–33) as an alternative pulping technology for the conventional Kraft pulping process. Currently, the organosolv process is further developed as fractionation technology for the production of bio-based products in the context of biorefineries.

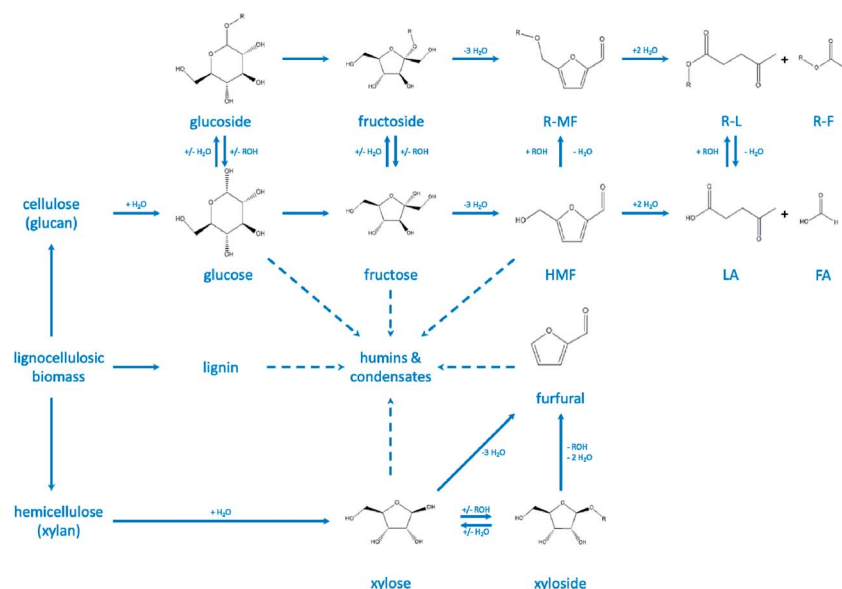


Fig. 2 Overview of the reactions from lignocellulosic biomass to furan derivatives. The equilibrium reactions mentioned here are for the purpose of quantifications of product groups only.

Organosolv fractionation allows for the recovery of all three main constituents of lignocellulosic biomass, *viz.* cellulose, hemicellulose and lignin, in separate streams. In consecutive steps, these fractions can be further upgraded and converted into chemical building blocks, such as HMF, levulinic acid (LA), furfural and phenolics.²

In organosolv technology, biomass is fractionated with aqueous organic solvent mixtures, typically containing short chain alcohols, acetone, formic and acetic acid or ethylene glycol.^{24,25} Fractionation of lignocellulosic biomass using low boiling solvents, such as methanol and ethanol, is typically carried out at 160–200 °C for 60–180 minutes at autogenous pressures with an organic solvent concentration of 40–80% in water.^{24,34–36} During the process, lignin is solubilized and the hemicellulose fraction is hydrolyzed predominantly into xylose, although a significant part of the xylose may also be converted into furfural. Under typical reaction conditions, cellulose is insoluble and can be recovered by solid–liquid separation. Optionally, lignin can be recovered from the solution by precipitation, yielding a high purity lignin that may be used for the production of chemicals, such as phenolics.³⁷ Cellulose can be depolymerized enzymatically or chemocatalytically, the latter typically in the presence of acids. The currently dominant manner of cellulose hydrolysis is by using enzymes.

The biorefinery concepts presented in this paper focus on combinations of lignocellulosic biomass fractionation by organosolv technology and furan chemistry to produce polyethylene furanoate (PEF), a bio-based alternative to PET, and furfuryl ethyl ether (FEE), a bio-based transportation fuel from the streams obtained after fractionation. In order to explore the feasibility of such combinations a simulation model was built using the ASPEN Plus modeling software. Input for the chemical reaction pathways and process lay-out were supplied by ECN and Avantium.

The goal of this study is to determine the mass and energy balances of different routes for the production of PEF and FEE from lignocellulosic biomass. In addition, the benefits, as well as potential bottlenecks related to the coupling of organosolv fractionation technology and the furans platform technology will be identified.

2. Biorefinery concepts

Three case studies employing organosolv and furan conversion technology were defined. All cases are directed towards the production of PEF and FEE from wheat straw. Wheat straw was chosen as feedstock, since it is a relatively cheap, abundantly available agricultural residue, especially in Europe.^{36,38,39}

The three cases are (1) the base case, based on ethanol organosolv, enzymatic hydrolysis and isomerization converting cellulose to fructose (aqueous step) and fructose based furans production in methanol; (2) the glucosides case, based on methanol organosolv, cellulose methanolysis and furans production in methanol from methyl-glucopyranosides; and (3) the integrated case, based on direct single-step conversion of the (hemi)cellulose fraction in biomass into methyl-glucosides and subsequent conversion into furans.

Each of the three biorefinery concepts can be divided into four distinct components: (1) the pretreatment section, where biomass is fractionated; (2) the conversion section, where C5 sugars are converted into furfural and C6 sugars are converted into fructose or methyl-glucosides, followed by a conversion to furans and furan-derived products; (3) the upgrading and recovery section, where furans are recovered by distillation; and (4) the final conversion section, where the recovered products are converted into PEF and FEE.

2.1. Case I; the base case

The base case incorporates state-of-the-art technologies. Ethanol is the standard organic solvent used for organosolv because of its low boiling point, high delignification efficiency and its relatively low toxicity as compared to methanol (used in Case II and III).^{34,40}

The production of furan derivatives from cellulose, recovered from the organosolv process, ultimately goes *via* monomeric sugars. The highest yield of furans is normally reached when fructose is used as starting material.³ Standard industrial fructose production processes are based on the enzymatic hydrolysis of starch to glucose, followed by enzymatic isomerization. These processes are applied in the base case to convert cellulose into fructose. Furans are recovered and purified by distillation, after which HMF and HMF ethers are oxidized to FDCA, followed by a polymerization with ethylene glycol to PEF.

During organosolv fractionation a significant part of the hemicellulose is converted into furfural, which is recovered by distillation. Cellulose and residual hemicellulose in the solid fraction are hydrolyzed by a cocktail of xylanase and cellulase enzymes. The resulting aqueous mix of monomeric sugars is then fed to an enzymatic isomerization process, where glucose is further converted into fructose. The effluent is passed over a chromatographic separator using ion exchange resins, resulting in a separate stream of fructose, glucose and xylose. The xylose stream is led to a secondary furfural conversion section to increase the overall yield of furfural (A400-I (a) in Fig. 3). Furfural is further converted into furfuryl alcohol using hydrogen and subsequently etherified with ethanol to yield FEE (A700-I). Details can be found in the ESI.†

The lignin that is recovered from the organosolv process is of high purity and could be used for the production of chemicals. Yet the development of a lignin based chemical industry is still in the research phase^{31,41} and therefore in this analysis it was decided that recovered lignin, along with other residual streams, is burned using a CHP, to provide on-site heat and power.

2.2. Case II; the glucoside case

Case II is based on organosolv fractionation and subsequent alcoholysis of the cellulose-enriched pulp to methyl-glucosides, followed by the direct conversion into furans (Fig. 4). Importantly, the aqueous enzymatic conversion steps between the organosolv and furan conversion are avoided in this case. The alcoholysis and furan production are both methanol-based, facilitating integration between the different steps.

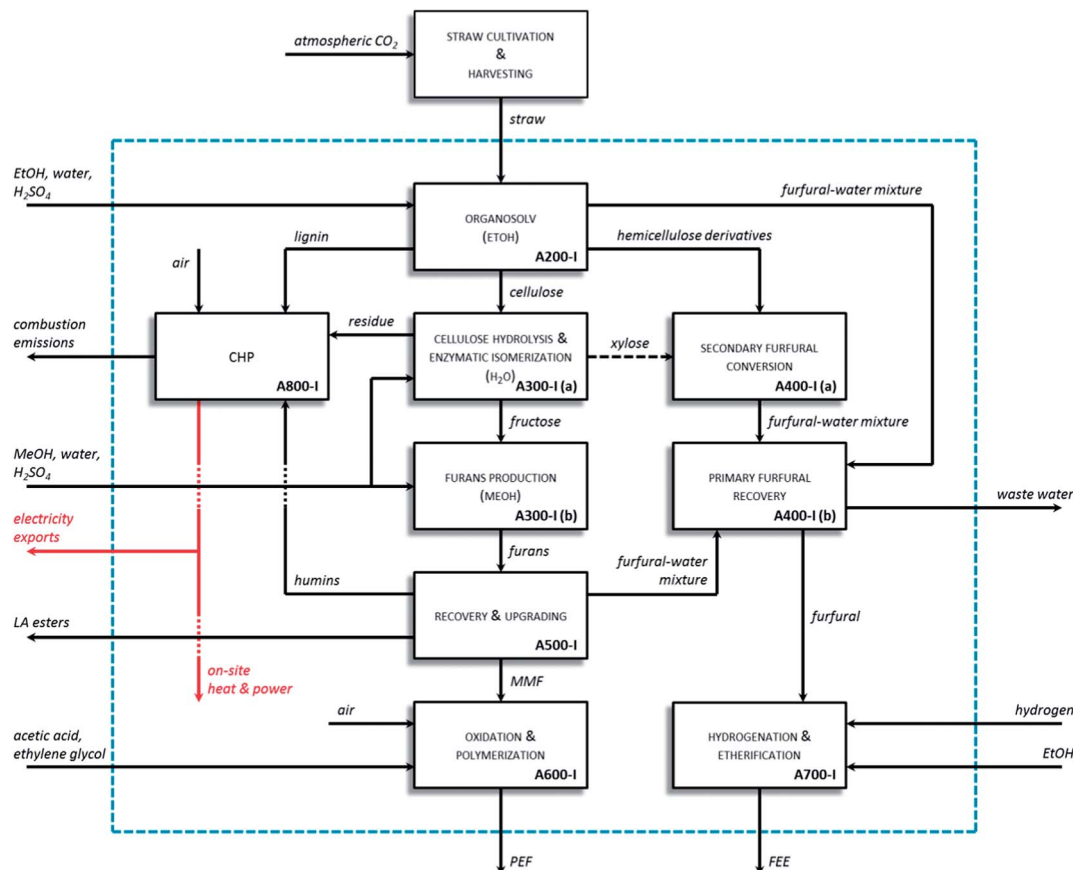


Fig. 3 Case I; ethanol based organosolv, cellulose conversion to fructose and fructose based production of furans (or furan derivatives).

It has been reported that cellulose can be converted into methyl-glucosides in methanol with yields between 40–50%, in the presence of an acid catalyst at 200 °C.⁴² However, at these conditions the etherification of methanol to dimethyl ether (DME) is kinetically favored, which may lead to substantial solvent losses⁴³ and has to be taken into account in techno-economic evaluations. Once formed, the methyl-glucosides are led to the furan process, converted and subsequently separated by distillation, along with the formed DME. The further conversion steps are similar to those of Case I. Details can be found in the ESI.†

2.3. Case III; the integrated case

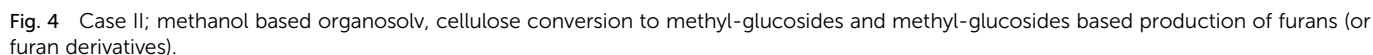
Case III represents an integrated process from lignocellulosic biomass to furans consisting of biomass liquefaction by alcoholysis and furans production (Fig. 5). In methanol-rich solutions, cellulose and hemicellulose present in straw are mainly converted directly into methyl-glycosides, methyl-xylosides and furfural. Grisel *et al.* (2013)⁴⁴ reported a simultaneous methyl-glucosides yield of 56 mol.% (based on initial glucan) and a furfural yield of 40 mol.% (based on initial xylan) from wheat straw after 120 min fractionation in 95% methanol at 175 °C and 40 mmol L⁻¹ H₂SO₄. Major byproducts detected were methyl levulinate (ML) and 5-methoxymethyl furfural (MMF). In addition, smaller amounts of xylose, glucose, HMF, and LA were

formed as well. Similar to Case II, a substantial amount of DME is potentially formed; the actual amount being formed depends on the acid concentration and the fractionation temperature.⁴⁴

After fractionation, the effluent is led to the furans production section, where the main conversion to furan derivatives occurs. In this case no separate hemicellulose stream is recovered, thus the additional furfural conversion step is not required. Lignin is also not recovered as a separate stream and ends up in the residue stream, which is burned in the CHP. The effluent from the furans production section is distilled, where DME and levulinate esters are recovered, alongside HMF, HMF ethers and furfural, which in turn are converted into PEF and FEE, similar to Case I and II. Details can be found in the ESI.†

2.4. Key unit processes of the biorefinery concepts

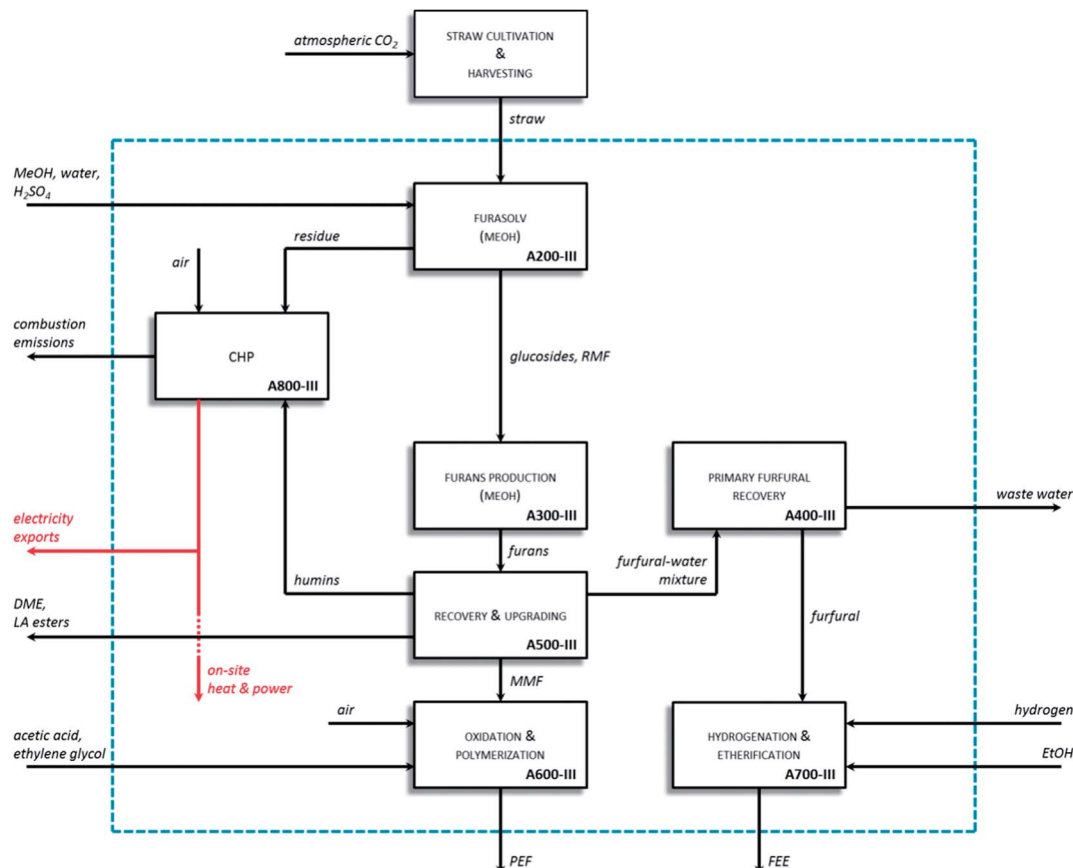
2.4.1. Organosolv process. In Case I and II, the organosolv process is used to fractionate the straw into its three main constituents. The solvent in Case I is ethanol, while methanol is used in Case II. The advantage of using low-boiling methanol and ethanol is their ease of recovery by distillation,²⁴ which in turn is a prerequisite for an efficient and economic process. There are differences between the behavior of the two solvents in the examined organosolv process. Ethanol seems to achieve a higher level of delignification, because it is more effective in dissolving the depolymerized lignin fragments.³⁴



The filtrate is led to a distillation column, where the alcohol content of the solvent is decreased and the lignin precipitates. The bottom stream of the lignin precipitation column consists of water dissolved hemicellulose sugars (mainly xylose), acetic acid and (solid) lignin. This stream is pressed through a filter, where the lignin is filtered off and led to a CHP unit. The hemicellulose is converted to furfural (A400). The top phase of the lignin precipitation column is combined with the flash-vapors of the flash vessel and are led to a second distillation column where the organic part of the solvent is recovered over the top and recycled. The bottom stream mainly contains

2.4.2. Alcoholysis process. Instead of using a traditional organosolv process to fractionate biomass, the entire biomass or cellulose-enriched pulp can be solubilized (liquefied) in a related process that uses acidified alcohol-rich solvents (>90% w/w). The cellulose fraction in biomass is then converted into alkylated sugars in one step. Inevitably, some HMF and HMF ethers, LA and LA esters are formed, but their yields can be controlled by tuning the reaction conditions.⁴⁴ The alcoholysis process and furan production processes show similarities in terms of reactions that occur (after depolymerization) and solvent used. Different are the reaction time, temperature and substrate used. The goal of alcoholysis is to convert lignocellulosic biomass into glucosides and furan compounds in one step and at high yields. The glucosides may then be separated and further converted into furan compounds.

In the envisaged alcoholysis process, biomass is mixed with the solvent and a catalyst and this mixture is heated to 200 °C at autogenous pressure for 1 hour (Fig. 7). The effluent is filtered and the solid fraction (*ca.* 15–20% w/w) is flash-dried. The liquid fraction is led to the furans reactor. Both lignin precipitation and solvent/furfural recovery are avoided. Azeotropic furfural is recovered in the main recovery section (A500), before led to the primary furfural recovery section (A400).



2.4.3. Furfural production. In order to maximize the furfural yield from the hemicellulose fraction, as recovered from the organosolv process, the hemicellulose in the aqueous hemicellulose stream (Fig. 6), is catalytically converted into furfural, using sulfuric acid. The obtained mixture is combined with other aqueous furfural streams and led to a dedicated

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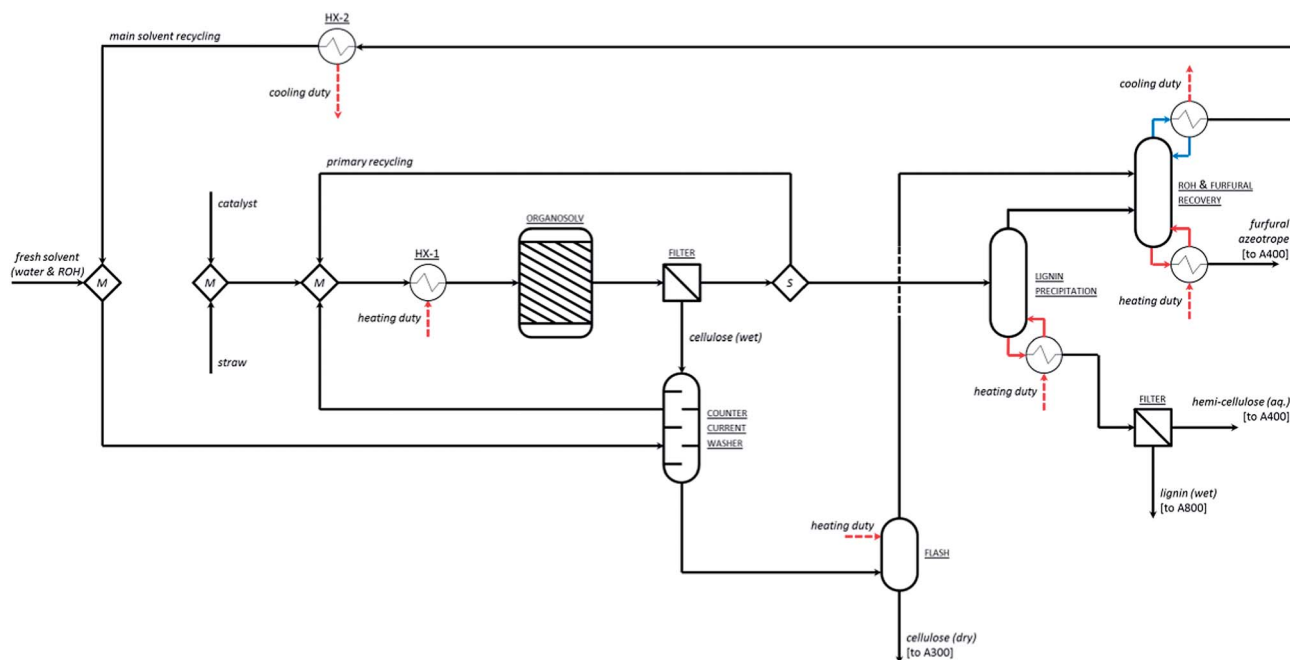


Fig. 6 Flow diagram of the organosolv process.

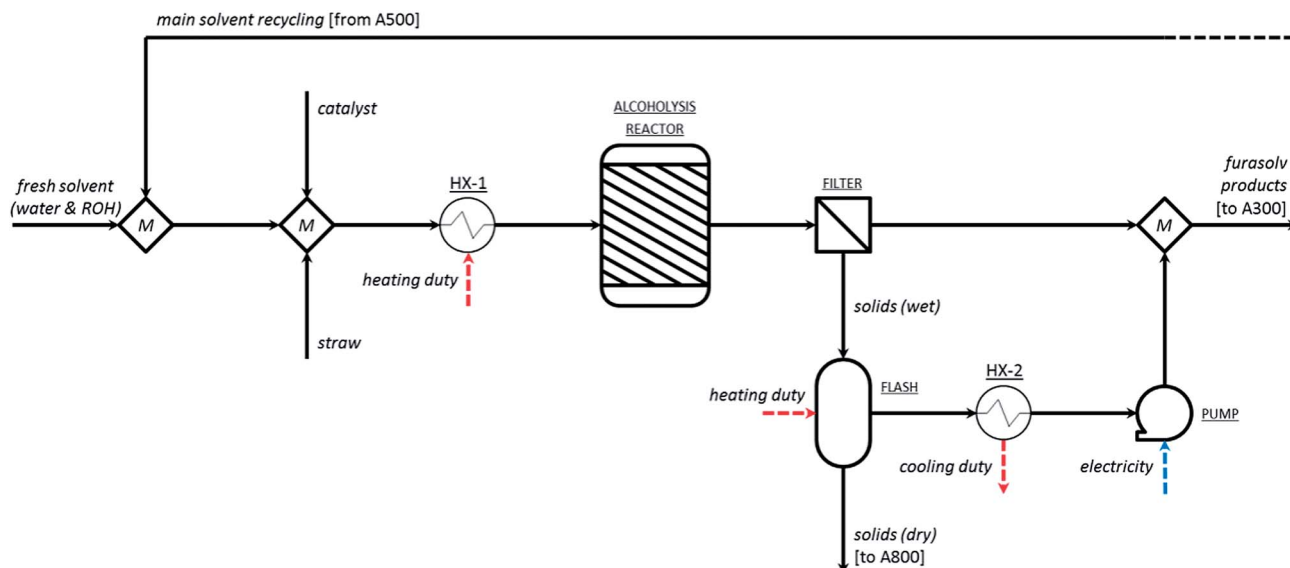


Fig. 7 Flow diagram of the alcoholysis process.

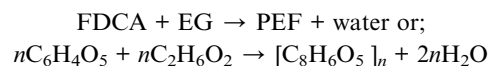
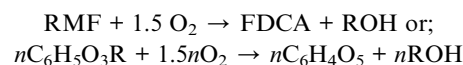
furfural distillation column. The recovered furfural is led to the fuels section of the biorefinery and here it is converted to furfuryl alcohol, which is subsequently etherified with ethanol to yield FEE.

2.4.4. Furan production. The furan conversion process is similar in all three cases, except for the make-up of the MeOH feed. For Case I, fructose is mixed with a methanol solvent (95% w/w methanol and 5% w/w water) and an acid catalyst. The catalyst was undisclosed by Avantium and therefore H_2SO_4 was used as model acid. For Case II and III, a make-up stream of methanol solvent is added to the methyl-glucosides containing stream to account for the loss of methanol due to the alcoholysis and DME formation. The resulting mixture is pressurized to 50 bars and heated to 200 °C for several minutes. The sugars are dehydrated according to the reaction schematics found in Fig. 2.

2.4.5. Production of PEF. HMF and HMF ethers are bio-based equivalents of petrochemical based *p*-xylene, which is the main precursor to terephthalic acid. Just like *p*-xylene is oxidized to obtain purified terephthalic acid (PTA), HMF and HMF ethers can be oxidized to yield 2,5-furandicarboxylic acid (FDCA). FDCA is one of the two monomers of PEF (the other being ethylene glycol).

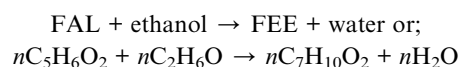
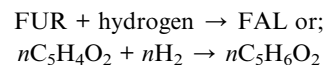
Because of the strong parallels between the production of PET and PEF, it is assumed that the production of PEF uses the same process steps and conditions resulting in similar yields. The process to produce FDCA from MMF is similar to the Amoco process for the production of PTA⁴⁵ and typically operates between 160 to 190 °C, pressures between 20 to 40 bars, with a catalyst containing cobalt, manganese and bromine and conversions of MMF to FDCA at 95 mol%.⁴⁵ The production process of PEF is expected to be more efficient, due to a lower operating temperature, lower pressures, less acetic acid burning to CO_2 and lower polymerization temperatures of FDCA and EG to PEF than the production process of PET.^{46,47} However,

demonstration plant data to quantify these benefits are not yet available, and thus this potential benefit has been neglected in this evaluation.



2.4.6. Production of FEE. Apart from HMF and HMF ethers, furfural is produced in sufficient quantities; about 50% of the xylose is converted into furfural, to justify its conversion into a value-added product. Furfural can be used for many industrial applications, ranging from solvents to thermosets and thermoplastics.^{48,49} In addition, furfural can be converted into liquid fuels with interesting fuel characteristics.⁴⁹

Avantium has developed a route for the valorization of furfural as a bio-fuel *via* the hydrogenation to furfuryl alcohol, followed by an etherification reaction with an alcohol. In the case of ethanol, the product would be furfuryl ethyl ether (FEE).^{50,51} FEE can be used as a fuel blend (up to 30% v/v) in a diesel engine.⁵²



2.4.7. Description of the CHP unit. The CHP unit consists of a boiler, operating at 870 °C and atmospheric pressure.⁵³ Lignin, humins and residue streams are burned in the boiler and the hot flue gases are led through a heat exchanger in which

pressurized water at 42 bars is converted into medium pressure (MP) steam. The steam is fed to a steam turbine to produce electricity. Part of the exiting steam (12.5 bars) is led through a series of heat exchangers to meet the on-site heat demands, thus ensuring self-sufficiency. Excess steam is fed to a low pressure (LP) steam turbine to produce surplus electricity. The CHP unit is similar in all three cases.

2.5. Aspen plus inputs for each case

Tables 1, 2 and 3 show the process conditions, conversion and the product spectrum assumed for the calculations and are discussed in Section 3.

Table 1 Organosolv assumptions for Cases I and II^a

	Units	Case I	Case II
Feedstock	—	Wheat straw	Wheat straw
Temperature	°C	200	200
Pressure (autogenous)	bar	28	30
Organic solvent used	—	Ethanol	Methanol
Organic solvent	w/w%	60	60
H ₂ SO ₄ concentration	mM	15	15
Cellulose hydrolysis	%	0	0
Xylan hydrolysis	%	80	80
Xylose dehydration to furfural	%	37.5	37.5
Lignin extracted	%	80	60
Precipitation efficiency	%	90	80
Lignin yield	%	72	48

^a The values for wheat straw are derived from Huijgen *et al.* (2011).³⁵ Wheat straw consists of glucan (36.9 w/w% dry biomass), xylan (19.9), arabinan (1.9), galactan (0.7), mannan (0.2), rhamnan (0.1), lignin (17.8; AIL 16.7, ASL 1.1), ash (6.1) and extractives (10.4).³⁵

Table 2 Alcoholysis assumptions for Cases II and III^a

	Units	Case II	Case III
Feedstock	—	Organosolv pulp	Wheat straw
Solid residue yield	%	10	10
Temperature	°C	175	175
Pressure	bar	<30	<30
Organic solvent used	—	Methanol	Methanol
H ₂ SO ₄ concentration	mM	40	40
Cellulose hydrolysis	%	95	95
Methyl-glucoside yield	%	55	55
Xylan hydrolysis	%	100	100
Xylose dehydration to furfural	%	50	50
HMF yield	%	<1	<1
MMF yield	%	5	5
LA yield	%	1	1
ML yield	%	10	10

^a The pulp used in Case II consists of 65% cellulose, 8% xylan, 12% undissolved lignin and 15% ash (similar as reported in Section 2.4.1). The values for Case III are based on experimental data reported in Grisel *et al.*⁴⁴ From data presented herein, it can be assumed that similar results can be obtained for pulp. It should be noted, however, that the amount of acid required in Case II may be lower than in Case III, due to the intrinsically lower acid neutralizing capacity of the pulp.

Table 3 Furan conversion assumptions for Cases I, II and III^a

	Units	Case I	Case II	Case III
Process conditions				
Temperature	°C	200	200	200
Pressure	bar	50	50	50
Sugar feed	—	Fructose	Methyl-glucosides	Methyl-gluc./RMF
Furan products formation				
HMF	mol%	9.6	9.6	1.4
HMF ethers	mol%	50.2	50.2	15.0
LA	mol%	1.0	1.0	0.0
LA esters	mol%	7.7	7.7	25.0
Methyl formate	mol%	1.7	1.7	3.6
Furfural	mol%	2.7	2.7	0.0
Methylal	mol%	0.5	0.5	0.0
Unreacted sugars	mol%	0.5	0.5	0.0
Humins	mol%	26.2	26.2	55.0

^a The values might not add up to 100% due to rounding. The values for Case I are based on Eerhart *et al.*¹⁷ It was assumed that yields for Case II are identical to Case I, operating on a relative pure stream of methyl-glucosides. For Case III, the effluent from the alcoholysis reactor (A200) is fed directly into the furan conversion reactor, resulting in a lower purity stream of methyl-glucosides entering the reactor. To represent a lower purity stream, the values for Case III are based on extrapolations of experimental data, provided by Avantium. Further catalytic research is thus still required to validate the assumptions above.

3. Results

The mass balances of each case are presented in Table 4 and Fig. 8. The inputs of straw are similar for each case, set at 625 ktonnes per year, assuming an operation time of 8000 h per year. Table 5 presents a detailed mass balance focused on PEF, starting from straw. The complete stream tables for each case are presented in the ESI.†

3.1. Mass balance results

Table 4 and Fig. 8 show that for a 625 ktonnes wheat straw per year plant the PEF production amounts to 80, 52 and 22 ktonnes per year for Case I, II and III respectively. These differences are caused by the underlying reaction yields of the furan conversion, based on the sugar input (fructose in Case I, methyl-glucosides in Case II and III). As explained in Section 1, the closed structure of fructose contains a furanoside ring, and thus conversion to HMF and subsequently MMF is more straightforward as compared to methyl-glucosides which contain a pyranoside ring within its structure and an isomerization step is required first.³ Further (catalytic) research is needed to increase the conversion of (methyl-)glucose into furans.

FEE production amounts to 82, 80 and 47 ktonnes per year respectively, for the three cases. In Case I and II, the xylan conversion to furfural is similar, resulting in similar FEE production, however, Case III does not produce a separate hemicellulosic sugar stream from the organosolv process, thus reducing the conversion of xylan to furfural and subsequently reducing FEE production.

Table 4 Input and output table of the three scenarios

	Case I	Case II	Case III
Inputs (ktonnes per year)			
Straw (d.w.)	625	625	625
H ₂ SO ₄	5	9	10
Ethanol (A200)	3	n/a	n/a
Ethanol (A700)	30	29	17
Methanol (A200)	n/a	6	285
Methanol (A300)	6	126	n/a
Acetic acid	12	8	3
O ₂	21	14	6
Ethylene glycol	27	18	7
Hydrogen	1	1	1
Total input	730	836	954
Outputs (ktonnes per year)			
<i>Target products</i>			
PEF	80	52	22
FEE	82	80	47
<i>By-products</i>			
ML	9	11	56
<i>Residues</i>			
Lignin	230 ^a	149 ^a	n/a
Humins, etc.	34	66	261
Residue	203	254	126
<i>Others</i>			
DME	n/a	63	170
Water formed	91	161	272
Total output	730	836	954
<i>Recycling rates</i>			
<i>Methanol</i>			
Methanol in	449	1431	2391
Methanol recovered	443	1299	2106
Methanol recycling rate	98.6%	90.8%	88.1%
<i>Ethanol</i>			
Ethanol in	1336	n/a	n/a
Ethanol recovered	1333	n/a	n/a
Ethanol recycling rate	99.8%	n/a	n/a

^a The purity of the lignin has not been measured in this study. Earlier work shows that the lignin purity is >90%.⁵⁴

LA esters make up 1–9% of the total product yield, defined as product divided by the straw input (d.b.), for all cases (9, 11 and 56 ktonnes per year). The reason for the absolute increase between Case I and Case II compared to Case III is that the

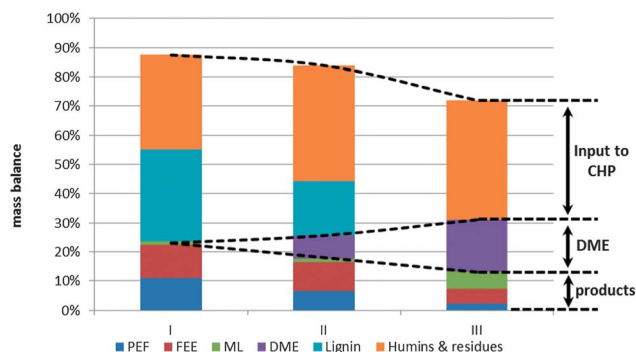


Fig. 8 Graphical representation of the mass balance results of the three cases analyzed, based on Table 4.

conversion of cellulose into methyl-glucosides already yields significant amount of ML, as compared to Case I in which cellulose conversion occurs *via* fructose. This is due to the fact that the conversion of cellulose into furans *via* methyl-glucosides requires high temperature which promotes the formation of ML. Another important factor is that more water is present in the furan conversion reactor in Case III, resulting in a larger conversion of HMF to ML, as compared to Case I and II.

An important aspect of the alcoholysis and furan conversion processes is that significant amounts of water are formed. Water is recovered in the general recovery and upgrading section (A500) and amounts to 91 ktonnes per year for Case I, 161 ktonnes per year for Case II and 272 ktonnes per year for Case III. These values represent the water that is formed during the organosolv, alcoholysis and furan conversion reactions and the formation of DME and does not represent the water that is part of the solvent. This formed water makes up the remainder of the mass balance results presented in Fig. 8.

The overall product yield, defined as product divided by the straw input (d.b.), of PEF and FEE is 26% for Case I, 21% for Case II and 10% for Case III. When ML is included the yields change to 27%, 23% and 19%, respectively (see the stacked bars on the left hand side of Fig. 8). The overall yield seems low for a combination of catalytic conversion processes, however, the remainder of the mass balance is recovered as lignin (37% for Case I, 24% for Case II, no recovery of lignin for Case III), humins (5% for Case I, 11% for Case II, 42% for Case III) and other solid residues (32% for Case I, 41% for Case II, 20% for Case III). These last three streams are burned on-site in an industrial CHP to provide process energy in the form of steam. Excess steam is converted into electricity and exported to the grid.

3.2. Energy balance results

The energy balance (both renewable and non-renewable energy) results in terms of input, output and efficiency can be found in Fig. 9. The input consists of straw (18 GJ per tonne straw), ethanol (29.7 GJ per tonne ethanol) (make-up only) and methanol (20 GJ per tonne) (make-up only) and ethylene glycol (19 GJ per tonne), while the output consists of PEF (22.5 GJ per tonne), FEE (29.8 GJ per tonne), ML (25 GJ per tonne), DME (28.4 GJ per tonne) and electricity. As is the case with the mass balance results, Case I has the highest efficiency at 41% (PEF, FEE, ML and electricity), followed by Case II at 33% and Case III at 28%.

The heat demand for Case I to produce LA, LA ester and the intermediates HMF ethers and furfural is 400 MW_{th}. This includes the organosolv process, fructose production, furans conversion, furfural recovery, the main recovery & upgrading section, the conversion of MMF to PEF and furfural to FEE. By applying heat integration, 290 MW_{th} can be recovered and used on-site. This means that 110 MW_{th} is required from other sources, in this case the on-site CHP. The combustion of solid residues, lignin and humins results in 184 MW_{th} of steam, leaving 74 MW_{th} of steam as excess. Steam is converted into electricity at an efficiency of 43% by using a combination of medium and low pressure steam turbines.

Table 5 Detailed mass balance results for Case I, focused on straw to PEF conversion

	ktonnes per year	Notes
Straw	625	Dry basis
Cellulose	236	37.8 mass% recovery
Glucose (primary conversion)	222	94.0 mass% conversion
Glucose (recycle)	212	Glucose recycle stream after chromatographic separation of fructose and glucose
Total glucose	432	Total glucose to isomerization
Fructose	158	36.3 mass% conversion
MMF	65.5	41.5 mass% conversion
MMF after distillation	64.8	99.0% recovery rate after distillation
FDCA	72	95.0 mol% conversion of MMF to FDCA
PEF	80	Polymerization with EG, water produced

Since Case II yields more waste streams, the CHP output is higher (Table 6); 197 MW_{th}, compared to 184 MW_{th} for Case I. The heat demand for Case II is also higher at 418 MW_{th}, compared to 400 MW_{th} for Case I. Heat integration yields are higher at 304 MW_{th}, and thus a similar amount of steam from the CHP is needed to run the process (58%, as compared to 60% for Case I). Finally, Case III has the lowest heat demand at 324 MW_{th}, due to the integrated alcoholysis and furan conversion. As the residue streams are bigger, the CHP produces more heat (228 MW_{th}), of which 35% is needed on-site for heat integration. As a consequence, the steam available for electricity production is highest for Case III, 56 MW_{elec.} (Table 6).

Looking at the heat demands per area across each of the three cases (Table 6 and Fig. 10), it can be seen that the pretreatment area (A200) for Case I and II makes up ~40% of the total heat demand. The heat demands in the furfural recovery section (A400) and FEE production section (A700) are around 10% in both Case I and II. Since the production of PEF (in ktonnes per year) drops from 80 for Case I to 52 for Case II to 22 for Case III the energy efficiency must follow a similar behavior. This is shown by the decrease in energy efficiency, as defined by the energy content of PEF divided by total energy inputs, from 14% to 8–3%, respectively.

When comparing the conversion of cellulose into intermediates (glucose, fructose or methyl-glucosides, A300) and the upgrading and recovery section (A500), an increase in the heat

demand for area A300 between Case I and Case II is observed. This is due to the production of methyl-glucosides, which requires two additional distillation columns to recover excess methanol before the furan conversion process, since the alcoholysis process operates at a higher liquid-to-solid ratio

Table 6 Energy balance for Cases I, II and III, expressed in MW^{a,b}

	Case I	Case II	Case III
Heat demand (MW_{th})			
A200 – pretreatment (a)	146	159	76
A300 – intermediate conversion (b)	84	125	7
A400 – primary furfural recovery	40	37	21
A500 – recovery and upgrading	52	35	177
A600 – PEF production	48	31	13
A700 – FEE production	30	30	30
Subtotal	400	418	324
Heat supply (MW_{th})			
Heat integration	290	304	247
A800 – boiler	184	197	228
A800 – used on-site	110	114	78
A800 – steam turbines	74	83	151
A800 – electricity production (MW _{elec.})	31	35	58
A800 – electricity exports (MW _{elec.})	28	32	56

^a Refers to either organosolv or alcoholysis process. ^b Refers to either fructose production, alcoholysis or furan conversion or a combination of these processes.

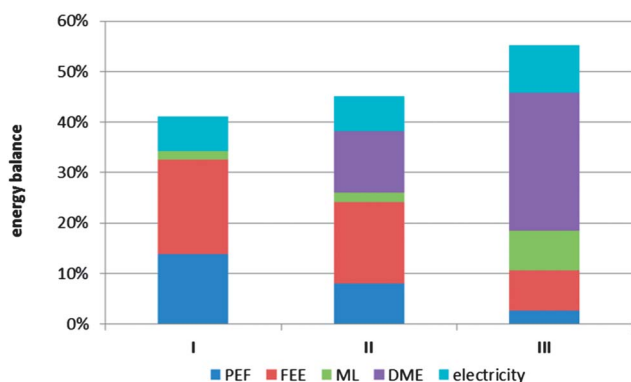


Fig. 9 Graphical representation of the energy balance results, based on calorific content.

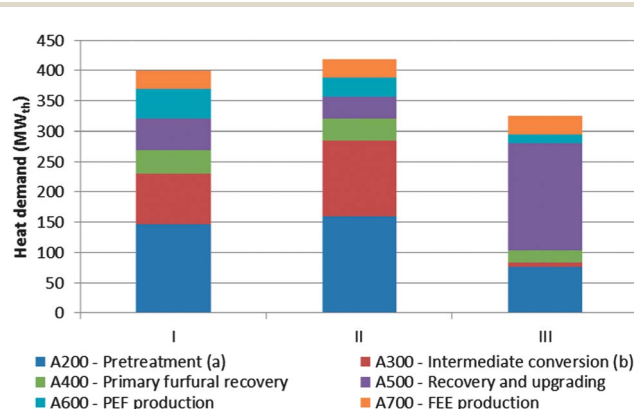


Fig. 10 Division of heat demand per area for each case.

($L/S = 5 \text{ L kg}^{-1}$, compared to $L/S = 3$ for furans conversion). A benefit is that these two columns reduce the heat demand of the first three distillation columns in A500 (Case I = 13%, Case II = 8%). Overall, A300 and A500 of Case II combined have a 30 MW_{th} higher heat demand than Case I. For Case III, the majority of energy use is in A500, because there are no intermediate distillation columns required in area A200 and A300. Case III also has the lowest energy requirement, because less process units are required (*e.g.* distillation columns; Case I and II = 13, Case III = 11).

4. Discussion

A second generation biorefinery was modeled using ASPEN Plus, based on lab-scale experimental data and expert opinions. This brings with it an inherent uncertainty. In addition, the cases modeled are extrapolated to represent full-scale industrial plants, which at this point in time, are not a reality. Therefore, validation of the model is not possible. However, it enables the evaluation and comparison of different cases and the potential of integration options in the production of lignocellulose-based furans at an early stage and identification of key bottlenecks.

In the light of the envisaged application, one of the key aspects of lignocellulosic biomass pretreatment is how lignin can be removed in an effective manner, thereby avoiding technical problems downstream, *e.g.* dissolved lignin precipitation on the catalyst used in the furan conversion process or irreversibly binding to enzyme during enzymatic hydrolysis. On lab-

scale, lignin separation is typically carried out by addition of water to precipitate the lignin. For industrial-scale organosolv processes, this is not the preferred route, as evaporation of water will significantly increase the process heat requirements. It is expected that this increase in energy consumption is detrimental for the economic viability. Instead, the ASPEN Plus model evaluated evaporation of the organic solvent (methanol, ethanol) as a means of lignin precipitation.

Within the studied biorefinery, the bottom phase of the lignin recovery tower (A200) consists primarily of lignin, hemicellulose and water. Lignin is recovered by means of filtration and is of sufficient purity (>90%) to be used for chemicals and other high-value added applications. However, the development of a lignin-based chemical industry is still in the research phase^{31,41} and therefore, in this study, the choice was made to burn the lignin, along with other residue streams to provide for on-site heat and power.

Key criteria for an efficient process are the total yield of products, mass and energy efficiencies. The yields for the three cases are between 19 and 27 w/w% (PEF, FEE and ML), and are comparable to first generation furans produced from corn, *viz.* 28%.¹⁷ The energetic efficiencies are between 28 and 41%. These efficiencies are low compared to established industrial petro-refinery processes (mass and energetic efficiency >90%⁴⁵), however, compared to upcoming bio-based processes, these yields are comparable or even better. For example, the mass yield of second generation bio-ethanol from poplar is in the range of 35–45% with an energy efficiency of 40–70,⁵⁵ whereas

Table 7 Strengths and weaknesses of the three cases

	Strengths	Weaknesses
Case I	<ul style="list-style-type: none"> ◆ Good fractionation of biomass ◆ High lignin removal and recovery ◆ Optimal furans yield, based on fructose ◆ All technologies are commercially available or in demonstration/pilot phase ◆ Lower solvent losses due to the use of EtOH (less etherification compared to MeOH) 	<ul style="list-style-type: none"> ◆ Alcohol-based organosolv, aqueous based conversion to fructose, alcohol-based furan conversion result in high separation costs ◆ Enzymes needed for the conversion of cellulose to fructose (costs) ◆ Large number of unit processes (investment and operation costs) ◆ Temperature swings between fractionation (150–200 °C), enzymatic conversions (50 °C) and furan conversion (200 °C) and requires additional heat integration efforts
Case II	<ul style="list-style-type: none"> ◆ Reasonable fractionation of biomass ◆ Improved integration by using only one type of solvent (aqueous methanol), thus avoiding the low-temperature alcohol-free conditions needed for enzymatic conversions to fructose ◆ Some lignin recovery 	<ul style="list-style-type: none"> ◆ Lower delignification efficiency as compared to ethanol-based organosolv ◆ Still large number of process steps (investment and operation costs) ◆ Glucosides based furan conversion has lower yield, as compared to fructose ◆ Alcoholysis technology needs to be proven on large scale ◆ MeOH losses due to DME formation
Case III	<ul style="list-style-type: none"> ◆ Fewer process steps required as compared to Case I and II 	<ul style="list-style-type: none"> ◆ MeOH losses due to DME formation ◆ No recovery of lignin, potential reduced efficiency downstream (furan product conversion, distillation) ◆ Glucosides based furan conversion has lower yield, as compared to fructose ◆ Lower overall conversion yield of straw to target products ◆ One-step alcoholysis technology needs to be proven on large scale

the mass yield for ethanol from wheat straw is around 15%⁵⁶ with an energy efficiency of 25–50%.⁵⁷ It should be noted that the energy efficiency reported for popular to ethanol is somewhat higher than reported for the biorefinery in this study, mainly because the production is limited to ethanol alone and a relatively large residual stream is burned. Since a larger part of the biomass is burned and the on-site heat demand for ethanol production is lower than the biorefineries studied in this paper, (more) excess heat can be valorized and sold as electricity, thus resulting in an overall higher energy efficiency.⁵⁵

In Case II and III, the formation of DME by methanol dehydration is a concern, since it represents a direct loss of organic solvent. At the typical process conditions applied in the alcoholysis process, the amount of DME that is formed may be as high as 10% of the total methanol in the system. Current market price for DME is around € 400 per MT,⁵⁸ while methanol is € 350 per MT⁵⁹ (as of September 2012). From mass the ratio and reaction stoichiometry, it is clear that the selling price of DME is lower than the price of methanol needed for its production. Therefore, the amount of DME byproduct should be minimized by adjusting the process conditions.

The combustion of lignin, humins and residue streams from the biorefinery in an industrial CHP unit is in principle possible.¹⁷ However, it still needs to be proven at industrial-scale. Heat integration is paramount for an effective second generation biorefinery and the CHP unit is an integral part of this.

The use of water resources, especially in the industry, has become an important subject in recent years. The biorefinery requires significant amounts of water to operate and this water needs to be reused as much as possible. The furfural recovery section (A400) and the main recovery and upgrading section (A500) produce relatively pure streams of water, which can be reused in the process. However, some of the waste water needs to be cleaned. Further research is needed to determine the actual level of contaminants in the waste water and what type of waste water treatment plant (aerobic, anaerobic) is required. Currently, waste water treatment is not incorporated in the models.

Finally, the three cases presented in this paper are compared to illustrate their strengths and weaknesses (Table 7).

5. Conclusions

The main products of the studied biorefinery are PEF, a bio-based alternative to PET, and FEE, a bio-based transportation fuel. Case I focused on ethanol-based organosolv, followed by cellulose hydrolysis and enzymatic conversion to fructose and fructose-based furan conversion. Case II focused on methanol-based organosolv, followed by the conversion of cellulose into methyl-glucosides and further into furan-derivatives. Within Case III, the organosolv fractionation was replaced by a methanol-based liquefaction process of wheat straw, followed by furan conversion.

Looking at the targeted products PEF and FEE, Case I has the highest production at 80 ktonnes per year PEF and 82 ktonnes per year FEE, with ML production at 9 ktonnes per year, which is considered as a valuable by-product. Case I has the highest

potential to be implemented on the short term, due to the step-wise approach. The production of PEF and FEE in Case II is 52 and 80 ktonnes per year respectively, with ML production at 11 ktonnes per year. The lower production of PEF is due to the lower conversion rates during the furan conversion. Case III is the most integrated process for production of furans from lignocellulosic biomass but the alcoholysis technology does not allow for full valorization of biomass. Combined with lower methyl-glucosides conversion into furans, this results in the lowest production of PEF (22 ktonnes per year) and FEE (47 ktonnes per year). On the other hand, Case III has the highest production of ML (56 ktonnes per year). When comparing the overall yields of wheat straw to products (PEF, FEE and ML), Case I has the highest overall yields at 27%, followed by Case II at 23% and Case III and 19% w/w.

One of the key issues identified within this study is the production of DME. At the conditions applied in Case II and III during the cellulose conversion to methyl-glucosides and the wheat straw liquefaction process, the dehydration of methanol to DME is thermodynamically favored. This leads to substantial solvent losses and should thus be avoided as much as possible.

The overall conclusion of this work is that each of the three cases could be a viable option to produce bio-based fuels and plastics *via* the furan pathway at efficiencies comparable or higher than other biorefinery concepts. However, the technical performance of each of the three cases presented here needs to be complemented by an economic and life cycle assessment to show whether the products can be produced at a competitive price and with a reduced environmental footprint, as compared to their petrochemical counterparts. Only then can one evaluate the overall potential of the furan-based lignocellulosic biomass biorefinery concept by showing the complete picture in terms of technical, economic and environmental performance.

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