



## 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 partition 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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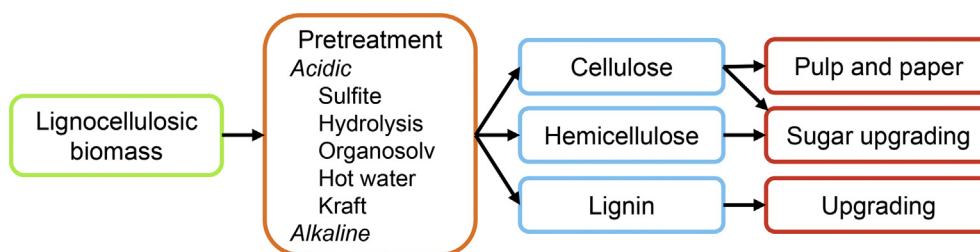


Fig. 1. Potential processing options for lignocellulosic biomass.

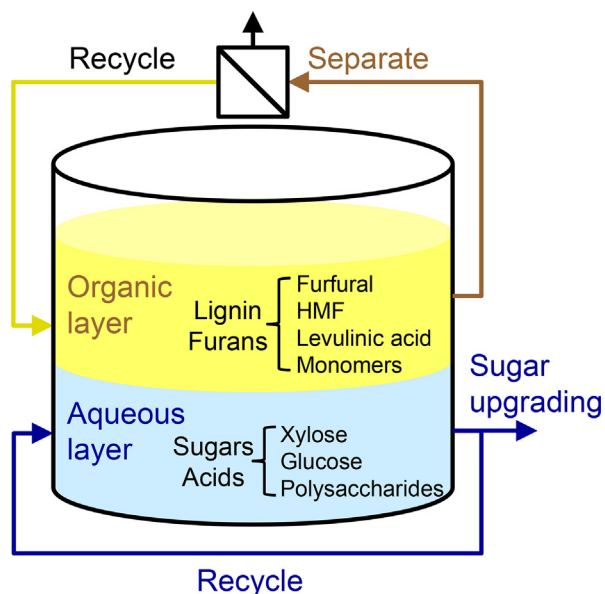


Fig. 2. Preferred partitioning of chemicals typically found in biomass upgrading. Adapted from Ref. [17].

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 ( $\pi^*$ ) [45], basicity ( $\beta$ ; hydrogen-

bond accepting ability) [46], and acidity ( $\alpha$ ; 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 heterogeneous 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 heterogeneous 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 heterogeneous reactions, partitioning 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<sub>2</sub>)), 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);

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