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Assessing the Economic Viability of Pretreatment Technologies to Make Sugars for Chemical Catalytic Upgrading to Fuels and Chemicals

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Abstract

The monomeric/polymeric sugars derived from cellulose and hemicellulose must be nearly pure (>95%) for chemical catalytic upgrading to chemicals and fuels. This work reports the results of a qualitative screening study of biomass pretreatment and fractionation technologies that can meet this purity requirement. Two technologies, combined autohydrolysis and Organosolv (AOF) and formic acid pulping (FAP), were found to be suitable for the effective fractionation of lignocellulose to yield cellulose, hemicellulose, and lignin. The estimated costs of making nearly pure (>95%) polysaccharides from a lignocellulosic feedstock were US$0.66/kg (AOF) and US$0.36/kg (FAP). The limiting factor for commercialization was the high ratio of liquid-to-dry-solid required for biomass fractionation using both AOF and FAP technologies.

Keywords

Biomass fractionation; Biomass pre-treatment; Formic acid pulping; Autohydrolysis; Organosolv

1. Introduction

Replacing petroleum-derived chemicals and fuels with lignocellulose-derived alternatives can improve global energy security and minimize the potential for climate change impacts[1]. Lignocellulosic feedstocks are comprised of three major components: cellulose, hemicellulose, and lignin, the relative amounts of which vary by biomass source. For example, the composition of corn stover is 37% cellulose, 31% hemicellulose, and 18% lignin whereas that of most hardwoods is 40-50% cellulose, 15-20% hemicellulose, and 18-25% lignin[2,3]. Recently, there has been great interest in leveraging petrochemical catalysis technologies to produce biobased chemicals and biofuels from these biomass fractions of cellulose, hemicellulose, and lignin[4-15].

Cellulose can be effectively hydrolyzed to glucose followed by dehydration to hydroxymethylfurfural/levulinic acid in presence of different catalyst types (e.g., mineral acids and soluble metal acid salts) using ionic liquids as a reaction medium[4]. Like cellulose, hemicellulose can be upgraded to high value added chemicals, such as furfural, with high yields, and lignin can be effectively hydrogenated to low molecular weight aromatic compounds for potential use as fuels using ionic liquids and different catalyst types[4]. Gamma-valerolactone (a potential liquid hydrocarbon fuel) can be made from cellulose using a cascade strategy involving dehydration of cellulose to equimolar mixture of formic and levulinic acids followed by decomposing formic acid to hydrogen and CO_2 to reduce levulinic acid to γ-valerolactone over Ru/C catalyst in sulfuric acid[5]. Solid acidic nanostructured catalysts have been explored for hydrolysis, isomerization, dehydration, and etherification of cellulose to glucose, fructose, HMF, 5-ethoxymethylfurfural[6]. Nearly pure cellulose hydrolysate can be converted to a gasoline blendstock via integrated aqueous phase reforming and acid condensation. The aqueous phase reforming of cellulose hydrolysate involves hydrogen production via reforming and dehydrogenation of alcohols/hydrogenation of carbonyls, deoxygenation reactions, hydrogenolysis, and cyclization. The effluent of aqueous phase reforming undergoes acid condensation over a zeolite catalyst to produce the gasoline blendstock[7].

Technologies for catalytic cracking of xylan over mesoporous catalysts and thermal cracking of xylan have been developed[12,13]. Further, a great amount of research has been focused on xylan dehydration to furfural using various solid acid catalysts, metal salts, organic acids, and heterogenous catalysts[14]. Simple aromatic chemicals can be made via acid/base catalyzed lignin hydrolysis under mild operating conditions[15]. Technologies for catalytic pyrolysis and hydro processing of lignin to potential transportation fuels are currently at the research and development stage[15].

One requirement for chemical catalytic upgrading of hemicellulose and cellulose fractions is that the various biomass fractions must be purified prior to catalysis. Further, the lignin condensation must be reduced during the biomass fractionation for the effective upgrading of lignin to a high value-added chemicals and transportation fuels. Additionally, the quantities of certain impurities in the fractions must be minimized because their presence can poison metal catalysts[10]. Finally, the cost of cellulose and hemicellulose fractions should be around $0.30 per kg for the economically viable production of commodity-type chemicals and biofuels[16-19]. The current commercialized sugar production pathway is the corn wet milling process. However, no commercial pathway exists to produce sugars from a lignocellulosic feedstock. From our personal communication with corn plants in Iowa during the Center for BioRenewable Chemicals (CBiRC) annual meeting[18], we learned that the best target price of sugars is \$0.40 to \$0.44 per kg to compete with the corn wet milling process. It is also evident from the recent department of energy DE-FOA-0002396 that the target cost of cellulose/hemicellulose sugars is \$0.44 per kg[19]. It takes about \$0.14 for the conversion of 1 kg cellulose and hemicelluloses to catalytic upgradable sugars. Thus, in this study we have chosen the target cost of cellulose and hemicellulose production at \$0.30 per kg. Nearly pure sugars can be predominantly made via a corn wet milling process in U.S[20]. The net cumulative deficit of corn derived sugars from 2021 to 2030 is estimated around 5.4 billion kg in U.S. By 2030, the net deficit of sugars needed for growing demand from biomass-based products is assessed at 1 billion kg[20].

Various technologies have been proposed to fractionate lignocellulosic feedstocks[21]. Most of these technologies are aimed at the production of sugars for biocatalytic use, especially for fermentation to yield ethanol. Unlike chemical catalysis, biocatalysis does not required complete biomass fractionation. Additionally, the types of impurities that can be tolerated are different for biocatalysis and chemical catalysis. For instance, the presence of residual sulfur and biogenic impurities like proteins in the feedstock stream can poison reduced metals but biocatalysts can tolerate sulfur and biogenic impurities[22-24]. On the other hand, metal catalysts can tolerate presence of phenolic compounds in the feedstock stream, but biocatalysts yield reduced rates in presence of aromatic compounds[25]. Thus, the biomass pretreatment technologies developed for bioconversion may or may not be suitable to make sugars for chemical catalytic upgrading. In this study, we for the first time screen a range of biomass fractionation technologies to down-select for those that produce pure cellulose and hemicellulose fractions suitable for chemical catalytic upgrading.

There have been a few studies of techno-economic assessment and life cycle analysis for biomass pretreatment technologies[26-28]. The techno-economic assessment of biomass pretreatment using ionic liquid, three stage milling, and dilute acid technologies have assessed the capital and operating costs of biomass pretreatment to produce sugars for biocatalytic upgrading[26,27]. Among these three technologies, dilute acid pretreatment technology is found to have a potential to make sugars at a cost of less than $300 per metric ton. However, the environmental impact of the acid pretreatment technology is high due to the lime treatment necessary for precipitating sulfuric acid[28]. Further discussion of acid pretreatment disadvantages will be found in the technology down selection section of the paper. Finally, application of the results to the production of sugars to produce fuels and value-added chemicals via chemical catalytic upgrading is limited as the published techno-economic and life cycle assessment studies evaluated biomass fractionation technologies with a focus to make glucose for biocatalytic use, especially for fermentation to yield ethanol.

Here, for the first time, we screened and down-selected biomass pretreatment technologies suitable for producing cellulose and hemicellulose sugars for chemical catalytic upgrading. The techno-economics of the down-selected biomass pretreatment technologies to produce sugars are also presented. For the first time, the effect of biomass compositional variance on the economic performance of the biomass pretreatment technologies is also assessed. The results will enable identification of technological barriers which limit the commercial relevance of biomass pretreatment technologies. Finally, the results will be used to set performance targets to the biomass pretreatment technology teams in terms of desired solid to liquid ratio.

2. Technology Down Selection

The most advanced and innovative lignocellulosic biomass pretreatment technologies have been selected and grouped into five categories: mechanical (not shown in Figure 1 and Table 1), chemical, physical, biological, and physicochemical (Figure 1 and Table 1). The structural disruption caused due to mechanical pretreatment may be enough for the enzymes or microbes to access cellulose and hemicellulose fractions and upgrade them to chemicals. However, mechanical pretreatment is energy intensive[29] and not enough by itself to achieve effective biomass fractionation to produce reasonably pure cellulose, hemicellulose, and lignin, thereby making it a poor choice for pretreatment for chemical catalysis.

Biological processes such as bacterial and fungal depolymerization are used to degrade lignin to yield CO_2 and water[30], which is a significant economic loss. Also, these processes require the addition of nutrients (e.g., nitrogen) and salts (e.g., sodium and ammonium) [30], which are inhibitory to reduced metal catalysts[22-24]. Further, the separation and purification of cellulose and hemicellulose fractions from such complex reaction media could be very expensive due to the many impurities in the fermentation media.

The physical, chemical, and physicochemical biomass fractionation technologies are evaluated against the following screening criteria: safety and handling, hazardous waste formation, ability to separate hemicellulose and cellulose, degradation of hemicellulose/cellulose, incomplete delignification, and previously determined expense (Table 1). Biomass pretreatment with sulfuric acid and N-phenylmorpholine have significant material safety and waste generation issues. N-phenylmorpholine can form an explosive mixture with air. The precipitation of sulfuric acid using bases (e.g., sodium or calcium hydroxides) would consume about 300 kg of sulfuric acid per MT of biomass while producing about 500 kg of solid waste[31]. The solid waste can reduced by recovering the sulfuric acid for reuse, which is however found to be highly energy intensive and concomitantly expensive[31-32]. The sulfite or the SO_2-ethanol-water fractionation processes avoids the need of recovering sulfate, as both produce lignosulfonates[33]. Though lignosulfonates have an existing market, the technology risk of these processes is high because the valorization of lignosulfonates are limited[34]. Additionally, the presence of dissolved SO_2 in the hemicellulose stream is unacceptable for catalytic chemical upgrading.

Techno-economic studies have indicated that the cost of ionic liquids and ozone pretreatment technologies are about twofold higher than the target cost[16-17]. Similarly, the economics of repurposing a kraft pulp mill for biomass fractionation and subsequent ethanol production was found to be economically not feasible[34]. Most biomass pretreatment technologies either result in the incomplete fractionation of lignin, hemicellulose, and cellulose or in the complete degradation of hemicellulose to organic acids (Table 1). The issue of incomplete fractionation can be addressed by combined autohydrolysis and Organosolv fractionation (AOF) as well as formic acid pulping (FAP) technologies. In addition to effective fractionation, these two technologies also address issues around safety and handling, generation of hazardous waste, and product degradation[35-36]. A techno-economic analysis of these two technologies has been conducted to determine their economic practicality.

For the base case techno-economic assessment, we considered corncob feedstock for the FAP technology and wood for the AOF technology as the bench scale sugar yield data is available for the modeling purpose. To expand the scope of results applicability, the sensitivity of assessed minimum selling price of sugars to a change in the composition of hemicellulose and cellulose. Generally, the selling price of hemicellulose and cellulose is higher than that of lignin and thus the biomass composition will influence the economic performance of a biomass fractionation process. For this reason, in this work while we assess independently the economics of the FAP and AOF technologies, we explicitly have not attempted to compare the economics of the two processes.

3. Process description of the selected biomass fractionation technologies

3.1 Autohydrolysis and Organosolv fractionation (AOF)

The autohydrolysis is highly effective on both graminoid monocot species (e.g., switchgrass and corn stover) and dicots and gymnosperms biomass (e.g., soft and hard wood chips) due its ability to effectively hydrolyze acetyl groups of hemicelluloses. The Organosolv process involves the cleavage of aryl ether linkage in presence of organic solvents and both graminoid monocot and gymnosperms biomass can be effectively pretreated with the Organosolv process. Thus, the AOF pretreatment process can be a biomass feedstock agnostic. For the base case, we selected wood chips for modeling AOF pretreatment and the sensitivity of biomass composition to the base case results was done to assess the impact of feedstock type on the economic feasibility of AOF pretreatment.

Romani *et al.* has reported the AOF fractionation of *eucalyptus globulus* wood with 2.4% extractives, 0.23% ash, 44.4% cellulose, 18.5% xylan, 3.3% acetyl groups, and 27.7% lignin[36]. A simplified process flow diagram (PFD) is presented in Figure 2 for the AOF fractionation. The hammer milled wood chips are delivered to a biorefinery facility. The milled wood with a moisture content of (>30 wt %) is hydrolyzed under the following conditions: liquid-to-dry-solid ratio of 8, hydrolysis temperature of 200°C and residence time of 42 min[36]. Under these operating conditions, nearly 86 wt% of the xylans undergo hydrolysis to produce xylo-oligomers and a small fraction of the oligomers are further hydrolyzed to xylose. This hydrolysis step is thought to be catalyzed by acetic acid, produced *in situ* from the acetyl groups of hemicellulose that are readily liberated under hydrothermal conditions[36]. The hydrolyzate is then transferred to a vacuum evaporator to remove acetic acid and other volatile wood extractives. The solid/liquid mixture is then separated using conventional filtration. The recovered liquid mixture contains predominately xylo-oligomers and xylose while the solids contain primarily cellulose and lignin. A multiple effect evaporator is used to concentrate the xylo-oligomers and xylose stream before used for chemical catalytic upgrading. The same multiple effect evaporator will also be used to dry cellulose and lignin if necessary, by using the waste heat available in the plant.

The autohydrolysis solids (cellulose and lignin) are mixed with ethanol and water as they are transferred to the Organosolv reactor where they are reacted under the following conditions: liquid-to-dry-solid ratio of 8, 60 wt% aqueous ethanol, pulping temperature of 180°C and residence time of 120 min[36]. Cellulose with a purity of close to 90% can be obtained at these operating conditions. The high-pressure mixture of solid (which is composed mostly of cellulose) and the liquid (which contains lignin, ethanol, and water) leaves the Organosolv reactor and is flash evaporated at 4 bar to collect a fraction of aqueous ethanol as a vapor. The bottom stream leaving the evaporator column is routed to a belt filter press where the cellulose solids (with a moisture content of 50 wt.%) are recovered as retentate. The vacuum distillation operating with a reboiler temperature of 40 °C is used to recover aqueous ethanol as a top product and lignin as a bottom product from the containing lignin and aqueous ethanol liquors.

3.2 Formic acid pulping (FAP)

The FAP technology involves dissolving hemicelluloses via hydrolyzing acetyl groups and solubilizing lignin via cleavage of lignin aryl ether linkages[35], like the combined AOF technology. Thus, FAP has a potential to become biomass agnostic. For the base case, we selected corncob for modeling FAP pretreatment due to the availability of the process data necessary for the ASPEN modeling. The sensitivity of biomass composition to the base case results was done to assess the impact of feedstock type on the economic feasibility of FAP pretreatment.

The FAP fractionation of corncobs containing 3.8% extractives, 39.2% cellulose, 37% hemicellulose, 3.2% acetyl groups and 16.5% lignin was reported by Zhang *et al.*[35] A simplified PFD to make cellulose, hemicellulose, and lignin from corncob using FAP is presented in Figure 3. The corncob is first crushed to fine powder with a particle size of about 2 mm at a biorefinery facility. The fine corncob solids are mixed with formic acid (88 wt%), water (11.8 wt%), and HCl (0.2 wt%) at a liquid-to-dry-solid ratio of 10. The resulting liquid-solid mixture is hydrolyzed in a reactor operating at a temperature of 60 ^{0}C with the mixture residence time of 150 min[35]. The hydrolysate is transferred to a vacuum evaporator to collect HCl and a fraction of formic acid/water as a vapor. This vapor is then condensed and recycled to the hydrolysis reactor. The solid-liquid mixture is then filtered to separate the solids (nearly 95 wt.% cellulose with a moisture content of 50 wt.%) from the liquid containing lignin, xylan, xylose, extractives, formic acid, and water. The liquid (filtrate) is sent to a second vacuum evaporator operating at 50 °C. The vapor stream of the second vacuum evaporator is routed to a distillation column to recover formic acid and water mixture as a top product and wastewater as a bottom stream. The recovered formic acid and water mixture is recycled to the hydrolysis reactor. Water is added to the bottom stream leaving the second vacuum column, which results in lignin precipitation. The precipitated lignin is separated from the liquid mixture containing xylan and xylose using a centrifuge. Finally, a multiple effect evaporator is used to concentrate xylan and xylose by evaporating water. The same multiple effect evaporator will also be used to dry cellulose and lignin if necessary, by using the waste heat available in the plant.

3.3 Process and Economic Modeling

The ASPEN Plus software package was used to model PFDs of both AOF and FAP technologies[37]. The physical property data for cellulose, lignin, xylan, glucose, xylose were obtained from Wooley and Putsche[38]. The cellulose, xylan, and lignin were modeled as solid compounds, and glucose and xylose/xylose oligomers were modeled as liquid compounds. It is assumed that the properties of lignin and soluble lignin are same. The remaining physical properties needed for calculation were obtained from the Aspen Plus Physical Property database. The autohydrolysis, Organosolv, and formic acid pulping reactors were modeled using a stoichiometric reactor model (RSTOIC). The reaction schemes used in the modeling are presented in the supplementary material.

The process equipment of the AOF and FAP technologies was sized using the material and energy balances obtained from the ASPEN simulation. Except where indicated, the installed cost of all process equipment was estimated using the ASPEN

Capital Cost Estimator tool. The installed equipment cost of the hydrolysis reactors was estimated from a combination of the published literature and vendor quotes and updated to the designed capacity and to 2019 dollars using the scaling factors and chemical engineering cost indices, respectively. Similarly, the operating costs were estimated using the material and energy balances from the ASPEN simulation. The assumptions made to calculate the fixed and variable operating costs are listed in Table S1. The discounted cash flow analysis method was used to compute the minimum selling price (MSP) of hemicellulose and cellulose production, following the assumptions listed in the Table S2.

4. Results

4.1 Mass and Energy Balance

ASPEN was used to simulate a process for the fractionation of 2000 dry MT per day (d) of wood using the AOF technology to produce 920 MT/d of cellulose, 120 MT/d of mixed xylose and xylan, and 470 MT/d of lignin. The AOF technology produces cellulose and lignin with a purity of greater than >95%. However, the concentration of xylose and xylan attained with the AOF technology is only 16 g/l, which requires further evaporation of water depending on the desired concentrations of xylose and xylan mixture for further upgrading. In this study, water is evaporated from a mixture of water and xylose and xylan to increase the concentration to 100 g/L just to be consistent with the FAP process. Further, the increase in cost to concentrate xylose and xylan stream beyond 100 g/l is found to be negligible, which is consistent with the findings of Gunukula *et al.*[17] The process requires 160 MW of thermal energy for the autohydrolysis process, 110 MW for the ethanol fractionation, and 109 MW for recovering ethanol using the distillation column. The specific thermal energy demand and electricity requirement of the AOF technology was assessed at 15 MJ and 0.082 kWh per kg of dry feedstock processed at the biorefinery plant, respectively. Such a high thermal energy consumption for the AOF technology is due to the requirement of a high liquid-to-dry-solid ratio for the effective wood fractionation.

Similarly, ASPEN was used to simulate the fractionation of 2000 dry MT/d of corncob via FAP technology to produce 505 MT/d of cellulose, 500 MT/d of mixed xylose and xylan, and 310 MT/d of lignin. The attained concentrations of xylose and xylan at the simulated process conditions are 40 g/l. A multiple effective evaporator is used to remove water to concentrate xylose and xylan to 100 g/l. The total thermal energy consumption for corncob fractionation by FAP is 260 MW, of which about 70 MW is necessary for concentrating xylose and xylan mixture. It was assessed that 9 MJ of thermal energy and 0.065 kWh of electricity are necessary for the effective fractionation of one kg of dry feedstock at the biorefinery plant using FAP technology. The high thermal energy which is due to the large ratio of liquids-to-dry-solids necessary for efficient fractionation of corncobs by FAP.

4.2 Economic Analysis of Suitable Technologies

The calculated total installed equipment cost, total capital investment, and annual operating cost of biomass fractionation plants for both the AOF and FAP technologies, each with a biomass processing capacity of 2000 dry MT/d are listed in Table 2. The installed equipment costs and the total capital investments for the biomass fractionation plant built around AOF technology are found to be higher when compared with the FAP technology (Table 2), which is due to the necessity of two fractionation steps with the AOF technology. The combined installed equipment cost of the autohydrolysis and Organosolv reactors corresponds to 85% of the total installed equipment cost of the wood fractionation plant (*i.e.*, the AOF plant). Similarly, the combined installed cost of the formic acid pulping reactor accounts for nearly 70% of the total installed equipment cost of the corncob fractionation plant (*i.e.*, the FAP plant). The breakdown of annual operating costs shows that the contribution of utilities to the annual operating costs of wood fractionation plant is 70%, while that for the corncob fractionation plant is 53%. Such a high utility cost is a result of the thermal energy requirements for both the hydrolysis process itself as well as for the recovery of ethanol and formic acid from the spent pulping liquor.

The annual co-product revenues generated from selling lignin at $120 per MT are $18 million and $11 million for the wood and corncob fractionation plants, respectively. The assessed MSP of cellulose as well as the xylose and xylan mixture made from wood via AOF is $0.66 per kg, and from corncob via FAP technology is $0.36 per kg. This low MSP with the FAP technology is because the AOF pretreatment requires two hydrolysis reactors as compared to the one hydrolysis reactor with the FAP technology and a high composition of cellulose as well as xylose and xylan of corncob as compared to that of wood. Importantly, the MSP of hemicellulose and cellulose obtained by AOF and FAP are both greater than the target price of $0.30 per kg, suggesting that these two technologies are not economically feasible as modeled in the base case. We next explore the sensitivity of the MSP to various process conditions to find a regime in which the production of sugars by AOF and FAP can be accomplished economically.

4.3 Sensitivity analysis

The sensitivity of MSP to the liquid-to-dry-solid ratio, economic value of lignin, and the variance of composition of cellulose, hemicellulose, and lignin in the feedstock is measured for both the AOF as well as FAP technologies (Figures 4 and 5). These figures are generated by determining the relative change in the MSP (expressed as a percentage) for a given change in the input parameter value (e.g. lignin price, liquid-to-dry-solid ratio, or biomass composition) from the base case value while keeping all other parameter values constant. As expected, the MSP decreases as the lignin price increases (Figures 4 and 5). For the base-case technology, economic viability (i.e., a MSP below the target of $0.3/kg) can be achieved for a lignin price greater than $300 per MT for the FAP technology (Figure 4). The economic value of lignin can be increased by developing technologies that can upgrade lignin to a high value product like phenolic resins[39]. In contrast, the economic viability of the AOF technology cannot be sufficiently improved by an increase in the value of lignin (Figure 5).

The decrease in the values of liquid-to-dry-solid ratio reduces the MSP of hemicellulose and cellulose polysaccharides for both the FAP and AOF technologies (Figures 4 and 5). For AOF, the liquid-to-dry-solid ratio corresponds to both the water-to-wood ratio as well as the ratio of ethanol-to-autohydrolyzed-wood. Minimum liquid-to-dry-solid ratios of 1 and 7 are necessary to make AOF and FAP economically competitive, respectively (Figures 4 and 5). This result indicates that research efforts must be directed to lower the liquid-to-dry-solid ratio for the effective conversion of biomass using FAP and AOF technologies.

Figures 4 and 5 also show that the MSP is inversely proportional to the amount of cellulose and hemicellulose in the feedstock. However, FAP and AOF are not economically competitive for production of polysaccharides for subsequent chemical catalytic upgrading even starting with a feedstock composed of 80 wt% cellulose and hemicellulose, due to the requirement of a high liquid-to-dry-solid ratio. Thus, the most important factor in obtaining low-cost polysaccharides is a small ratio of liquid to dry solids. Figure 6 is generated by determining the minimum liquid-to-solid ratio required to obtain polysaccharides at \$0.30/kg using FAP, given the amount of cellulose and hemicellulose in the feedstock. Figure 6 can be used to identify performance targets for this ratio. For example, if wood containing a total of 60 wt.% cellulose and hemicellulose is used as a feedstock for FAP to make hemicellulose and cellulose polysaccharides for chemical catalytic upgrading, the liquid-to-dry-solid ratio must be at least 5 to obtain a MSP of \$0.30/kg. The minimum water-to-wood ratio as well as ethanol-to-autohydrolyzed-wood ratio is found to be two to attain the target MSP with the fractionation of feedstock having cellulose and hemicellulose composition of 80 wt.% (on a dry basis) using the AOF technology. For a feedstock with a cellulose and hemicellulose composition of less than 60 wt.% (on a dry basis), it is found that even a liquid-to dry-solid ratio of one is not enough to make hemicellulose and cellulose polysaccharides at a target price using the AOF technology.

Figures 7 and 8 illustrate the sensitivity of the process to the price of natural gas, the feedstock cost, the cost of the hydrolysis reactor, the total project investment, the discount rate, fractionation temperature, fractionation residence time, and the total biomass processing capacity. The sensitivity was measured by calculating the change in the MSP for a +/- 33% change in the parameter of interest. The MSP of hemicellulose and cellulose production using both FAP and AOF is highly sensitive to the feedstock cost, natural gas price, and the plant capacity. A 33% decrease in the feedstock price decreases the MSP by 18% and 14% for FAP and AOF, respectively. Thus, producing hemicellulose and cellulose from inexpensive feedstocks such as food waste can significantly reduce the MSP of hemicellulose and cellulose polysaccharides. Similarly, increasing the plant capacity by 33% reduces the MSP by 11% and 12 % for FAP and AOF, respectively. However, such an increase in plant size may create logistical challenges associated with feedstock procurement. Finally, if natural gas can be obtained at $8 per MMBtu, the MSP can be reduced by 11% for FAP and by 15% for AOF.

The process parameter (biomass fractionation temperature of both AOF and FAP and the residence time of biomass particles during the biomass fractionation via AOF and FAP) values have a significant impact on the economics of biomass fractionation. A 3 to 6% change in the MSP values of hemicellulose and cellulose was found for a +/- 33% change in the process parameter values. Please note that the impact of fractionation temperature and residence time on the biomass fractionation yields have not considered while performing the sensitivity analysis due to the data unavailability.

The discount rate, total project investment, and hydrolysis reactor cost all have an insignificant impact on the MSP of hemicellulose and cellulose (Figures 7 and 8). For example, a 33% decrease in the discount rate results in only a 4% and 6% reduction in MSP for FAP and AOF, respectively. This result indicates that providing biorefinery subsidies cannot considerably reduce the MSP of hemicellulose and cellulose.

5. Conclusion

We have performed preliminary screening of both Formic Acid Pulping and Autohydroysis and Organosolv Fractionation and found both to be suitable for the production of sugars for chemical catalytic upgrading. The MSP of polysaccharides obtained from corncobs by FAP and from wood by AOF are estimated at $0.36/kg and $0.66/kg, respectively. These estimated MSPs are higher than the target price of $0.3/kg. For both technologies, the MSP is most sensitive to the ratio of liquid to dry solids, and the target MSP can be obtained using FAP with a liquid-to-solid ratio of 7 and using AOF technology with a liquid-to-solid ratio of 1.

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Figures

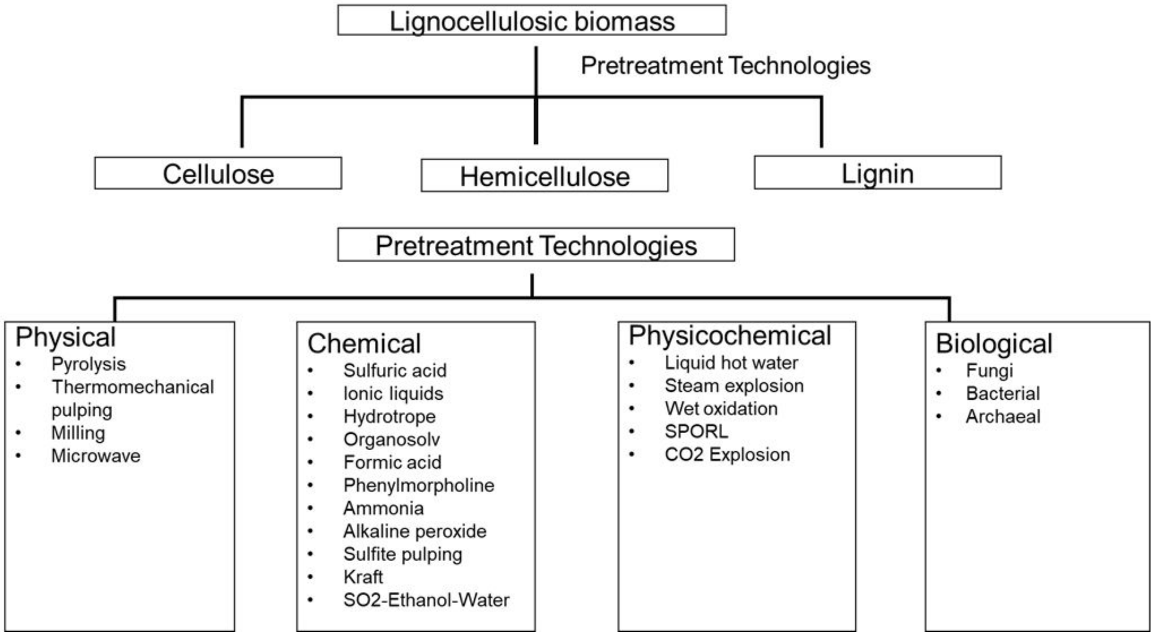

Figure 1: Biomass fractionation using various pretreatment technologies

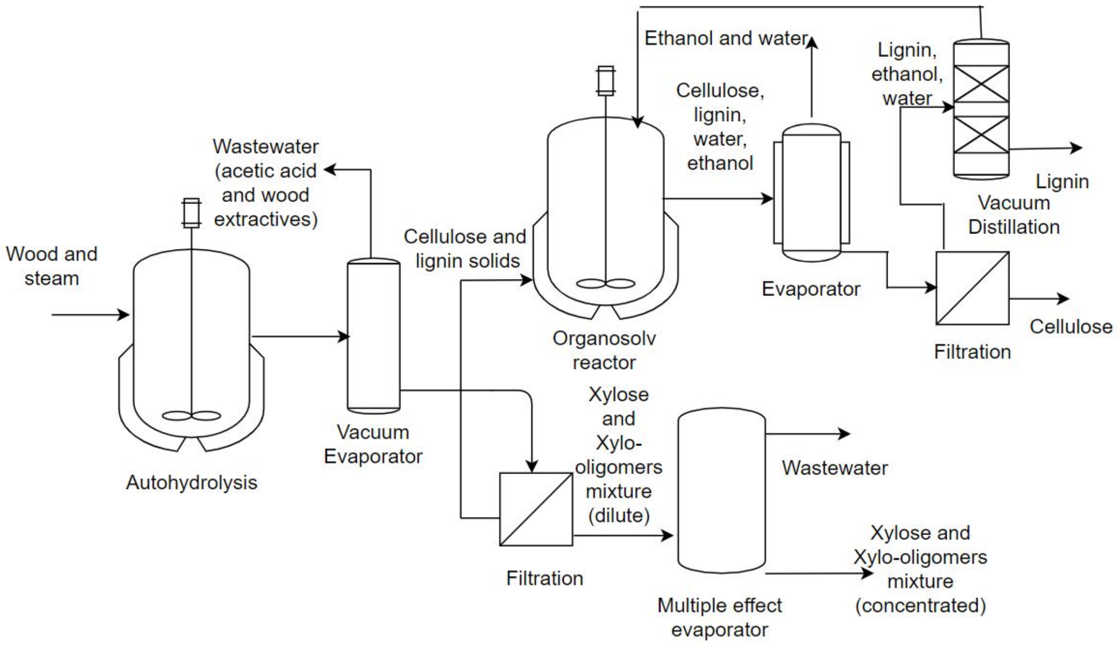

Figure 2: Process flow diagram of the wood fractionation using the combined autohydrolysis and Organosolv technology. The material balance and operating conditions are presented in the Table S6.

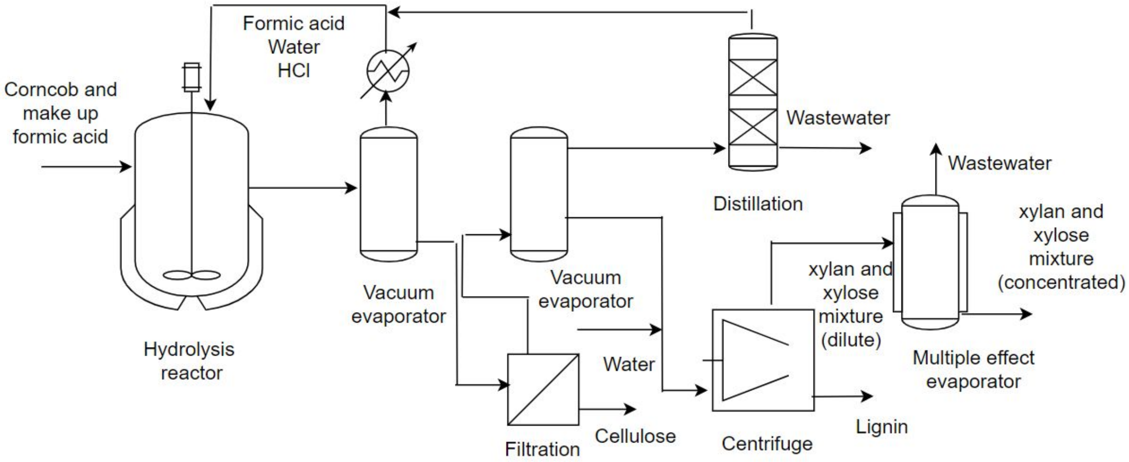

Figure 3: Process flow diagram of the corn cob fractionation using the formic acid pulping technology. The material balance and operating conditions are presented in the Table S7.

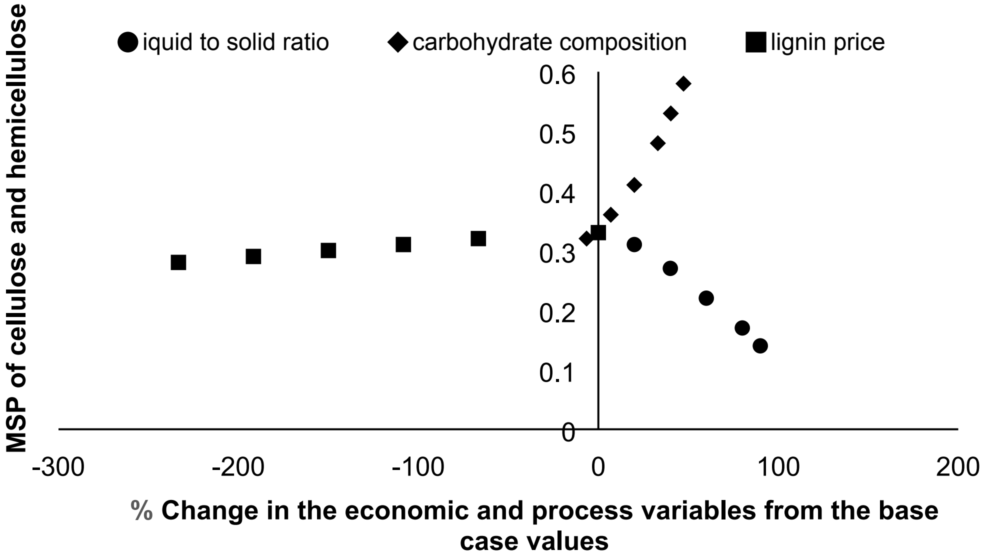

Figure 4: The influence of lignin price, liquid to solid ratio, and total composition of cellulose and hemicellulose on the MSP of sugars made from corncob using the formic acid pulping technology. The absolute values of parameters are presented in the Table S4.

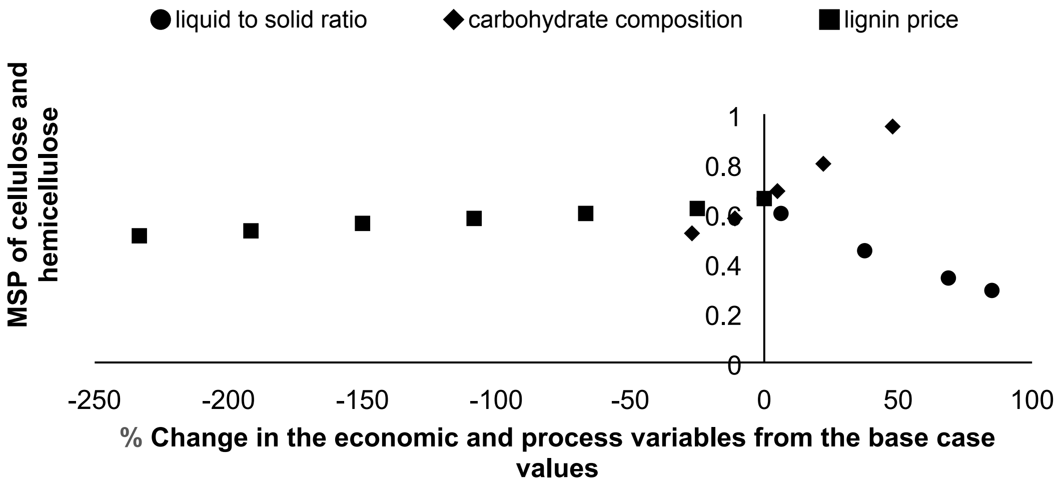

Figure 5: The influence of lignin price, liquid to solid ratio, and total composition of cellulose and hemicellulose made from wood using the combined autohydrolysis and Organosolv technology. The absolute values of parameters are presented in the Table S5.

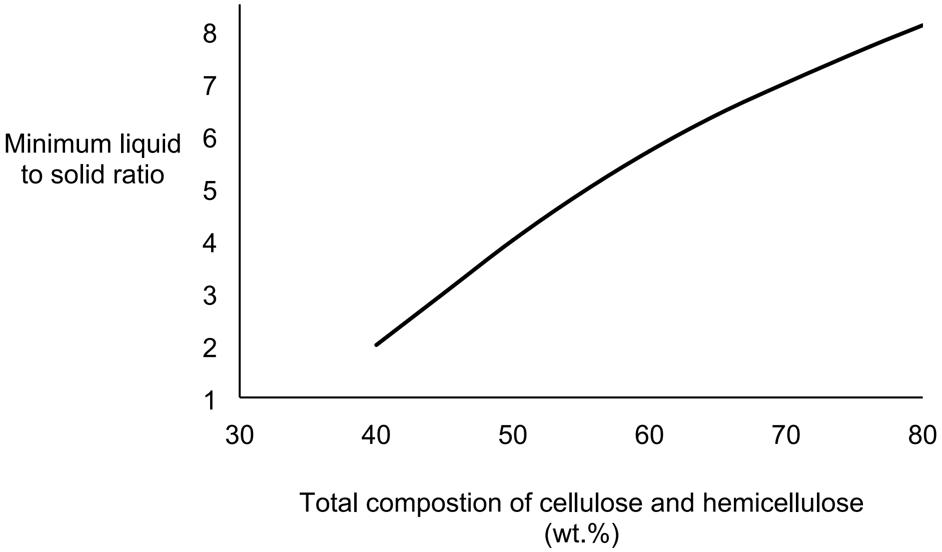

Figure 6: The minimum liquid to solid ratio required to obtain polysaccharides at $0.30/kg using FAP, given the amount of cellulose and hemicellulose in the feedstock

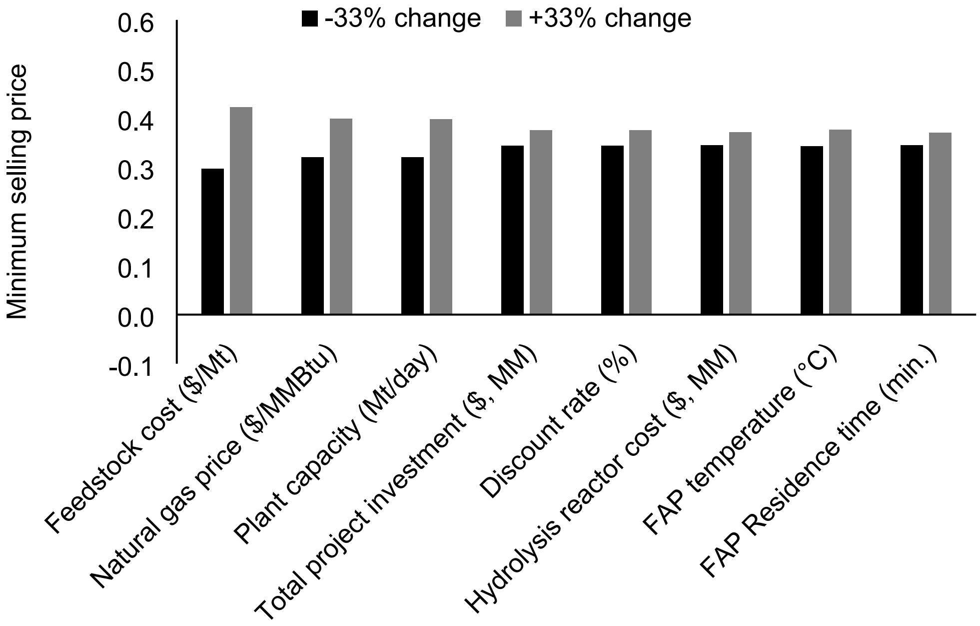

Figure 7: Sensitivity of MSP of sugars made from corncob using the formic acid pulping technology to a ±33% change in the values of economic parameters.

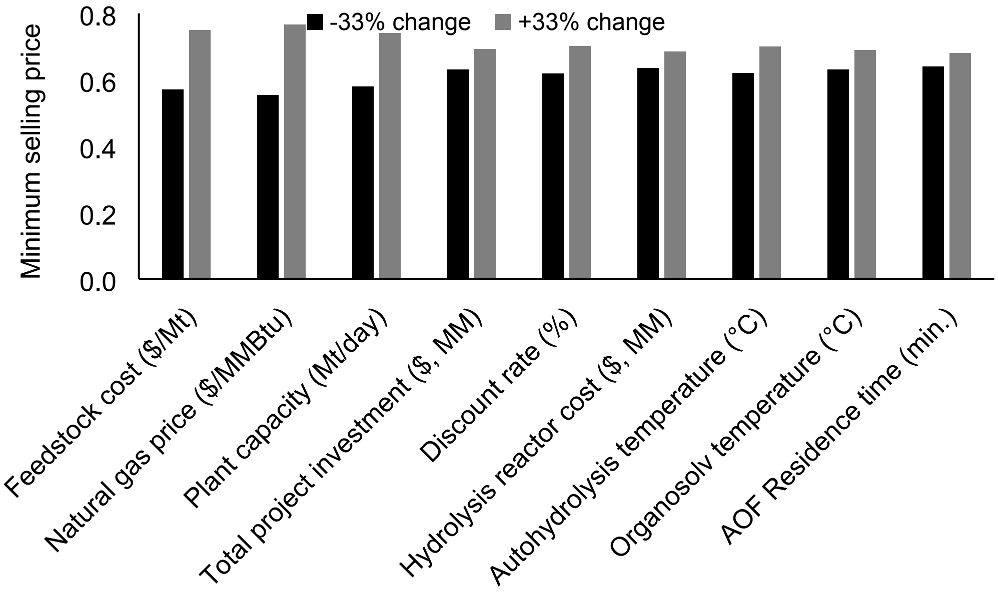

Figure 8: Sensitivity of MSP of sugars made from wood using the combined autohydrolysis and Organosolv technology to a ±33% change in the values of economic parameters.

Tables

Table 1. Screening of biomass pretreatment technologies

Physical pretreatment	**Reason for elimination**
Pyrolysis	Loss of hemicellulose and not enough to fractionate cellulose and lignin
Pulping	Can only produce pure cellulose
Milling	Not enough to fractionate hemicellulose, cellulose, and lignin
Microwave	Not enough to fractionate hemicellulose, cellulose, and lignin
Chemical pretreatment	
Sulfuric acid	Separation and purification of sulfuric acid for recycling is complex and expensive
Ionic liquids	Proven to be expensive for biomass fractionation
Hydrotrope	Incomplete fractionation of lignin, hemicellulose and cellulose
Organosolv	Incomplete fractionation of lignin, hemicellulose and cellulose
Formic acid	Incomplete fractionation of lignin, hemicellulose and cellulose
Phenylmorpholine	Safety issues
Ammonia	Incomplete fractionation of lignin, hemicellulose and cellulose
Alkaline peroxide	Complete degradation of hemicellulose
Sulfite pulping	Market risk to lignosulfonates
Kraft	Proven to be expensive for biomass fractionation
SO2-Ethanol-Water	Market risk to lignosulfonates
Physiochemical pretreatment	
Liquid hot water	Incomplete fractionation of lignin, hemicellulose and cellulose
Steam explosion	Incomplete fractionation of lignin, hemicellulose and cellulose
Wet oxidation	Incomplete fractionation of lignin, hemicellulose and cellulose
SPORL	Incomplete fractionation of lignin, hemicellulose and cellulose
CO2 Explosion	Incomplete fractionation of lignin, hemicellulose and cellulose
Biological pretreatment	
Fungi, Bacterial, Archaeal	Complete degradation of lignin

Table 2: Results of Economics of biomass fractionation technologies

	Formic acid pulping	Combined autohydrolysis and Organosolv
Total Installed equipment cost (TIC) ($ MM)	102	137
Total Capital Investment ($ MM)[a]	174	239
Annual operating costs ($ MM)	140	186
Minimum selling price ($/kg)	0.36[b]	0.66[b]

[a] Table S3 shows the factors used to assess the capital cost from the total installed cost.

[b] The minimum selling price indicates the selling price of one kg of cellulose and hemicellulose.