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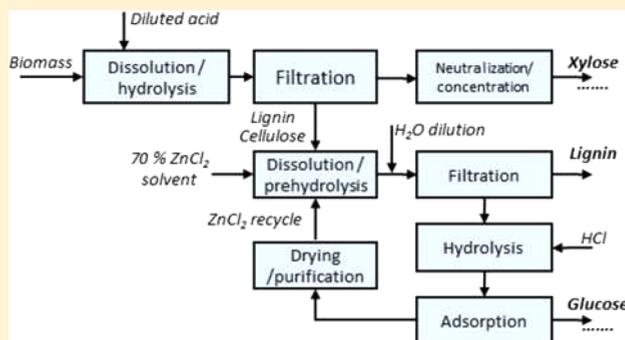
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Production of Monosugars from Lignocellulosic Biomass in Molten Salt Hydrates: Process Design and Techno-Economic Analysis

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ABSTRACT: ZnCl₂ hydrate, the main molten salt used in biomass conversion, combined with low concentration HCl is an excellent solvent for the dissolution and hydrolysis of the carbohydrates present in lignocellulosic biomass. The most recalcitrant carbohydrate, cellulose, is dissolved in a residence time less than 1 h under mild conditions without significant degradation. This technology is referred to as BIOeCON-solvent technology. Separation of the sugars from the solution is the main challenge. The earlier conclusion regarding the potential of zeolite beta for selective adsorption has been used as the basis of a scale-up study. The technology of choice is continuous chromatographic separation (e.g., simulated moving bed, SMB). The sugar monomers are separated from the sugar oligomers, allowing the production of monosugars at high yield, using water as an eluent. Results of a pilot plant study are presented showing a stable operation at high selectivity. Several process designs are discussed, and the techno-economic performance of the BIOeCON-solvent technology is demonstrated by comparison with the state-of-the-art technology of NREL (National Renewable Energy Laboratory), which is based on enzymatic conversion of cellulose. It is concluded that the BIOeCON-solvent technology is technically and economically viable and is competitive to the NREL process. Because the BIOeCON-solvent process is in an early stage of development and far from fully optimized, it has the potential to outperform the existing processes.



Results of a pilot plant study are presented showing a stable operation at high selectivity. Several process designs are discussed, and the techno-economic performance of the BIOeCON-solvent technology is demonstrated by comparison with the state-of-the-art technology of NREL (National Renewable Energy Laboratory), which is based on enzymatic conversion of cellulose. It is concluded that the BIOeCON-solvent technology is technically and economically viable and is competitive to the NREL process. Because the BIOeCON-solvent process is in an early stage of development and far from fully optimized, it has the potential to outperform the existing processes.

1. INTRODUCTION

The possible depletion of fossil reserves, growing global energy demand and competition between food and fuel for first generation biofuels are strong drivers to develop so-called second generation biofuels and biochemicals. A wealth of different chemicals and fuels can technically be produced from biomass.¹ The key challenge is developing a cost-effective process.

Similar to crude oil, biomass can be and is processed in several ways.² The processes range from high-temperature thermochemical processes, viz., combustion, gasification, and pyrolysis, to more subtle (bio-) chemical processes in the liquid phase, viz., hydrolysis and fermentation (Figure 1). The former category is very robust in the sense that the detailed structure of the biomass plays only a minor role and the complete organic part of the biomass is converted into a large pool of various chemical compounds. The latter category involves the selective conversion routes under milder conditions. For this class, the biomass structure offers the potential of efficient processes with high yields of target products.

Biomass can be gasified at high temperature in the presence of a substoichiometric amount of oxygen and the produced synthesis gas (a mixture of CO and H₂) can be further processed to obtain the “normal” product spectrum, including, for example, methanol and Fischer–Tropsch liquids.⁴ During pyrolysis, which takes place at intermediate temperature in the absence of oxygen, biomass is converted into a mixture of gas,

solid material, and liquid, referred to as “bio-oil”.⁵ This robust process can be used with a large variety of feedstocks. The product spectrum strongly depends on the reaction conditions, in particular the heating rate. In “fast” pyrolysis (ca. 500 °C, time ca. 1 s), yield of bio-oil has been reported to be 75 wt %, whereas in “slow” pyrolysis (ca. 290 °C, time 10–60 min) the main product is solid (“biochar”, 80 wt %).⁵

All these processes are analogous to major processes applied in the oil refinery. However, because of the completely different structure of biomass compared to crude oil, fundamentally different processes are also possible.

Lignocellulosic biomass consists mainly of three components: cellulose (35–50 wt %), hemicellulose (15–25 wt %), and lignin (15–30 wt %) (Figure 2). Plant oils, proteins, different extractives, and ashes make up the rest of the lignocellulosic biomass structure.

The macrostructure of lignocellulosic biomass is complex. A schematic representation is given in Figure 3. The cell walls are built up from cellulose and hemicellulose, held together by

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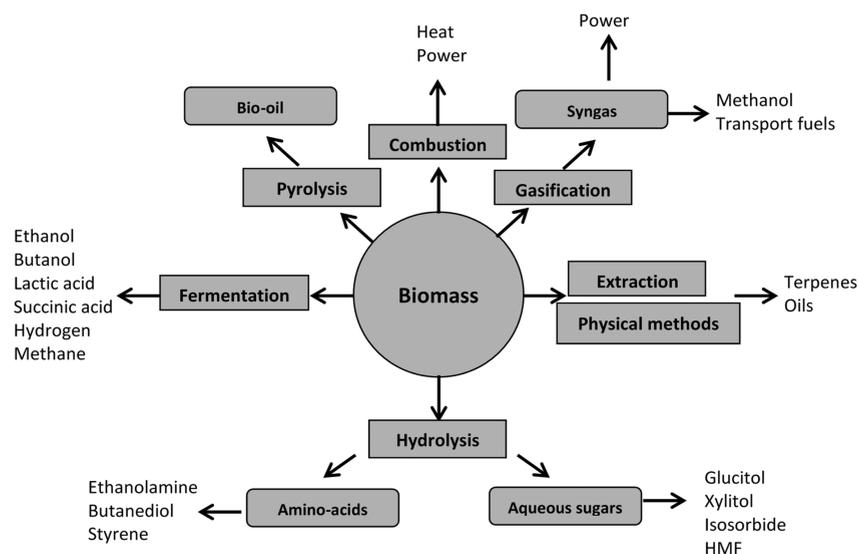


Figure 1. Main routes and their products for biomass conversion processes.³

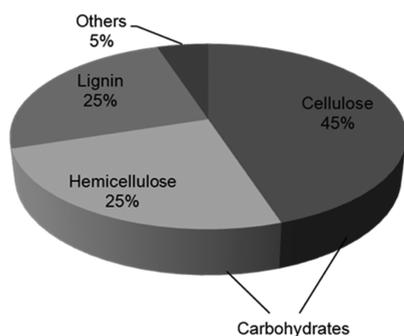


Figure 2. Average composition of lignocellulosic biomass.³

lignin. The hemicellulose, in turn, is a matrix containing the cellulose fibers.

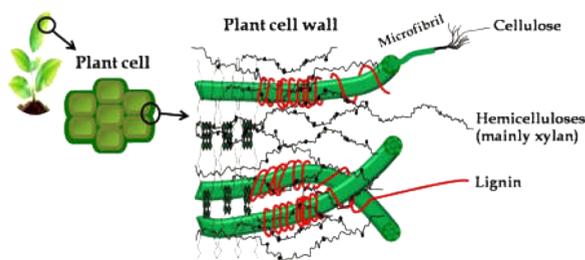


Figure 3. Structure of lignocellulosic biomass.⁶

Cellulose is the most abundant organic polymer on earth and its chemical structure, which is largely crystalline, is remarkably simple. It consists of linear polymers of cellobiose, a dimer of glucose (see Figure 4). The multiple hydroxyl groups of the glucose molecule form hydrogen bonds with neighbor cellulose chains making cellulose microfibrils of high strength and crystallinity.

Hemicellulose is chemically related to cellulose in the sense that it is composed of a carbohydrate backbone. However, because of its random and branched structure, hemicellulose is amorphous. It has a more complex composition than cellulose. Figure 5 shows the structure of xylan, a polymer representative of hemicellulose. Whereas cellulose is completely built up from

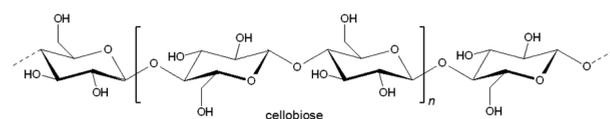


Figure 4. Chemical composition of cellulose; $n = 2500-5000$.

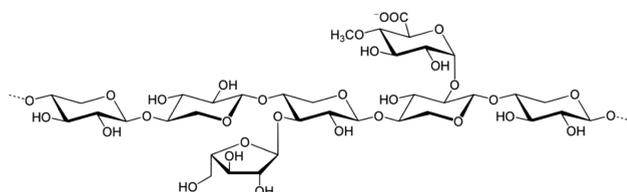


Figure 5. Chemical composition of xylan, a typical hemicellulose.

glucose monomers, hemicellulose consists of a mixture of five-carbon sugars (xylose, arabinose), six-carbon sugars (glucose, mannose, galactose), and uronic acids (e.g., glucuronic acid), see Figure 6. In hemicellulose, xylose is the most abundant monomer.³

In view of the fact that the largest part of the lignocellulosic biomass has a well-defined structure composed of attractive

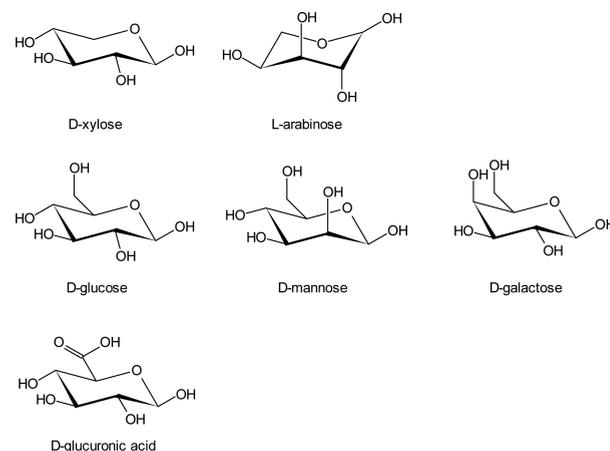


Figure 6. Monomers present in hemicellulose.

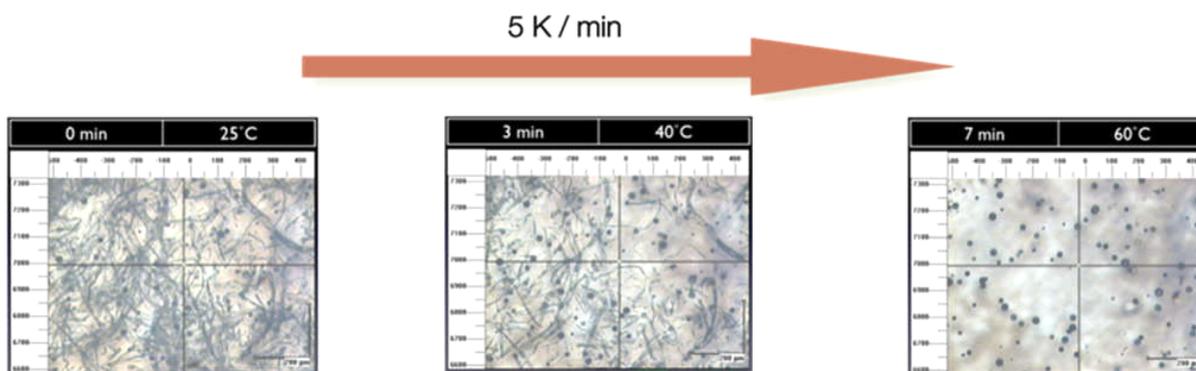


Figure 7. Dissolution of cellulose in ZnCl_2 hydrate in a temperature-programmed experiment followed by a microscope. The images at the left, the middle, and at the right represent successively the initial situation at room temperature, the situation after 3 min ($40\text{ }^\circ\text{C}$), and after 7 min ($60\text{ }^\circ\text{C}$).

monomeric units, why not try to produce them directly without turning to high-temperature scission chemistry? In fact, such a strategy opens up the production of materials with a higher value than fuels. In general, we postulate that the production of chemicals is to be preferred over the production of fuels.^{7,8} Does this mean that production of chemicals from second generation biomass is economical? In fact, at present, sugar prices are modest and, as a consequence, processes based on sugar are strong competitors to processes based on second generation biomass.

The production of cellulosic sugars to produce ethanol has received a lot of attention in the past decades.^{9,10} Efficient depolymerization of the recalcitrant cellulose polymer to glucose is a critical step in this process. This can be done enzymatically, but the cost of the enzymes can be high and the process is slow and, as a consequence, a pretreatment step is required to make the cellulose accessible, which can be costly as well.¹⁰ In fact, Figure 3 showing the macrostructure of lignocellulosic biomass suggests that mass transport limitations will be considerable in enzymatic processes.

An alternative approach is to use solvents that can dissolve biomass under mild conditions ($T < 100\text{ }^\circ\text{C}$) leading to a minimum of degradation products formed. Examples of solvents are concentrated mineral acids (aqueous HCl , H_2SO_4 , H_3PO_4),^{11–13} molten salt hydrates, and ionic liquids.¹⁴ The critical aspects of such processes are undesired degradation reactions and the difficult separation of the products from the solvent system. High monosugar yields can be obtained, but separation of the monosugars from the solvent and economical recycling of the solvent are essential to enable commercial application. The molten salt hydrate of ZnCl_2 is, for example, a solvent with excellent cellulose dissolution properties and hydrolysis to glucose can easily be done in the same solvent.^{15,16}

Figure 7 shows the superb performance of ZnCl_2 : at room temperature the cellulose fibers are clearly visible and upon heating they quickly disappear: at $60\text{ }^\circ\text{C}$ cellulose is dissolved, corresponding with a residence time lower than 7 min. Diluted HCl (typically 0.4 molal) is sufficient to catalyze cellulose depolymerization at a rate large enough for a commercial process.¹⁷ The typical hydrolysis time is 60 min with glucose as the main component of cellulose hydrolysate mixtures. In addition to glucose, some cellobiose and higher cellooligomers (Figure 8) are present in the hydrolysate, due to the fact that there is an equilibrium between hydrolysis and condensation reactions in such concentrated ZnCl_2 solutions. An equilibrium composition is determined by both total sugar concentration in

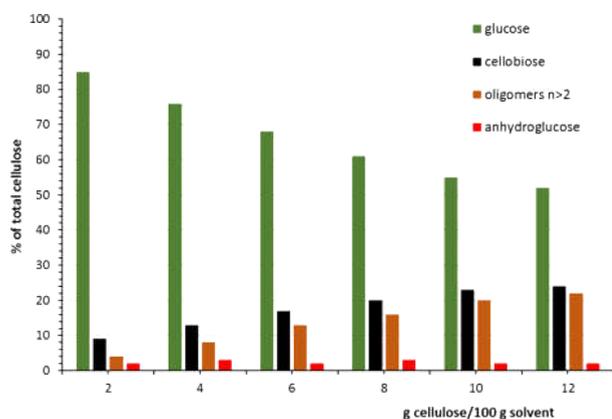


Figure 8. Hydrolysate composition at equilibrium after cellulose hydrolysis in 70 wt % $\text{ZnCl}_2/0.4$ molal HCl at $70\text{ }^\circ\text{C}$.

the hydrolysate and ZnCl_2 concentration because water molecules are required for both hydrolysis reactions and for coordination with ZnCl_2 .

Separation of the polar glucose molecule from this polar molten salt hydrate is challenging. The stepwise conversion of cellulose has been demonstrated in the same solvent, producing the much less polar isosorbide, which is easier to separate. In such a way, an efficient process converting cellulose into the attractive monomer isosorbide is within reach.¹⁷ By combining hydrolysis and hydrogenation in one reactor, a one-pot-production of sorbitol from cellobiose, the monomer of cellulose, can be carried out at high yields thus, in this way an avenue has been found for a direct process converting cellulose to sorbitol in one reactor.¹⁸ These processes result in derivatives (isosorbide, sorbitol, etc.) from the intermediate glucose. Clearly, an efficient method to separate glucose would greatly enhance the potential of molten-salt-based technologies in biomass conversion processes, for instance in biorefineries. In this paper, it is reported that such a separation process has been found.

In earlier work, the potential of zeolite beta in a chromatographic process environment was shown.¹⁹ In the work presented here, the performance (sugar recovery, stability) of the zeolite under practical conditions is reported and a techno-economic evaluation is presented.

2. MATERIALS AND METHODS

The molten salt solvent ZnCl_2 is referred to as “BIOeCON-solvent”. It may contain diluted HCl .

2.1. Pulse Injection Adsorption Studies. Adsorption experiments were performed using a setup consisting of several HPLC pumps (Knauer S100 Smartline, 10 mL Ti pump head) connected to a jacketed glass column (Bioline) via a selection valve. The column had an effective bed height of 850 mm and 10 mm inner diameter.

The hydrolysate used here was prepared from bagasse in the following way: A dried bagasse sample was mixed with 50 wt % $\text{ZnCl}_2/0.4$ molal $\text{HCl}/\text{H}_2\text{O}$ solvent in a ratio 1 to 10. The slurry was kept under stirring at 90 °C for 60 min, filtrated; the solid residue was washed with water and dried at room temperature. This material was used as the feed to contact with BIOeCON-solvent (70 wt % ZnCl_2 , 0.4 molal HCl , 10 wt % feed) at 80 °C. After filtration, the hydrolysate solution was diluted with water to 50 wt % ZnCl_2 and the HCl was neutralized by addition of ZnO . Part of the so-called acid-soluble lignin (ASL) precipitates after dilution and is filtered off. Remaining ASL was removed by passing 5 L of hydrolysate solution over a 250 mL column filled with Amberlite XAD7HP at 5 $\text{mL}\cdot\text{min}^{-1}$. The resulting composition of the solution was determined as described elsewhere¹⁹ to be ZnCl_2 (47.3 wt %), oligomers, including cellobiose (1.71 wt %), glucose (3.4 wt %), xylose (0.35 wt %), arabinose (0.02 wt %), anhydroglucose (0.05 wt %), acetic acid (0.008 wt %), traces of furfural, and HMF (hydroxymethylfurfural). Synthetic hydrolysate feed was prepared by mixing ZnCl_2 , cellobiose, and glucose in water to get a solution that contains 50 wt % ZnCl_2 , 2 wt % cellobiose, and 6 wt % glucose.

2.2. SMB Pilot Studies. The simulated moving bed (SMB) process is a multicolumn chromatographic process where feed and eluent are continuously fed, resulting in two product streams: the extract containing the sugars and the raffinate containing the ZnCl_2 solution (Figure 9). Note that an SMB

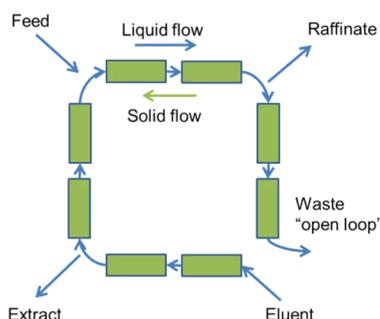


Figure 9. Schematic representation of SMB setup used in experiments for monosugar separation. The countercurrent solid flow is simulated by switching the positions in and outgoing flows clockwise. Note in this example each zone has 2 columns: a 2–2–2–2 configuration. The rectangles represent the columns described here.

system involves changing many parameters (switching time, temperature, four different flow rates [feed, eluent, extract, raffinate], feed composition, number of columns, column length, distribution of columns per zone) and leads to a system with many trade-offs.²⁰ A rigorous modeling study is required to optimize fully such a system. In addition, the position of the SMB within the whole process including recycle flows should be optimized. The objective of the pilot study was to demonstrate that real feeds can be treated over a longer period of time and to get a first reasonable operating point to enable a fair economic evaluation of the full process. The current data are presented to demonstrate that with a real hydrolysate feed,

with reasonable liquid hourly space velocities, good sugar recovery can be achieved for longer period of time.

The SMB pilot unit consists of 8 jacketed Knauer Bioline MPLC glass columns (1000 × 10 mm, effective bed height, 850 mm per column) that are connected by 8 Knauer Azura Assistant ASM 2.1L, each equipped with two 6-position valves. In this way, the feed, extract, raffinate, and eluent flow positions can be switched in time to simulate the moving bed behavior. Additionally, the number of beds per zone can be changed by simple reprogramming of the control software without hardware changes. Four Knauer Azura P2.1L pumps are used to control the feed, eluent, extract, and raffinate flows. Three Bronckhorst mini CORI-FLOW mass flow meters were used to measure the raffinate, feed, and eluent flow. A Knauer Smartline 2520 UV detector was used for qualitative online measurement of the extract concentration and a Knauer Smartline 2900 conductivity detector equipped with a pH sensor was used to monitor the raffinate concentration and pH. With use of a VICI Cheminert C25F flow through 8-positions selection valve and a Foxy R1 fraction collector, an automated sampling system was created. Samples were analyzed by HPLC as described earlier.¹⁹ The whole setup was controlled by Chromgate version 3.3.2. The specific experimental conditions used are indicated in the Results section.

The feed for SMB pilot studies was prepared in a similar way as for the pulse experiment with the only difference the solid to solvent ratio (1 to 20) and that acid soluble lignin was removed with Kuraray carbon. The resulting feed composition for the SMB pilot study was ZnCl_2 (47.3 wt %), oligomers, including cellobiose (0.24 wt %), glucose (2.0 wt %), xylose (0.88 wt %), acetic acid (0.15 wt %), traces of arabinose, anhydroglucose, furfural, and HMF (hydroxymethylfurfural).

2.3. Microspheres. “BEA microspheres” are 300 μm sized silica bound (20 wt %) zeolite beta (Zeolyst, CP-814E) spheres prepared by the company Brace GmbH by a drip casting technique, using an alginate binder that was removed by a calcination step. Not surprisingly, it is not available in the optimal shape for chromatographic processes (spherical, 300–800 μm). Spherical zeolite particles with a diameter of 300, 500, and 800 μm were developed (Brace GmbH). Silica was used as binder material.

2.4. Economic Evaluation. The economic evaluation is performed on the basis of the capital investment and the total production cost. General parameters of the cost estimation procedure are

- Cost date: December 2014 (CEPCI = 575)²¹
- Currency: US Dollar
- Location: US Gulf Coast, grassroots
- On-stream time: 8400 h/year

The costing estimation tool used is based on the method of Ulrich.²² For specific unit operations, we have taken cost data from vendor quotations or the NREL report.²³

The total capacity investment (TCI) was taken as the sum of total grass roots capital (GRC), working capital, 10% of TCI and start-up expenses, 2% of GRC. The capacity was chosen to be 263 kt/a corresponding with a sugar mill size of 1000 metric kiloton per year on a dry basis, with a bagasse content of 26.3%.

3. RESULTS AND DISCUSSION

3.1. Dissolution and Hydrolysis: Flow Schemes of Associated Potential Processes. Initially, dissolution and hydrolysis were performed in one reactor, as indicated in Figure

10. This scheme represents a rather simple process design. However, the simultaneous dissolution and hydrolysis leads to

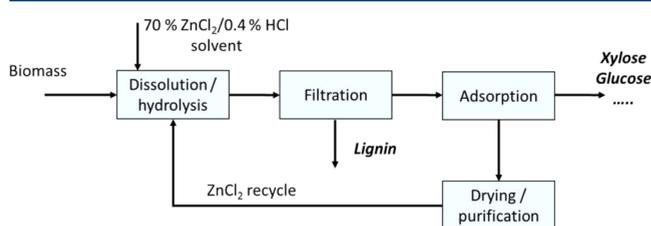


Figure 10. Flow diagram for the depolymerization of lignocellulosic biomass based on one simultaneous dissolution and hydrolysis process.

relatively large equipment and the needs of highly corrosion resistant materials for reactors due to the presence of ZnCl₂ and HCl. It should be noted that dissolution does take place in the experiments shown in Figure 7, but subsequent hydrolysis of the monomer is very slow. Under these conditions, dissolved microfibrils are formed rather than monosugars. Because HCl only has a minor role in dissolution, in principle, there is no need to use it in the dissolution step. Thus, it might be considered to add HCl after dissolution has taken place in a separate hydrolysis reactor. This way, an additional reactor is needed, but due to the low dissolution time the total volume is less than that of a single reactor of the simultaneous dissolution and hydrolysis. In addition, the dissolution reactor could be made from a cheaper material of construction, also leading to lower investment on reactors. However, the further development of the consecutive dissolution/hydrolysis confirmed that a modest HCl concentration is still preferred also in the dissolution step to reduce the operating temperature and residence time. The effluent of the dissolution reactor is diluted to enable filtration (see the Discussion section below). The further hydrolysis is then performed in a more diluted ZnCl₂ solution, which is beneficial to shift the sugar equilibrium toward glucose monomer.

In the most simple scheme (Figure 10), the hemicellulose and cellulose are reacted as a mixture. Not surprisingly, it was found that the reactivity of hemicellulose and cellulose are quite different. The optimal concentration of ZnCl₂ for hemicellulose and cellulose dissolution is 50 and 70 wt %, respectively. Therefore, a stage wise process might be more optimal, see Figure 11. An attractive aspect is that it is possible to produce

glucose and xylose in separate flows. In the framework of a biorefinery, such a product spectrum gives ample possibilities.

The crucial function of ZnCl₂ solvent regards the dissolution of the recalcitrant component cellulose. In contrast with cellulose, hemicellulose is very easy to depolymerize, for instance in diluted acids.²⁴ In acid-based processing, cellulose requires severe conditions (pH, temperature, acid concentration) that are incompatible with a clean process. The molten salt solvent is associated with mild conditions resulting in a clean process. For the much more reactive hemicellulose, acid-based processing is also satisfactory at mild conditions. Therefore, a variation of Figure 11 suggests itself. When first the lignocellulosic biomass is subjected to a treatment with diluted acid, converting the hemicellulose, the ZnCl₂ solvent will be limited to the conversion of cellulose, simplifying the ZnCl₂ recycle. Figure 12 gives the respective flow scheme.

3.2. Solid/Liquid Separation. In all process schemes considered, after dissolution the remaining solid phase is separated by filtration. The slurry coming from the dissolution reactor is diluted with water. This dilution is advantageous to precipitate and filter off part of acid soluble lignin, to increase the filtration rate, and in the subsequent hydrolysis to shift the equilibrium toward monomers.

3.3. Key Separation Step: How to Separate the Hydrophilic Monosugars from the Polar Molten Salt Solvent? An option is to extract ZnCl₂ by liquid/liquid extraction, e.g., a process based on extraction by tributyl-phosphate is described in the literature.²⁵ However, such a separation process involves removal of the major part (all ZnCl₂ and some water) of the mixture solvent and leads to excessive amounts of extractant needed. Moreover, a mixture of monosugars, dimers, and higher oligomers remains, where, in general, direct isolation of the monomer would be preferred. A known method to separate monosugars from a hydrolysate product is by chromatography using ion-exchange/exclusion resins.²⁶ A downside is that a high degree of dilution is required before the chromatographic separation,²⁷ leading to high costs in solvent recycling. Chromatography is conceptually interesting because it allows removal of the minor component from the solution. However, in-house tests as a part of this study have revealed the type of resins reported for the sulfuric acid system^{26,27} perform much worse for the ZnCl₂ system; it can only work at high dilutions (<<30 wt % ZnCl₂) and then still the performance is poor compared to the acid-based systems, i.e., long contact times and very bad peak separation.

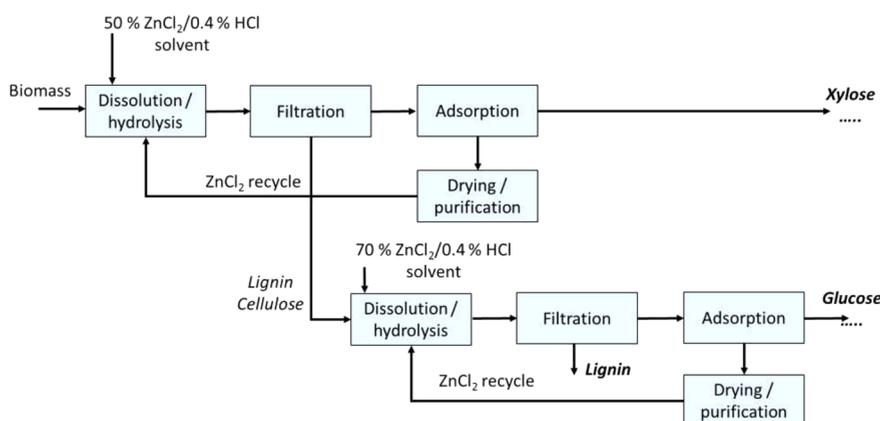


Figure 11. Flow diagram for the depolymerization of lignocellulosic biomass based in a stage-wise dissolution and hydrolysis process.

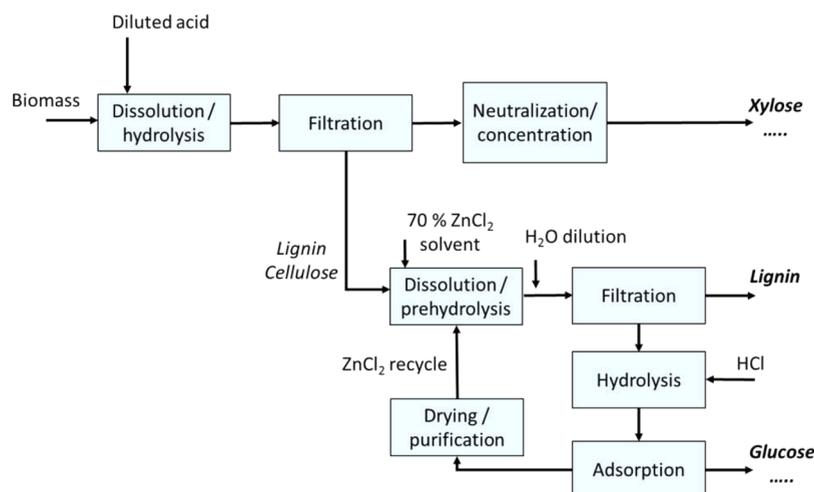


Figure 12. Flow diagram for the depolymerization of lignocellulosic biomass in a stage-wise dissolution and hydrolysis process involving a diluted acid catalyzed step for hemicellulose conversion.

As an alternative, we have explored another class of sorbents, viz., zeolites. Zeolites are microporous crystalline aluminosilicates with pores of molecular dimensions. Specifically, zeolites with high silica to alumina ratios (SAR) could be attractive because they possess a high stability toward acids and could exclude (hydrated) ions from their structure,²⁸ or at least limit adsorption due to a low ion-exchange capacity. A detailed study was performed.¹⁹ Zeolite beta appeared to be the most suitable material for the separation. The reason for the favorable behavior of zeolite beta is discussed elsewhere.¹⁹

The detailed adsorption equilibrium data for different zeolites and ZnCl_2 /glucose/cellobiose mixture, a model for a cellulose hydrolysate, was presented earlier.¹⁹ The results show that zeolite beta allows discrimination between monosugars and oligomers: compared to monosugars, the dimer cellobiose is not significantly adsorbed. The relation between performance and zeolite structure is discussed elsewhere.¹⁹

A selection of adsorption equilibrium data of different sugars and acetic acid for zeolite beta (microspheres) in an aqueous and 50 wt % ZnCl_2 solution are reported in Table 1. The

Table 1. Loading of Sugars and Acetic Acid on Zeolite Beta in Water and 50 wt % ZnCl_2 Solution^a

component	in aqueous solution, g/g _{sorb}	in 50 wt % ZnCl_2 solution, g/g _{sorb}
arabinose	0.049	0.069
xylose	0.034	0.072
fructose	0.029	0.073
glucose	0.022	0.061
cellobiose	0.017	0.017
sucrose	-0.008	0.002
acetic acid	0.051	0.096

^aThe initial content of the organic component was in all cases 8 wt %. Copyright permission Springer.¹⁹

monosugars (glucose, xylose, arabinose, fructose) have a relatively low loading in the presence of water, but the loading strongly increases when 50 wt % ZnCl_2 is present in the solution.

Clearly, a positive effect of ZnCl_2 on the adsorption of 5 and 6 carbon-membered sugars is found. The studied sugar dimers (sucrose, cellobiose) show a low loading, both in water and in a 50 wt % ZnCl_2 solution, resulting in a significant mono-

saccharide/disaccharide selectivity for zeolite BEA. The observation that cellobiose adsorbs only slightly and sucrose not at all is in line with results of Buttersack et al.²⁹ The acetic acid loading is relatively high in water and is strongly increased by the presence of ZnCl_2 . Note that the absolute loading of xylose and arabinose is higher in water than glucose and fructose. For the separation from ZnCl_2 , this can be beneficial because it will lead to a better peak separation in column chromatography.

The most (cost) efficient way for industrial application of the separation is by continuous chromatography (e.g., SMB) at high column loading. Breakthrough experiments were carried out to verify the behavior of the separation under column overloading conditions.¹⁹ The data confirmed the separation of glucose from both ZnCl_2 and cellobiose. It also showed that when the glucose is separated from ZnCl_2 , its separation becomes more difficult, obviously because the glucose loading in the absence of ZnCl_2 is much lower (Table 1). Water acts as a desorbent for glucose, leading to a strongly concentrated glucose peak, up to three times the concentration present in the feed. Full peak separation of glucose and ZnCl_2 is difficult and the choice of technology to perform this chromatographic step is very important. SMB technology, for example, would be particularly suitable to perform this separation because full peak separation on the column is not required to realize high glucose purity and recovery. Because of the strong desorption of glucose, very concentrated product streams can be obtained, whereas, typically in chromatography, product streams are diluted compared to the original feed.

In conclusion, it has been demonstrated with a model feed that monosugars can be isolated efficiently from a ZnCl_2 containing hydrolysate by a chromatographic separation using zeolite beta. The zeolite also separates the sugar monomers from the sugar oligomers. The separation is strongly determined by the presence of salt, which promotes monosugar adsorption and shows a maximum monosugar adsorption at 45 wt % ZnCl_2 . The separation can be performed at limited dilution of the original hydrolysate (70 wt %), thereby limiting water that needs to be removed from the solvent during solvent regeneration. An important benefit of the separation is that the monosugar adsorption is reduced when ZnCl_2 is removed. As a result, a monosugar product stream can be obtained with a

strongly increased concentration compared to the original feed in one step, using water as an eluent.

3.4. Pilot Plant Study SMB. After the demonstrations with model feed mixtures, the separation of a real cellulose hydrolysate was studied by pulse injection on a zeolite beta microsphere column. The results are given in Figure 13.

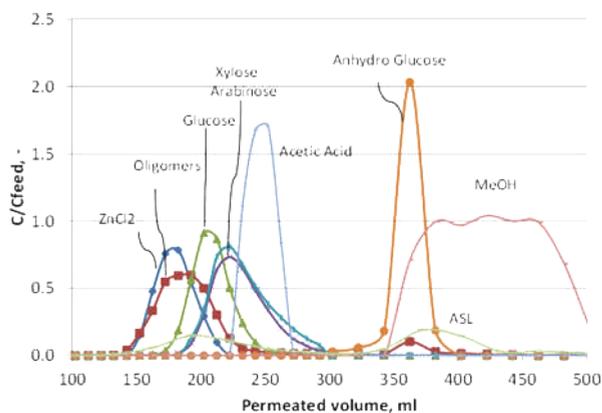


Figure 13. Pulse injection of a real cellulose hydrolysate on a zeolite beta microsphere column (1×260 cm). Flow: 5 mL min^{-1} . Feed injection: 5 min, 50°C , 50 wt % MeOH is used as desorbent after water injection. Copyright permission Springer.¹⁹

Glucose, xylose, arabinose, and acetic acid are separated well from ZnCl_2 , in line with the equilibrium adsorption data. Xylose and arabinose separate better from ZnCl_2 than glucose.

This difference is due to the higher adsorption affinity of xylose in the absence of ZnCl_2 . Acetic acid adsorbs very strongly also in the absence of ZnCl_2 , which explains its high retention time. Sugar oligomers are well separated from the monosugars. ASL adsorbs relatively strongly, as do furfural and anhydroglucose (data not shown). These stronger adsorbing components can be desorbed using a 50 wt % MeOH solution. The zeolites particles were extensively tested for their stability under a broad range of conditions. The results were positive. In addition, pilot testing was successfully carried out over several months.

The chromatographic process was further optimized on the pilot scale with SMB technology. Various real hydrolysate product mixtures have been studied for longer periods of time. Figure 14 shows an example of the SMB performance for the hydrolysate of bagasse. The feed was pretreated with activated carbon (Kuraray GLC), in order to remove acid soluble lignin impurities and the very low amount of furans formed. The data show that the separation performance is very stable for more than 150 h. A glucose recovery of 90%, which is typical, is observed. The xylose recovery is at the same level (not shown). After optimization, it is expected that these numbers will be closer to 100%.

Table 2 shows the composition of the feed and collected extract product. The data show that an extract product with a strongly increased monosugar loading and very low ZnCl_2 content (0.04 wt %) can be obtained. The ZnCl_2 content in the extract flow accounts for 0.15% of the total ZnCl_2 recovery. Note that the final monosugar content is still relatively low due to the low monosugar concentration in the used feed. Demonstrations with model feeds representing the expected design feed composition showed sugar concentrations in the extract stream up to 15–20 wt %. The effective eluent to feed

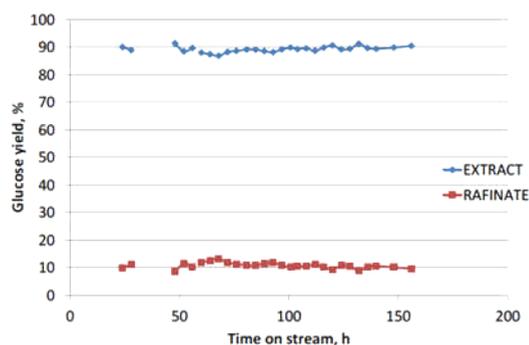


Figure 14. Glucose recovery in a SMB experiment starting from a real hydrolysate feed at 40 h at 60°C . After 40 h, the feed was switched from model to real feed. The feed was pretreated using Kuraray GLC activated carbon. Note that the SMB was operated in a 1–4–2–1 open-loop configuration with a valve switching time of 6 min, and the recovery found in the waste flow is added to the extract recovery. The system is operated with 8-column system with a total volume of 0.5 L. The eluent, extract, feed, raffinate, and waste flow rates are 10.74, 1.0, 2.0, 3.5, and 8.24 mL min^{-1} , respectively.

Table 2. Composition (wt %) of the Feed and of the Collected Extract Product

	ZnCl_2	glucose	xylose	acetic acid	oligomers
feed	47.3	2.0	0.88	0.15	0.24
extract	0.04	5.1	1.6	0.47	0.09

ratio on mass basis in this experiment is low (0.833) due to the high feed density ($\sim 1500 \text{ kg/m}^3$).

Additional work revealed that particularly furans can lead to deactivation of the sorbent of the SMB and acid soluble lignin to a much lesser extent. The activity of the sorbent can be recovered by a treatment with water and an organic solvent like MeOH. Working with a zeolite guard bed to remove these furans instead of the carbon bed showed very promising results to simplify the pretreatment step and potentially recovery of valuable furanic byproducts. Note also that because of the relatively low temperature, in the dissolution and hydrolysis step, only very few furanic species are formed.

After a demonstration of the SMB with real feeds, the operating conditions need to be defined. From an economic point of view, a critical parameter is the eluent that is consumed because the recovery of this eluent (water) is energy intensive (evaporation). A strong relation exists between the extract product purity and eluent consumption. It was concluded that it is the most economical to fix the SMB operating point at not too high ZnCl_2 recovery ($\sim 97\%$) and to add a post-treatment (e.g., electrodialysis) to remove the last amount of ZnCl_2 . In this way, only 300 ppm ZnCl_2 is left in the stream.

On the basis of the above-mentioned considerations and a broad data set, we have come to the following operating conditions and performance for our laboratory system: $T = 60^\circ\text{C}$, $\text{LHSV} = 0.3 \text{ h}^{-1}$ ($\text{LHSV} = \text{liquid hourly space velocity}$, based on volumetric feed inlet and total SMB volume), an eluent to feed ratio of 0.6 (w/w), the total system has 8 columns with 1 m bed height. Separation performance can be defined based on the recovery in extract of all components: glucose (90%), xylose (95%), ZnCl_2 (3%), acetic acid (90%), oligomers (30%). Based on our lab data, total costs of SMB unit for the BIOeCON-solvent process has been quoted to a total sum of 5 MEUR for the equipment cost. Installed cost could add up to 10 MEUR. A couple of points should be made. First,

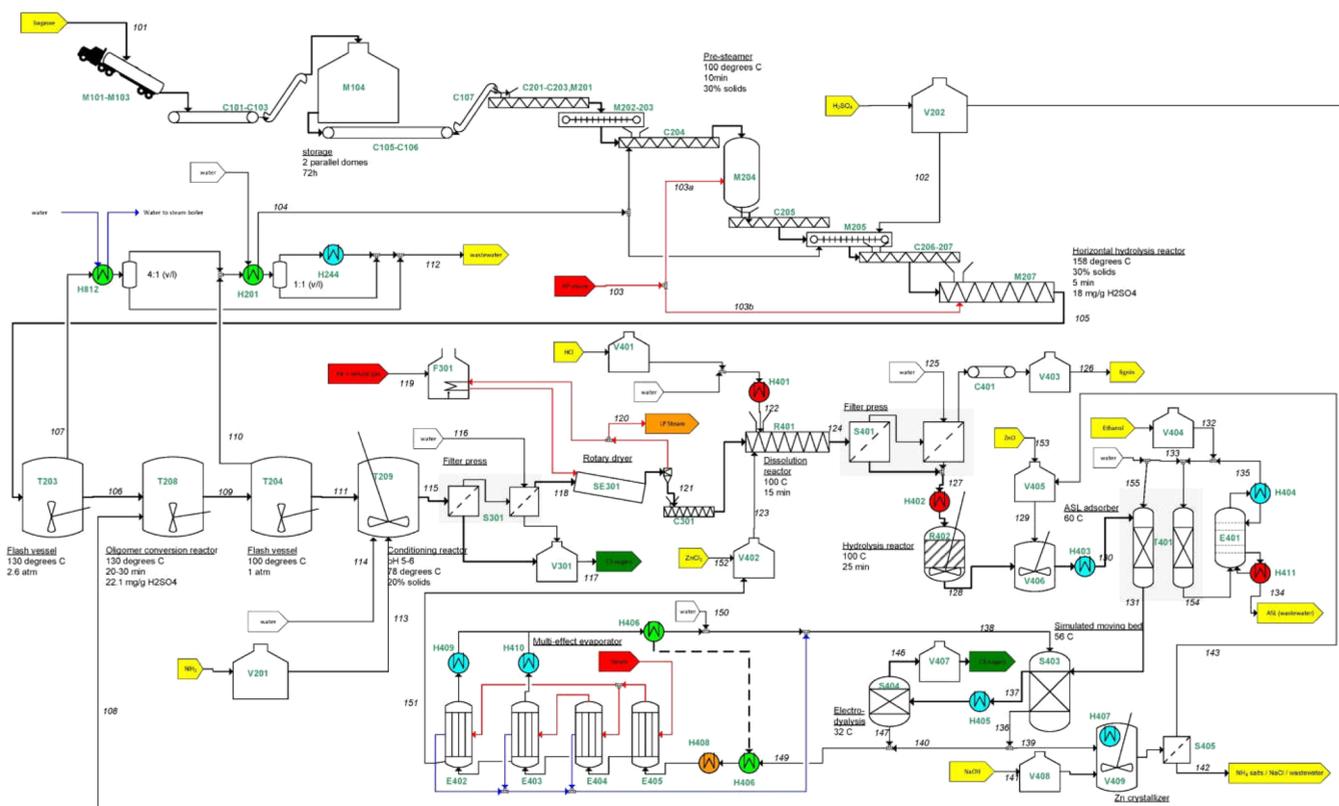


Figure 15. Process flow diagram of the two-stage process according to a combination of sulfuric acid-catalyzed hemicellulose and BIOeCON-solvent-based cellulose conversion.

the productivity, purity, and eluent consumption of the SMB is expected to be further improved significantly by a rigorous modeling of the process. Second, 8 column systems are not commonly designed. Typically, 5 or 6 columns are used. This is in line with the observation in the lab that in several zones the same performance can be achieved with one instead of 2 columns. Moreover, vendors claim that an advanced sequential-SMB (SSMB) system is typically 25% more productive than classical SMB as we performed. Considering the discussion above, the investment cost may be significantly overestimated.

In the current design, it is assumed that further purification of the extract product is done in a polishing step.

3.5. HCl Removal. ZnCl_2 hydrate is an excellent solvent for cellulose, the most refractory carbohydrate. When depolymerization is the aim, in general the addition of HCl (low concentration is sufficient) is favorable because of a large increase of rate of depolymerization. In general, it is attractive to remove the HCl after the hydrolysis step in order to allow cheap metals for the construction of the equipment. The following options were evaluated:

- Neutralization
- Liquid/liquid extraction
- Evaporation

All these options are technically feasible. However, liquid/liquid extraction appeared to be not economical (TEHA (tri-2-ethylhexyl amine) was studied). Evaporation also was not economical, mainly because HCl was only removed to the desired degree after evaporation of most of the water ($\text{ZnCl}_2 > 70$ wt %). Also, the equilibrium of monosugars shifted back to the oligomers. Neutralization works well; it can be done by adding ZnO or Zn(OH)_2 (forming ZnCl_2).

3.6. ZnCl_2 Recovery. ZnCl_2 losses should be minimized for economic and for environmental reasons. Two main flows have been identified causing the loss of ZnCl_2 :

- ZnCl_2 remaining in the lignin produced
- ZnCl_2 left in the extract product flow leaving the SMB process

The extent of the first flow can be reduced by more efficient washing of the lignin product stream. When this is done by using additional water, recovery of the salt from this diluted water flow is needed. We considered several technologies, viz., water evaporation, reverse osmosis (RO), and electro dialysis (ED). For a concentrating step of 4–70 wt % ZnCl_2 solution, it was found that it is economically most interesting to combine either an ED or a RO preconcentrating step with a final evaporation step; ED and RO lead to similar costs. An attractive alternative might be based on our recent finding that precipitation of ZnCl_2 by NaOH is also feasible. Use of NaCl makes the technology significantly more cost-effective. In addition, the formed Zn hydroxides can be used to neutralize the HCl as discussed in the paragraph above.

Recovery of ZnCl_2 from the SMB extract stream has been discussed above.

3.7. Techno-Economic Analysis. From the work described here, it is concluded that the BIOeCON-solvent process is technically feasible. The question arises if this also applies to the economy of the process. We performed several analyses in which we involved a company specialized in process design.^{22,30}

We decided to concentrate on stage-wise process schemes in which two streams are produced, one from hemicellulose and one from cellulose, with the advantage that separate C5 and C6

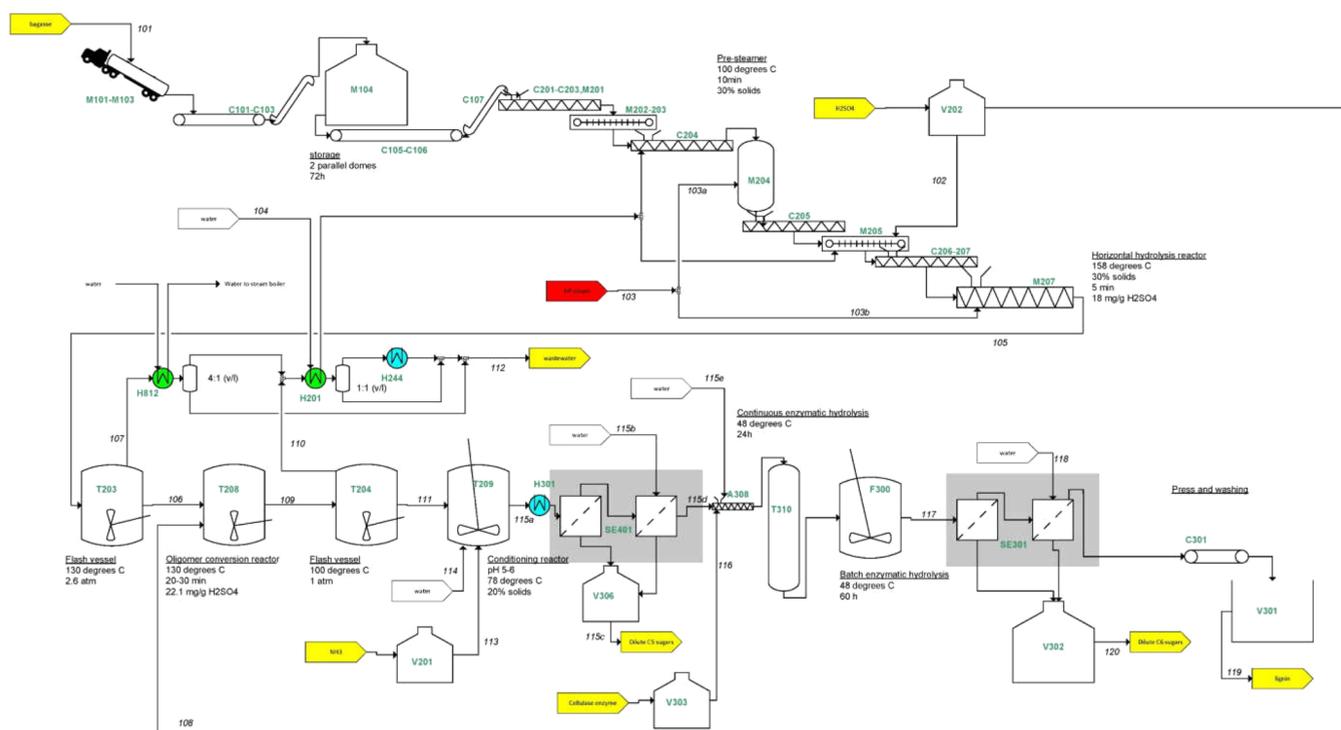


Figure 16. Process flow diagram of the two-stage process according to a combination of sulfuric acid-catalyzed hemicellulose and enzyme-based cellulose conversion.

sugar product streams are produced. In addition, because of the high relative reactivity of the hemicellulose stream compared to the cellulose stream, a stage-wise process might be the most efficient scheme. For the first step, mild conditions will do; for instance, 50 wt % ZnCl_2 or the conventional technology of diluted acids such as diluted HCl of diluted sulfuric acid. The uniqueness of the BIOeCON-solvent technology in comparison with other biomass to sugar conversion technologies is the effectiveness of the cellulose hydrolysis, which due to the use of ZnCl_2 can be performed with very short residence times and without significant sugar degradation.

We wanted to compare our process with an established process for lignocellulosic biomass conversion. In the literature, not many processes are described in sufficient detail. A set of reports is available from NREL.²³ To enable a direct comparison, we have chosen the same hemicellulose conversion process as NREL, i.e., diluted sulfuric acid technology.

To allow a useful comparison of the BIOeCON-solvent technology with the NREL process, we performed an alignment in feedstock (bagasse), battery limits of the process, separate sugar production, and the method and basis for equipment and operating cost estimation. Added unit operations are the biomass dryer, ASL recovery column with solvent recovery, multieffect evaporator for ZnCl_2 reconcentration, and ZnCl_2 recovery from the purge. For the NREL reference case, the mass and energy balance was developed by scaling of the NREL data.²³

Thus, in the first stage the hemicellulose is converted based on diluted sulfuric acid-catalyzed hydrolysis into soluble C5 sugars, primarily xylose and mannose and arabinose. Also, glucose is formed to a short extent. Acetic acid is produced from acetyl groups present in the hemicellulose components. In addition, some lignin is dissolved and some sugar degradation products (furfural, HMF (5-hydroxymethyl furfural) are

formed. The second stage converts cellulose to glucose and separates lignin.

The following steps can be distinguished:

- Pre-steamer; steam is injected to reach a temperature of 100 °C; 10 min
- Hydrolysis; H_2SO_4 added, 158 °C; 5 min
- Oligomer conversion; 130 °C, 20–30 min
- Neutralization with ammonia
- Filtration
- Drying the solid product from the first stage hemicellulose conversion in diluted H_2SO_4
- Dissolution; 70 wt % ZnCl_2 ; 100 °C; 1 bar; 15 min; solid:liquid = 1:5 wt/wt; HCl 0.4 wt %
- Filtration
- HCl neutralization
- ASL and furan removal (adsorbent: zeolite beta)
- Recover residual ZnCl_2 by electro dialysis

Figure 15 and Figure 16 give the process flow diagrams of respectively:

- First stage according to the NREL process followed by the second stage according to the BIOeCON-solvent technology
- First stage according to the NREL process followed by the second stage according to the NREL enzyme-based technology

The outcomes of the techno-economic evaluations of the various process designs and configurations are summarized in Table 3.

Overall, the numbers do not differ very much. At first sight, this might be surprising: the technologies are very different. The key advantage of the BIOeCON-solvent technology is the effectiveness of the cellulose hydrolysis, which can be performed with high conversion and without significant sugar

Table 3. Comparison of the Results of the Techno-Economic Analysis of Stage-Wise Conversion of Bagasse for the BIOeCON-Solvent Process and the Adapted NREL Process

technology second step	BIOeCON-solvent ZnCl ₂ /diluted HCl	NREL enzyme-based reference process
CAPEX (MM\$)	95.4	90.8
OPEX (MM\$/year)	90.0	84.6
utility costs (MM\$/year)	12.2	5.9
raw materials (MM\$/year)	28.9	34.2
labor costs (MM\$/year)	3.1	2.5
manufacturing costs mixed sugars (\$/ton)	471	436
product scale, all sugars (kt/year)	195	194
sugar concentration in product (%)		
C6	25.3	7.3
C5	6.3	5.6

degradation at a time scale less than 1 h, instead of 80 h for the NREL process. In addition, for the BIOeCON-solvent process no enzyme costs are involved. The concentration of sugars in the product is much higher for the BIOeCON-solvent processes than for the NREL processes. This high concentration is achieved because of a concentrating action of the SMB and electrodialysis unit. The concentration produced in the NREL process is too low for a final product and is even low when it is directly used for fermentation. When the sugars in the NREL process are included to achieve a concentration similar to that of the BIOeCON process, CAPEX and OPEX for the NREL process would increase. On the other hand, additional equipment is needed for the ZnCl₂/sugar separation. Together with higher operation costs, utility consumption increases. Both CAPEX and product manufacturing prices are in the same order for the two process designs. In this comparison, the sugars in the NREL process are included to achieve a concentration similar to that of the BIOeCON process, CAPEX and OPEX for the NREL process would increase.

On the other hand, additional equipment is needed for the ZnCl₂/sugar separation. Together with higher operation costs, utility consumption increases. Both CAPEX and product manufacturing price are in the same order for the two process designs. In this comparison, the BIOeCON-solvent process is slightly higher in cost, but also produces a substantially higher sugar concentration in the product stream. In the present evaluation, the differences largely cancel and the sugar prices are comparable. We see this as promising because the ZnCl₂-based process is very new and far from optimized. We conclude that the BIOeCON-solvent process is at least competitive with the state-of-the-art enzyme-based process.

Robustness of BIOeCON-solvent based process is one of the additional and probably main advantages compared to enzyme based processes. The process was tested at laboratory and pilot scale extensively for bagasse as a feedstock, but with similar efficiency it can handle any type of lignocellulosic biomass including wood and straw. In Table 4, results are compared for wood, straw, and bagasse. The measured sugar in the hydrolysate liquid showed high yields for all three feed stocks (Table 4). It should be noted that the process conditions (*T* and treatment time) were optimized for bagasse case. If the conditions are optimized for particular feedstocks, we expect

Table 4. Sugar Yield in Hydrolysate Liquid for Different Type of Lignocellulosic Feedstock

feedstock	sugar yield in hydrolysate liquid	
	C ₆ , g xylose per g feed	C ₆ , g glucose per g glucan in the feed
bagasse	0.92	0.95
wood	0.71	0.96
straw	0.90	0.77

significantly higher sugar yields within reach than presented in the Table 4.

A fair point to consider is the price of the sugar produced. Sugar prices are rather volatile and typically between 400 and 500 \$/ton. Moreover, it should be noted that we gave lignin only the fuel value. When for lignin an economically more attractive application is found, the sugar cost price goes down. Thus, in the short term, compared with lignocellulosic-biomass-based processes, sugar-based processes are as economic, without the need to build a new plant. Moreover, the sugar both in the BIOeCON-solvent and in the NREL process are C5/C6 mixtures, whereas the sugar at the market probably is pure C6 sugar. Dependent on the specific application, this difference might make sugar from the market more attractive. On the other hand, it is generally postulated that for sustainable biomass-based production in the chemical industry in the long-term, starting from lignocellulose is a must.

4. CONCLUSIONS

Technically, the BIOeCON-solvent technology can be used to convert lignocellulosic biomass to monomeric sugars. The breakthrough was the development of zeolite-based chromatographic separation. Monosugars can be isolated efficiently from a ZnCl₂ containing hydrolysate by a chromatographic separation using zeolite beta. In addition, the sugar monomers are separated from the sugar oligomers. This process was demonstrated on a continuous scale with real feedstocks.

An economic evaluation is made, based on realistic pilot data, including pretreatment steps and solvent recycle loops. A comparison is made with the NREL process, a well-documented and -developed process, to obtain an objective evaluation. The BIOeCON-solvent technology is technically and economically competitive with state-of-the-art technology. The main advantages are its robustness, the high reaction rates and the high yields. The manufacturing cost is around 450 \$/ton, in the range of sugar price in 2015–2016 years. There is a clear potential for developing a significantly more favorable process by further optimization. A rigorous modeling study is, e.g., required to optimize fully an SMB system as used. The high costs of the utilities show that it is worthwhile to optimize heat integration. Future development should also focus on process simplification.

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Notes

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