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Review

Liquid phase conversion of lignocellulosic biomass using biphasic systems

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ABSTRACT

Lignocellulosic biomass, such as corn stover, pulp and paper mill waste, and switchgrass, is a readily available feedstock for the production of monomeric sugars and platform chemicals that can then be transformed into valuable organic molecules. However, efficiently fractionating lignocellulosic biomass is difficult due to the recalcitrance of lignin at mild reaction conditions and the reactive sugars/platform chemicals at more severe conditions. Biphasic systems present a possible solution to creating an economically viable biomass upgrading process since sugars prefer the aqueous phase while the lignin and furans partition to the organic phase. This review focuses on recent work to fractionate biomass using biphasic reactions as well as monophasic reactions that use biphasic systems to separate products. The use of different biphasic media, heterogeneous and homogeneous catalysts, and reaction conditions are reviewed and trends in isolating the fractions found in biomass are discussed.

1. Introduction

For decades, researchers have focused on producing chemicals and fuels from renewable resources, such as lignocellulosic biomass, to replace petroleum-derived chemicals. Many research articles are devoted to the topic of biomass fractionation in order to maximize product yields and economics, but a small fraction of published processes have been commercialized. Since biomass feedstock costs can make up 60–70% of the production costs [1], efficient pretreatment of the biomass is necessary in order to compete with traditional petroleum and chemical production processes [1–5]. One goal is ensuring all fractions of the biomass are used, including the cellulose, hemicellulose, and lignin, to increase profitability. Although progress has been made in upgrading the polysaccharide sugar fractions (cellulose and hemicellulose) and their constituent monomers to fuels and valuable chemicals [6–17], improving the initial pretreatment step to obtain even higher yields could have a significant impact on biomass processing economics. Another issue is that many of the pretreatment processes that achieve high yields require costly unit operations to recover the products, which renders them cost-prohibitive. In order to be industrially successful, all fractions of the biomass will need to be utilized and the overall process costs taken into account.

Common pretreatment methods (Fig. 1) include acidic [18–20], alkaline [21], ionic liquid [22–25], hot water [26,27], ammonia fiber expansion (AFEX) [28,29], and Organosolv [30–36]. For more details on these monophasic pretreatment methods, excellent reviews have recently been published by Luterbacher et al. [17,37]. In general, pretreatments including hot water and acid hydrolysis are lower in cost than processing with a solvent, but often lead to undesirable humin formation (solid, carbonaceous by-products), which requires filtration prior to further upgrading. Organosolv uses organic solvents to separate the lignin and hemicellulose fractions from the biomass while minimally disrupting the cellulose and often times, solubilizing by-products [38]. Additionally, the selection of solvent can improve separations for product recovery. For example, the volatility of ethanol allows for easy recovery of the solvent from the cellulose after it is filtered from the lignin/hemicellulose solution; however, recovery of the hemicellulose and lignin is more difficult. The pH can be decreased in order to recover the lignin [39,40], but then the hemicellulose remains in an acidic ethanol solution. Recovery of products and solvents are necessary considerations for solvent selections in order to improve process economics. Biphasic systems are advantageous for these separations since the cellulose, hemicellulose, and resultant sugars reside in the aqueous phase while the lignin and products such as furans partitions to the organic phase in due differences in hydrophobicity (Fig. 2). This results in easier separations, less degradation of products, and, potentially, concentration of the products.

There are two main ways that biphasic systems have been used for biomass fractionation. The first is using a biphasic reaction system that contains a partially or fully immiscible aqueous and organic phase (Fig. 3, top pathway). As the biomass reacts, the cellulose remains in the aqueous layer while the furans and lignin partition to the organic

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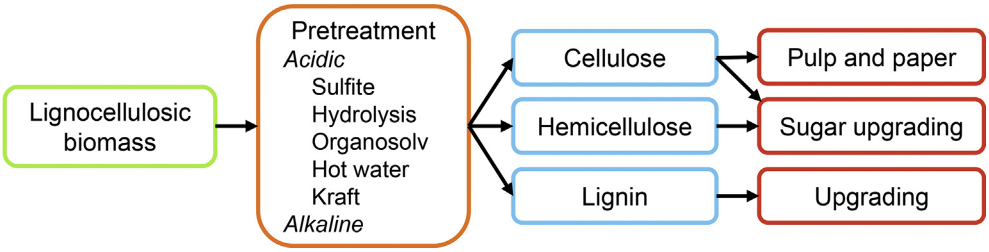

Fig. 1. Potential processing options for lignocellulosic biomass.

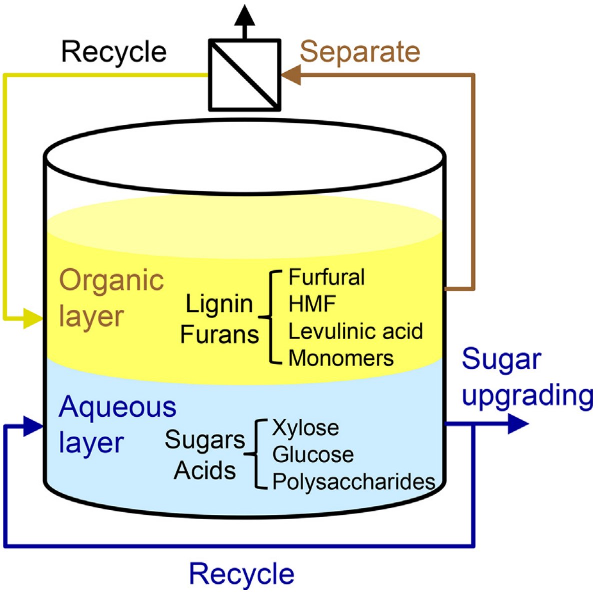

Fig. 2. Preferred partitioning of chemicals typically found in biomass upgrading. Adapted from Ref. [17].

phase. This allows the cellulose to then be enzymatically treated since inhibitors, such as furfural, have a much lower concentration in the aqueous phase than if a monophasic system was used [41,42]. Alternatively, the reaction could be carried out until monomeric sugars are produced and then recovered and upgraded.

The second way biphasic systems have been used is for the reaction to take place in a monophasic solvent and then, after reaction, a modifier is added to create a biphasic system that separates products using liquid-liquid extraction (Fig. 3, middle and bottom pathways). Even if monophasic systems are used, processes can benefit from biphasic systems for product recovery. Therefore, biphasic separations open the door to multiple processing pathways with lower energy requirements needed for separations versus monophasic systems based on solvent properties.

Solvent selection is an important consideration for biphasic systems. Product yield and ease of separation need to be balanced with solvent properties including flammability, viscosity, volatility, and toxicity [43]. Additionally, research has focused on decreasing the amount of solvent used in order to reduce costs and decrease environmental impacts. Jessop et al. [44] surveyed many solvents to determine the "green-ness" of a solvent using environmental risks, health risks, and manufacturing energy as evaluation parameters. They identified 2-methyltetrahydrofuran (MTHF), gamma-valerolactone (GVL), acetone, and poly(ethylene glycol) (PEG) as some of the aprotic green solvents that could replace traditional solvents, such as toluene. For green protic solvents, water and many alcohols including iso-propanol, butanol, ethanol, and propanol were identified [44].

Other properties to consider for solvent selection were identified by Kamlet and Taft and are the polarity (π^*) [45], basicity (β; hydrogen-bond accepting ability) [46], and acidity (α; hydrogen-bond donating ability) [47] of the solvent. Previous literature has hypothesized that the basicity parameter has the most significant effect on cellulose solubilization and as basicity increased, so did cellulose solubility [48,49], which could improve fractionation. It is important to note that the calculation for basicity depends on the polarity value and therefore, basicity is not independent from polarity [44]. Doherty et al. attributed this to the basicity being able to disrupt the cellulose crystallinity, but no direct studies have proven this [49] and no known model exists to aid in solvent selection for biomass fractionation.

Many reviews have focused on monophasic lignocellulosic pretreatment with brief discussions of biphasic systems, but this review focuses specifically on the use of biphasic systems to recover the different fractions of lignocellulosic biomass. As mentioned, in recent literature biphasic systems have been used in two main ways: 1) using a biphasic system to perform the fractionation reaction (Fig. 3, top pathway) and 2) completing the fractionation reaction using a monophasic system and then creating a biphasic system through solvent or modifier addition for chemical separation (Fig. 3, middle and bottom pathways). This review focuses on recent research that isolated biomass fractions using either biphasic system. The use of different biphasic solvents, heterogeneous and homogeneous catalysts, and reaction conditions are explored and observed trends are discussed.

2. Biphasic reactions

Although less researched than monophasic reactions, biphasic reactions offer the opportunity to increase product yields due to a decrease in side reactions since the fractionated lignin and furans partition to the organic phase. Homogenous and heterogenous catalysts have been used to catalyze biomass fractionation in biphasic reaction systems and both have advantages. Homogenous catalysts are used in biphasic reactions due to their lower cost, miscibility, and high activity compared to heterogenous catalysts. However, heterogeneous catalysts can easily be recovered, are tunable, and can eliminate effects on downstream reactions. Both catalyst types benefit from biphasic reactions since for heterogenous reactions, partioning of products to the organic phase reduces catalyst deactivation [74] and for both, less product degradation reactions occur. Below we review literature regarding both homogeneous and heterogeneous catalysts.

Oxalic acid has been used as a homogeneous catalyst since, unlike hydrochloric and sulfuric acid, it can be recovered by crystallization and reused. vom Stein et al. [50] used 0.1 M oxalic acid in a MTHF:water (1:1; 10 mL) biphasic reaction system at mild temperatures (85–150 °C) to selectively catalyze hemicellulose into water-soluble sugar monomers. After reaction (beech wood 0.5–0.8 mm; 50–100 g/L loading; 6 h; 10–20 bar (CO_2)), the organic phase was decanted and the MTHF was evaporated to recover the lignin. The aqueous phase was filtered to recover the cellulose pulp and the permeate contained the glucose and xylose fractions. The cellulose remained crystalline and insoluble due to the mild reaction conditions allowing it to be further processed using enzymes or thermochemical treatment. The highest xylose recovery occurred at 145 °C at 10 bar and resulted in 18.0 wt% xylose (based on total biomass loading (TBL);

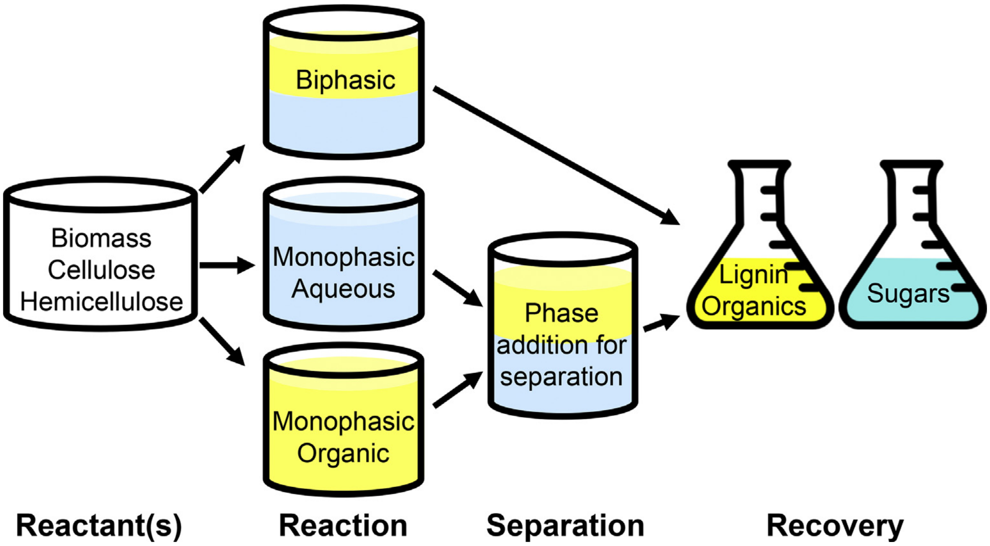

Fig. 3. Potential biphasic systems processing routes for biomass fractionation. The top route is biphasic reactions followed by separation while the middle and bottom routes are monophasic reactions with addition of a phase modifier to create a biphasic system.

Table 1
Results of MTHF/water (1:1) biphasic reaction systems using 100 g/L beech wood, 0.1 M oxalic acid as the catalyst, and 6 h reaction time.

Volume (mL)	Time (h)	Temp. (˚C)	Glucose (wt%)	Xylose (wt%)	Lignin (wt%)	Ref.
10	6	125	2.2	15.4	16	[50]
10	6	145	5.8	18	13.5	[50]
40	6	125	0.5	19	13	[51]
40	3	140	1.2	17	14	[51]
1500	3	140	4.5	22	12	[51]
1500[a]	3	140	6	60	30	[51]

[a] Four cycles as shown in Fig. 4.

Table 1). Since the focus was on recovering cellulose, lower temperatures were desired since at 145 °C, over 5 wt% glucose was detected (Table 1), which indicated that the cellulose fraction was beginning to undergo hydrolysis. The lignin recovered ranged from 4.0 wt% at 85 °C to 16.0 wt% (20 bar) at 125 °C [50].

Grande et al. [51] extended the MTHF/water research to higher biomass loadings using beech wood, mate tea, reed, and spruce wood and scaled-up the reaction to a 3 L reactor. A biomass concentration of 100–150 g/L was found to be the limit for efficient agitation of the mixture; however, by operating in repetitive batch mode, 400 g/L biomass could be processed. By adding 100 g/L boluses and filtering the solids to remove the cellulose, at least 400 g/L biomass could be processed in four cycles (Fig. 4) thus, increasing the concentration of xylose and potentially reducing capital costs for an industrial process. For 1.5 L total volume reactions, the conditions to minimize cellulose degradation, yet optimize xylose recovery, were determined to be 140 °C and 3 h, but for the 40 mL reactions, 125 °C and 6 h resulted in the lowest degradation (Table 1). The yields in the 3 L reactor were similar to the results vom Stein et al. [50] achieved in 10 mL glass reactors with xylose yields for a single reaction of 22 wt%, glucose yields of 4.5 wt%, and lignin yields of 12 wt% (all yields based on TBL). When the bolus method was used, the glucose yield remained low (6 wt%), the xylose yield was 60 wt%, and the lignin recovered was 30 wt% [51]. This work shows that higher amounts of biomass can be processed while achieving similar yields to low biomass concentration reactions. Shorter reaction times as well as low temperatures, typically favor xylose production, but high temperatures can quickly extract the xylose and must be balanced with dehydration reactions that lead to furfural and glucose production from xylose and cellulose, respectively.

Researchers have also investigated using poly-ethylene glycol (PEG) as the extracting phase of a biphasic, alkaline system with the goal of recovering a lignin-free cellulose. Preliminary work focused on determining partition coefficients using the concentration of lignin in the equation:

$$D = \frac{C_{PEG-rich\ phase}}{C_{salt-rich\ phase}}$$

for multiple lignins in PEG/water biphasic systems with various salts as modifiers. Since the research was focused on Kraft pulping, the salts were chosen according to those found in the Kraft pulping process and included sodium sulfide (Na_2S), sodium hydroxide (NaOH), and sodium carbonate (Na_2CO_3). It was found that the salt had a significant effect on the partition coefficient of lignin [52,53]. Fig. 5 shows that 3.8 M NaOH resulted in the lowest partition coefficient (less than 10) and an equivalent concentration of potassium carbonate (K_2CO_3) was orders of magnitude higher [52]. However, lignin in the system with the salt concentration similar to the Kraft process (3.5 M NaOH, 0.8 M Na_2S, and 0.4 M Na_2CO_3; labeled "Mix") had partition coefficients more similar to NaOH than K_2CO_3. The authors attributed the low partition coefficient to the OH^- group having a lower free energy of hydration than S^- and $CO_3{}^-$ groups [53]. The difference in partition coefficient of the lignins (Indulin AT and Reax 85A) was attributed to the degree of sulfonation. Reax 85A had a lower partition coefficients compared to

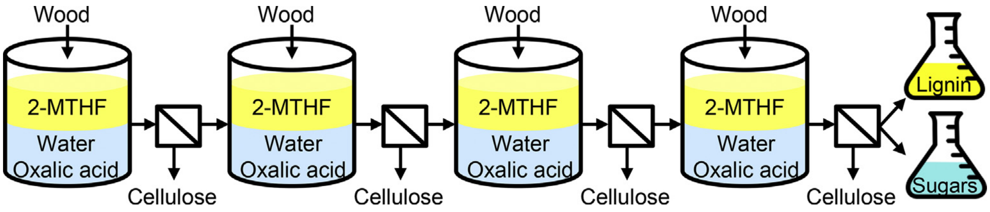

Fig. 4. Repetitive-batch mode for fractionation to increase biomass-to-solvent ratio. After four additions of 100 g/L wood boluses, the lignin was recovered in the organic layer while the xylose and glucose were recovered in the aqueous phase (Adapted from Ref. [51].).

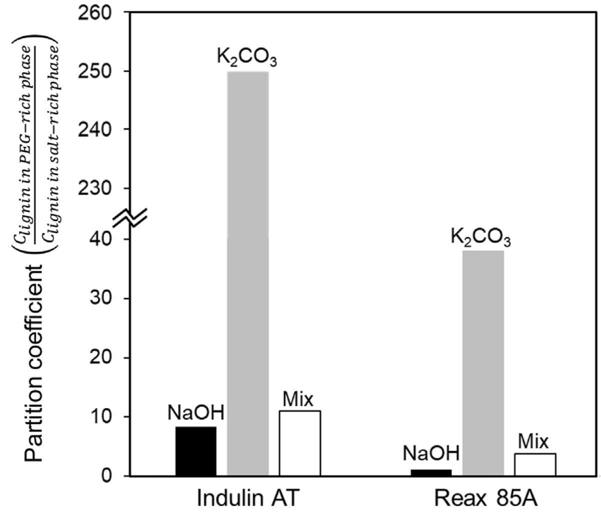

Fig. 5. Partition coefficients for Indulin AT and Reax 85A lignins in PEG with 3.8 M NaOH [52], 3.8 M K_2CO_3 [52], and a salt mixture of 3.5 M NaOH, 0.8 M Na_2S, and 0.4 M Na_2CO_3 [53]. Note the break in scale of the y-axis.

the Indulin AT, but is sulfonated, which results in lower hydrophobicity and less preference for the PEG layer [52]. The partition coefficient of lignin was found to not be significantly different at various temperatures [52], but the formation of the biphasic system was enhanced at higher temperatures indicating that less salt could potentially be used to get the same reaction results at higher temperatures [53].

Guo et al. then used the PEG in combination with the same salt mixture to remove the lignin from hardwood. The biphasic, polymer-based pulping exhibited faster delignification and 30–60% lower residual lignin content of pulps compared to reactions without PEG present. The hardwood chips in the biphasic PEG/salt system had a lower kappa number, which is a measure of lignin removal in pulps, and lower consumption of alkali than, polyethyleneimine, another polymer tested, in a biphasic system. Temperature and duration played key roles in removing the lignin as increasing the temperature (130 °C–160 °C) and reaction time (20–90 min) resulted in higher lignin removal from wood; however, as previously seen in other biphasic reactions, at high lignin removal conditions, the decrease in hemicellulose and cellulose yields was significant [53].

The researchers then evaluated the effects of lithium and magnesium sulfate as metal catalysts and found that, similar to the previous Kraft salt mixture, the presence of the salt made the PEG/aqueous solution biphasic. A factorial design experiment showed that time and temperature had a significant effect on pulp yield and kappa number, but with opposite trends. Lower temperatures and shorter times led to higher pulp yields and lower kappa numbers, while more severe reaction conditions (high temperature and long reaction times) led to lower pulp yields and higher kappa numbers. The trend in kappa number was unexpected and the authors attributed the results to condensation reactions dominating under acidic conditions. They hypothesized that the lignin underwent intermolecular condensation reactions with various monomeric phenols, and then precipitated on the pulp resulting in a higher kappa number. In order to evaluate this hypothesis, the effect of pH was studied using lithium sulfate. At the highest pH values (initial pH 13 and 14), the kappa number decreased with extent of reaction, but at the lowest initial pH values (initial pH 11 and 12), the kappa number actually increased with extent of reaction. In every case, the pH fell by about 2 units during reaction regardless of the initial pH. The decreasing kappa number with extent of reaction at high pH indicated greater delignification and reduced recondensation that occur at and under a pH of 9–10. Although PEG can prevent carbohydrate degradation and lignin condensation at high pH, unlike some monophasic Organosolv systems, it does not have this ability under acidic conditions due to lignin solubility and system pH [54].

Luterbacher et al. [55] used biphasic CO_2–H_2O mixtures with high-solid loadings (up to 40 wt% switchgrass) and high pressures (200 bar) to convert switchgrass and hardwood into sugar products. They used a two-temperature stage pretreatment method that consisted of a high temperature stage at 210 °C (16 min for hardwood and 1 min for switchgrass), followed by a low-temperature stage at 160 °C for 1 h. The two-stage process allowed for higher yields since the hemicellulose was extracted in the first stage, and the cellulose in the second, higher temperature stage. The solids were then enzymatically hydrolyzed resulting in total molar sugar yields of 65% and 55% for wood and switchgrass, respectively. The sugar yields were high despite the absence of traditional catalysts, the use of large biomass particles (0.95 cm), and high solid content (40 wt%). In further research [56], they found that the CO_2 acted as an acid catalyst and co-solvent, which allowed for high solids (up to 30 wt%) to be processed in a subsequent enzymatic treatment step resulting in high sugar yields.

By using recoverable, homogeneous catalysts like oxalic acid, using a bolus process to increase concentrations and reduce fresh solvent usage, and using environmentally friendly solvents, this research steps closer to allowing the efficient processing of biomass on an industrial scale. Homogenous catalysts are typically less expensive than heterogenous catalysts, but catalysts such as hydrochloric and sulfuric acid cannot usually be recovered, which gives heterogeneous catalysts an advantage. Although heterogeneous catalysts have been used to produce platform chemicals, such as furans, in biphasic systems [57–60], the use of heterogeneous catalysts in biphasic reactions to produce cellulose and monomeric sugars is limited. Sakdaronnarong et al. [61] fractionated and hydrolyzed sugarcane bagasse using carbon, polymer, and metal-based catalysts and solvents including ethylene glycol, xylene, and nitrobenzene. The most effective catalysts were: 1) a carbon-based catalyst (c-SO_3H) prepared from the pyrolysis of 100 mesh sugarcane bagasse, followed by sulfonation in concentrated sulfuric acid and 2) a nano-magnetic $SO_4^{2-}/TiO_2/Fe_3O_4$-based catalyst. The monomeric sugars were quantified as total reducing sugars and the highest yield (97.4%) was achieved when nitrobenzene was used as solvent in the presence of c-SO_3H at 140 °C for 4 h. Although the total reducing sugar yield was high with heterogeneous catalysts, the glucose (3.5%) and xylose (7.5%) yields were less than reported with homogeneous catalysts. The authors hypothesize that nitrobenzene resulted in higher yields than ethylene glycol and xylene due to the synergistic effects of lignin solubilization and the enhancement of the surface area accessible for the catalyst to hydrolyze the cellulose. Both catalysts saw that longer reaction times (8–12 h) and higher temperatures (180 °C versus 140 °C) resulted in more glucose, but lower xylose yields. The catalysts that led to higher yields were hypothesized to have the highest catalytic activity due to appropriate pore volume, surface area, and strong acidity [61], but the heterogeneous catalyst systems may be mass transfer limited.

3. Biphasic separations of monophasic reactions

Another way to use biphasic systems is through the middle and bottom pathways shown in Fig. 3, which use a monophasic solvent for the reaction and then require the addition of a phase modifier to create a biphasic system. A monophasic reaction first pretreats the biomass, followed by filtration to recover the solids (typically cellulose). A phase modifier such as a salt or additional solvent is then added to the permeate to create a biphasic system, which is then separated, and the products recovered. Using biphasic systems to separate chemicals after the monophasic reaction is advantageous for heat-sensitive and low concentration products. For example, the extracting solvent could have a lower boiling point than the original solvent, which requires less energy and may allow products to achieve higher purity. The following section discusses monophasic reaction systems that used liquid-liquid extractions as a separation step to recover the products.

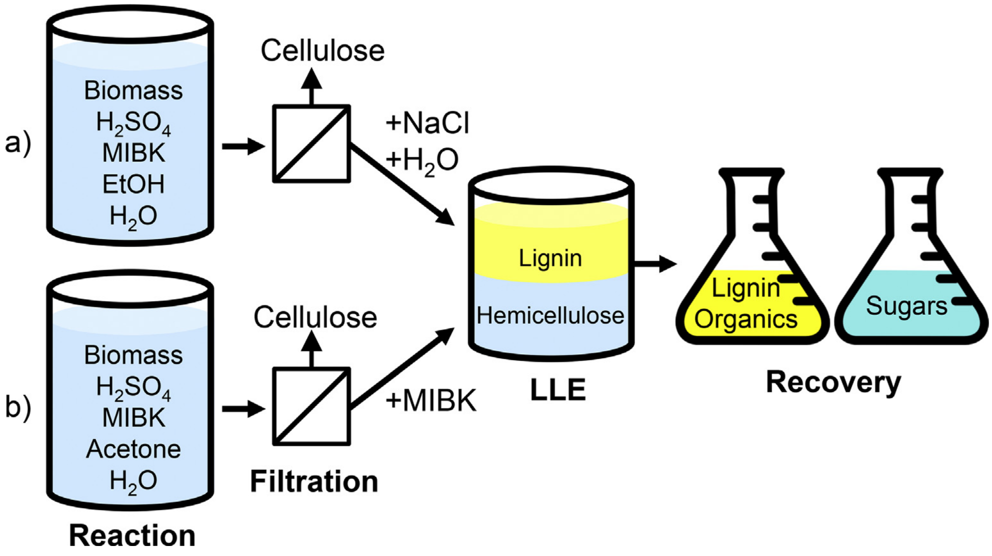

Fig. 6. Schematic of two solvent variations of the Clean Fractionation process where process a) uses ethanol and requires NaCl and water as a phase modifier and process b) uses acetone and only requires additional MIBK as a modifier.

Table 2

Yields of monophasic reactions followed by liquid-liquid extraction to recover products. All reactions also include water as the solvent.

Solvents	Time (min.)	Temp. (°C)	Catalyst (wt%)	Catalyst (M)	Solvent (wt%)	Cellulose/glucose/glucan yield (%)	Xylose/Xylan yield (%)	Lignin yield (%)	CEF[a] mass yield (wt%)	HEF[a] mass yield (wt%)	LEF[a] mass yield (wt%)	Ref.
MIBK/ethanol	60	140	–	0.05	44/32	64	18	18	–	–	–	[62]
MIBK/ethanol	60	140	–	0.1	44/32	53	24	23	–	–	–	[62]
MIBK/ethanol	50	140	0.57	–	25/35	89.3	62.6	93.1	–	–	–	[65]
MIBK/ethanol	40	150	0.39	–	34/35	93.9	45	86.4	–	–	–	[65]
EtAc/ethanol	20	150	0.31	–	32.5/22.5	92	55	58	–	–	–	[64]
EtAc/ethanol	20	140	0.46	–	50/10	70.6	49.5	72.7	–	–	–	[64]
EtAc/ethanol	20	140	0.46	–	15/10	71	67.9	15.2	–	–	–	[64]
EtAc/ethanol	20	140	0.46	–	36.7/25	85	44	59	–	–	–	[64]
MIBK/acetone	40	120	–	0.025	11/44	–	–	–	71.1	23.6	6.4	[63]
MIBK/ethanol	40	120	–	0.025	16/34	–	–	–	77.4	12.6	7.2	[63]
MIBK/acetone	40	140	–	0.025	11/44	–	–	–	54.5	10.7	39.0	[63]
MIBK/ethanol	40	140	–	0.025	16/34	–	–	–	66.5	8.6	24.2	[63]

[a] Cellulose (CEF), hemicellulose (HEF), and lignin (LEF)-enriched fractions.

The National Renewable Energy Laboratory (NREL) developed a method first patented in the late 1990's [62] named “Clean Fractionation” that was further explored more recently [32,63,64]. The Clean Fractionation process sought to provide a more energy efficient process that also produces valuable co-products from biomass. The method uses a monophasic solvent that consists of methyl isobutyl ketone (MIBK), water, and ethanol (Fig. 6a) or acetone (Fig. 6b) along with a homogeneous catalyst (typically sulfuric acid) to remove the hemicellulose and lignin fractions while, ideally, leaving the cellulose unreacted. After reaction, the cellulose and other solids that form during reaction are filtered and a modifier (in the case of the ethanol process, water and NaCl), is added to the permeate in order to create a biphasic system. The hemicellulose is recovered in the aqueous layer and lignin partitions to the organic layer. The original patent used poplar chips at 140 °C and, after approximately 1 h (0.05 M sulfuric acid; 8:11:6 ethanol:MIBK:water), the cellulose fiber (64%; TBL) was filtered and water was added to the permeate in a 1.3:1 ratio to induce phase separation of the organic layer. The lignin (18% yield; TBL) was recovered from the MIBK phase and the sugar monomers (18% yield; TBL) resulting from the hemicellulose were recovered from the ethanol/water layer (Table 2). Increasing the sulfuric acid to 0.1 M increased the lignin and hemicellulose fractions, but decreased the cellulose yield to 53% (Table 2). The patent also reports data for Aspen and sugar cane bagasse resulting in similar cellulose recoveries [62].

In more recent research, the solvents and reaction conditions have been varied to further increase yields and explore the industrial viability of the method. Brudecki et al. [65] explored a range of MIBK and sulfuric acid concentrations ranging from 7 to 43 wt% MIBK and 0.21–0.93 wt% sulfuric acid. Their goal was to develop a model that could predict the highest glucose yields from the enzymatic digestion of the pulp resulting from the Clean Fractionation process. They conducted these reactions over a range of temperatures (110–160 °C) and times (10–50 min) to improve the cellulose pulp yield and, as with previous research wanting to isolate cellulose, desired high glucan content in combination with low lignin and xylan content. The selected ethanol concentrations (30–35 wt%) were determined using a phase diagram so that the reaction was monophasic, and the resulting products were pulps rich in 78–94% glucan after removing 75–93% lignin and 83–100% xylan. They found that the xylose and lignin partitioning was determined by the MIBK content in the solvent mixture and that the more MIBK present, the better the separation into the aqueous and organic phases.

Through central composite design (CCD) experimental design, a series of 30 trials were conducted, varying time, temperature, sulfuric acid, and MIBK content. The highest pulp yield resulted from the lowest severity reaction conditions, which are based on acid concentration, time, and temperature [66], but, as expected, also led to the highest xylan and lignin remaining in the pulp (Table 2). The combination of the different factors, for example low temperature and long reaction times or high temperature and short reaction times, could result in similar yields, but temperature and catalyst amount had the largest impact on glucose yield. Higher acid loading was found to have a greater impact on fractionation efficiency than temperature [65], which was similar to the results Yang and Wyman [67] found for xylan and lignin removal in water. The higher the MIBK content, the more lignin in the organic layer and xylose in the aqueous layer. Time had little effect, but was only evaluated from 10 to 50 min [65].

Another study by the same group explored modifying the clean fractionation method using ethyl acetate instead of MIBK to fractionate switchgrass in order to maximize the glucose yield from enzymatic hydrolysis [64]. Ethyl acetate was chosen because it can be produced from biomass and has lower toxicity than MIBK. Using a similar method as in their previous study, they were able to achieve 96% glucose yield at 150 °C while the highest lignin yield, 72.7%, required a higher sulfuric acid concentration and higher ethyl acetate content (Table 2). The highest xylose yields (67.9%) were obtained at 140 °C, with 0.46 wt% sulfuric acid, and low amounts of ethyl acetate and ethanol (15 and 10 wt%, respectively). Similar to the previously mentioned research, the model found that temperature and catalyst concentration were the most important factors for high glucose yields. Optimization of all reaction parameters for lignin removal and high glucose yields from enzymatic treatment led to reaction parameters of 140 °C with 0.46 wt% sulfuric acid, 36.7 wt% ethyl acetate, and 25 wt% ethanol. The resulting yields were 44% xylose, 59% lignin, and 85% glucose. These results are similar to what were achieved with MIBK systems (Table 2, row 4) and make ethyl acetate a promising alternative solvent for the Clean Fractionation process.

In another adaptation of the original Clean Fractionation patent, instead of replacing the MIBK solvent, Katahira et al. [63] studied acetone as an alternative solvent for the ethanol using corn stover as the biomass (Fig. 6b). Acetone has a lower boiling point, did not require adding NaCl to create a biphasic system, and reduced the amount of MIBK required to extract the lignin. For both the ethanol and acetone systems, increasing the reaction severity (0.025–0.1 M sulfuric acid and 120 °C–140 °C) led to decreased recovery of the total hemicelluloses (e.g., xylose, galactose, and arabinose) and cellulose (i.e., glucose) since the monomeric sugars proceeded to dehydrate to other products such as furfural (Table 2). On the other hand, the total lignin recovered increase with severity and had the highest recovery (22 wt%) at 140 °C and 0.1 M sulfuric acid. Since there was only 15 wt% lignin in the corn stover, the increase was attributed to the formation of pseudolignin, which is a combination of lignin and carbohydrate degradation products. The sulfuric acid loading was found to have a larger effect on the fractionation efficiency than the 20° temperature increase. Comparing the acetone and ethanol solvents, the amount of cellulose fraction recovered were similar, but ethanol led to a higher recovery of the lignin fraction while the acetone system lead to a higher amount of the hemicellulose fraction and did not require the use of a modifier to create the biphasic system for product recovery [63].

Most recently, Zhang et al. [68] explored the use of alcohols in place of the organic solvents in the clean fractionation process. They studied ethanol, iso-propanol, n-propanol, 2-butanol, and n-butanol as potential solvents and confirmed previous research [69] that the separation of the alcohol and water phase increased as the alcohol chain lengthened and the partition coefficient of the monomeric sugars decreased, which is desired (Table 3). The furans had low partition coefficients in ethanol that, at minimum, doubled with longer chain alcohols. Additionally, the butanols have low solubility in water and create biphasic systems easily, which means in order to form a monophasic system, large amounts of water would be required. Therefore, n-propanol was used as the alcohol for further study due to the formation of a biphasic solution with ammonium sulfate ($(NH_4)_2SO_4$) which allows for efficient recovery of the n-propanol solvent [68].

Table 3
Partition coefficients (solvent phase concentration/aqueous phase concentration) for various components in a 20 wt% alcohol/saturated $(NH_4)_2SO_4$ solvent [68].

Solvent	Alcohol	Glucose	Xylose	Arabinose	HMF	Furfural
Ethanol	6.3	7.9	10.8	0.59	14.7	21.6
iso-Propanol	38.4	0.9	2.4	0.08	44.2	79.5
n-Propanol	76.6	0.4	1.1	0.04	45.4	101.5
2-Butanol	114	0.2	0.4	0.02	38.5	88.4
n-Butanol	475	0.1	0.3	0.01	35.7	95.5

Using n-propanol and water in an approximately 1.5:1 ratio and 0.1 M sulfuric acid as the catalyst, sugarcane bagasse was pretreated at 140 °C for 1.5 h in a monophasic system. The mixture was filtered to remove the cellulose and then water was added to precipitate the high molecular weight lignin (Fig. 7). The permeate became biphasic after $(NH_4)_2SO_4$ was added and the n-propanol layer contained most of the sugar dehydration products such as HMF and furfural, as well as low-molecular weight lignins, while the aqueous phase was rich in salt and soluble sugars. To increase efficiency of the process and increase product concentrations both phases were reused after reaction. After five recycles, the xylose concentration increased in the aqueous phase from 3.2 g/kg to 13.5 g/kg while the furfural concentration in the n-propanol increased from 2.4 g/kg to 15.1 g/kg. The aqueous phase needed to be distilled prior to recycling, but the organic phase was recycled with no treatment [68]. The higher concentration of products due to the recycle would likely lead to better overall process economics.

Recent literature has also explored using CO_2 as a modifier to induce biphasic separation. Luterbacher et al. [70] achieved high yields of carbohydrates (70–90%) from lignocellulosic biomass (corn stover, loblolly pine, or maple wood) using a solvent mixture of gamma-valerolactone (GVL), water, and dilute acid (5 mM sulfuric acid) in a flow-through reactor. The solvent flowed over the biomass, extracting the carbohydrates, and then CO_2 or NaCl was added to the effluent in order to form a biphasic system. Furan yields of up to 65%, xylose yields up to 90%, and glucose yields up to 80% were achieved due to GVL solubilizing the biomass [71], disrupting the crystallinity of the cellulose, and preventing the lignin from precipitating on the biomass surface [70]. Exploration of alternative phase modifiers such as CO_2 and two-step processing methods are worthy of research in other systems with different types of biomass due to the high sugar yields achieved.

By modifying the Clean Fractionation method and exploring different solvents and phase modifiers, several trends emerged. It can be generalized that more severe reaction conditions favor higher sugar monomer and lignin recovery, but further dehydration and condensation reactions may occur. Lower severity reaction conditions favor cellulose recovery, but significant amounts of hemicellulose and lignin could remain in the cellulose and inhibit the ability of enzymes to produce glucose. Other factors such as the renewability, toxicity, and recyclability of the solvent must be considered and ethyl acetate, n-propanol, and GVL may be better alternatives to MIBK in this regard.

4. Solvent discussion

As previously mentioned, the basicity parameter has been hypothesized to have a significant effect on cellulose solubilization [48,49], which in turn, lead to higher glucose recoveries. Table 4 lists the solvents used for reactions in the review and includes the Kamlet-Taft parameters of polarity (π) and basicity (β) for pure solvents. It should be noted that the addition of acids, modifiers, and other solvents affect the polarity, acidity, and basicity values, and therefore, we can only attempt to elucidate trends from the data shown in Table 4.

Sugar monomers are polar molecules and therefore, prefer to be in the aqueous phase due to high polarity of water (Table 4). As the difference in the polarity of the aqueous and organic phase increases, the sugar partition coefficient decreases. The opposite is true for lignin and

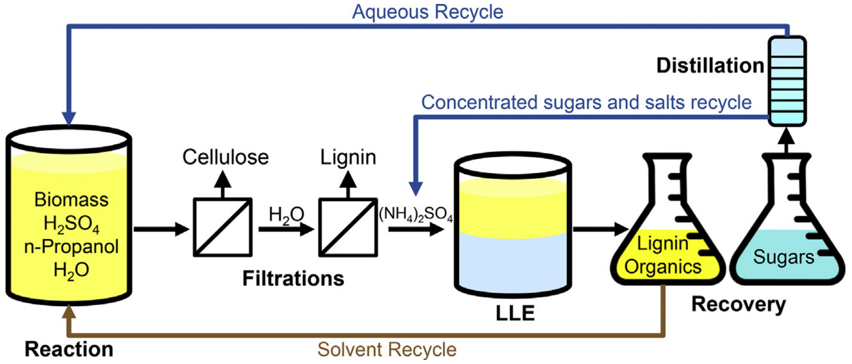

Fig. 7. Schematic of fractionation process used by Zhang et al. [68] including solvent recycle streams.

Table 4
Various properties of the solvents reviewed in this article including polarity and basicity [44,72,73].

Solvent	Boiling Point (°C)	Solubility (mg/mL)	Azeotrope	Modifier needed	π^{*a}	β^{a}
Acetone	56	1000	N	Y	0.71	0.48
Ethanol	78.4	1000	Y	Y	0.51	0.75
MTHF	80.2	15	Y	N	0.53	0.53
iso-Propanol	82.6	1000	Y	Y	0.48	0.84
n-Propanol	97	1000	N	Y	0.52	0.9
2-Butanol	99	181	N	N	0.4	0.84
Water	100	–	–	–	1.09	0.14
MIBK	116	19	Y	N	0.63^{b}	0.52^{b}
n-Butanol	117.7	68	Y	N	0.47^{c}	0.84
GVL	207	> 100	N	Y	0.83	0.6

[a] From Ref. [44] unless noted.
[b] From Ref. [72].
[c] From Ref. [73].

other organic compounds; as the difference is the polarity of solvents increases, the partition coefficient increases as well. A preferred system would have a low partition coefficient for sugars and a high partition coefficient for organics. The data by Zhang et al. [68] trended as expected with sugar partition coefficients decreasing as the length of the carbon chain increased due to the decrease in solvent polarity (Table 3; Fig. 8a). Although the xylose partition data is presented, the glucose partition data results in almost identical trends. The branched molecules resulted in higher partition coefficients for a given polarity value, which could be due to the secondary alcohols being more compact and therefore less of its hydrophobic surface is exposed. For example, a polarity value of 0.47 resulted in a partition coefficient of 0.3 for linear molecules (n-butanol), but iso-propanol with a polarity value of 0.48 resulted in a partition coefficient of 2.4.

The furan partition coefficients [68] did not correlate well with polarity, but the basicity parameter did as shown in Fig. 8b. We hypothesize that this may be due to the delocalized lone pair of electrons on the oxygen that could be stabilized in solvents that have a higher hydrogen-bond accepting ability (β). Similar to the sugar partitioning data, the branched molecules resulted in higher partition coefficients for a given basicity value. Based on this data, the ideal solvent would have both high polarity and basicity. As mentioned in the introduction, the basicity calculation has polarity in the equation and therefore, high polarity is an important factor to consider when selecting solvents for biphasic systems. These trends could lead to more efficient biomass processing and result in informed selection of reaction conditions; however, further research is needed to see if the trends are valid for solvents other than alcohols.

5. Conclusions

Biphasic systems show promise in providing an efficient and potentially profitable way to process lignocellulosic biomass by exploiting the differences in polarity of biomass products. Solvent choices that enable higher efficiency and require less energy to recover should be considered to improve the separation of the products and for solvent recovery. For example, by avoiding solvents combinations such as n-propanol/water that possess similar boiling points and using recoverable catalysts such as oxalic acid, the utilization of expensive solvents could still lead to profitable industrial processes. The developed optimization models that were discussed could provide valuable insight into the best reaction parameters to recover desired components of biomass and could potentially be applied to the other reaction systems

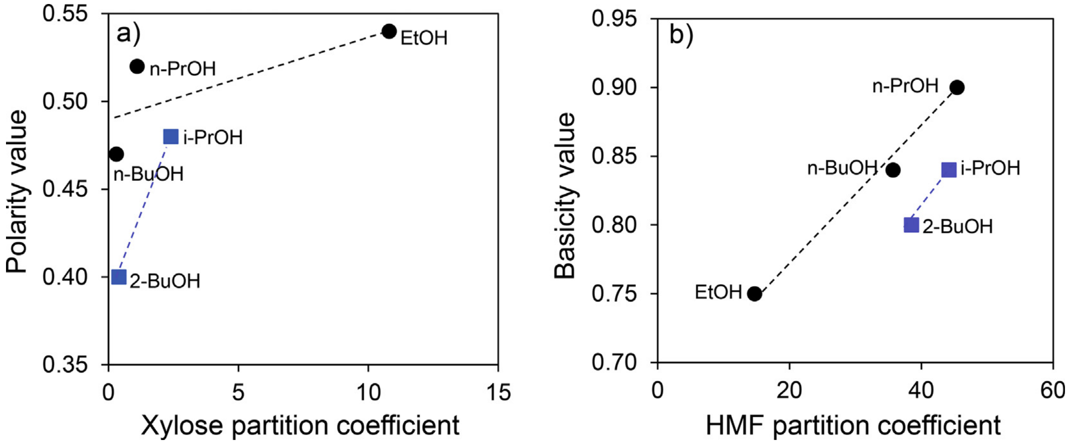

Fig. 8. The a) xylose partition coefficient [68] compared to the solvent polarity (π [44]) values and b) HMF partition coefficients [68] compared to the basicity (β [44,73]) values. Lines have been added to guide the eye.

and be expanded to include solvent properties, such as polarity and basicity.

The current review collected a growing body of literature on utilizing biphasic systems with lignocellulosic biomass. Finding a solvent, or a system of solvents, that is effective at fractionation of the three portions of biomass would be a great step toward limiting the necessity of fossil fuels; however, there is much research to be done in the area of using biphasic solvent systems for biomass fractionation. Finding a solvent system that balances polarity and basicity for selectively extracting solutes, has low environmental concerns, is recyclable, and has a low production cost would enable a viable, effective processing solution for lignocellulosic biomass. The biphasic studies presented in this work lays the foundation for further research into solvent parameter and severity effects on biomass fractionation.

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