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# Enhanced solid–liquid clarification of lignocellulosic slurries using polyelectrolyte flocculating agents

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ABSTRACT

Following pretreatment and enzymatic hydrolysis of lignocellulosic biomass within a biorefinery, the residual solids are often present in high concentration and have a wide particle size distribution. These solids, which can be difficult to remove from solution, can have a detrimental impact on downstream fermentations and separations. Here we show that polyelectrolyte flocculating agents can be used to enhance the solid–liquid clarification of a lignocellulosic biomass (Ponderosa Pine) hydrolyzate. Due to the negative zeta potential of Ponderosa Pine solids following pretreatment and enzymatic hydrolysis, flocculation with cationic polymers provided the largest flocs, which quickly settled out of solution. Adding Kemira flocculant C1592 up to 1000 mg/L created larger flocs; however, a higher dosage (5000 mg/L) resulted in solids re-dispersing into solution. It was estimated that a greater than 12-fold improvement in throughput with a scroll decanting centrifuge could be obtained when using flocculant, or that an approximately 40-fold higher flux could be obtained for a vacuum filtration operation. The addition of 100 mg/L of C1592 showed optimal suspended solids removal of the clarified solution (<0.1% w/w suspended solids) and the highest sugar recovery (up to 83% without washing). In all cases, the percentage of suspended solids remaining following either centrifugation or filtration was at least an order of magnitude lower with the aid of flocculant. The presence of residual polymer in solution did not affect the downstream ethanol productivity of a *Saccharomyces cerevisiae* fermentation.



## 1. Introduction

The United States currently imports over 10 million barrels per day of petroleum as a feedstock for fuels and chemicals [1]. However, environmental, economic, and national security concerns associated with petroleum have motivated research into alternative, renewable, domestic sources for fuels and chemicals [2]. Currently, ethanol is one of the primary alternative fuel sources being evaluated as a replacement for gasoline.

The majority of ethanol production within the United States comes from the fermentation of glucose derived from corn starch. While the process of converting corn starch into fermentable sugars has been well developed, there are many potential drawbacks. For instance, bioethanol production consumes more than 12% of the corn produced in the United States [3]. This has led to higher feed costs in the dairy, poultry, and livestock industries and has sparked debate over limiting subsidies for corn ethanol [4]. To help alleviate

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these concerns, other carbohydrate feedstocks are being considered.

Currently, different renewable lignocellulosic biomass sources (e.g., perennial grasses, woods, and cornstalks) are being tested to determine their viability as new, cost effective sources for fermentable sugars. Lignocellulosic materials are the most abundant renewable resource on earth, and new technologies are advancing their potential as an economical feedstock for fuel and chemical production [5]. Unfortunately, ethanol production from these materials has proven to be challenging because of the physio-chemical, structural, and compositional factors of the material. Compared to corn starch, cellulose is much more difficult to hydrolyze into glucose due to the recalcitrant nature of this polysaccharide and its associated biomass [6].

Lignocellulosic material is composed of three primary components: cellulose, hemicellulose, and lignin. The traditional process for breaking down lignocellulosic materials into fermentable sugars involves a pretreatment step to release cellulose/hemicellulose from the recalcitrant lignin sheath followed by enzymatic conversion of cellulose to glucose (Fig. 1) for a separate hydrolysis and fermentation (SHF) process [7]. SHF utilizes separate steps for pretreatment, hydrolysis, and finally fermentation of the lignocellulosic material. Solid–liquid clarification can take place before and/or after the fermentation process.

Completion of the pretreatment and enzymatic hydrolysis steps results in a slurry with a high concentration of non-dissolved, suspended solids in a sugar-rich solution. To improve process operability and economics, a solid–liquid separation step is beneficial; a solids-free, sugar-rich solution can then be sent to fermentation. This may elevate efficiency by improving mixing and reducing potential harmful adsorption or other detrimental interactions between fermentation organisms and suspended solids that reduce cell viability and availability [8]. Additionally, solids (primarily lignin) from the separation can be processed and possibly turned into a valuable byproduct without contamination from fermentation organisms. Finally, removal of unfermentable solids prior to fermentation would allow for easier concentration of the sugars-rich stream (using reverse osmosis or evaporation) as well as an opportunity to recover and recycle the fermentation organism. These operations would reduce the amount of water sent downstream to distillation (reducing energy requirements) and improve fermentation productivity.

Centrifugation and microfiltration are the primary operations for solid–liquid separations. Centrifugation is used extensively in many industries and allows for a continuous process; its main downfall can be extensive utility costs for operation. Alternatively, microfiltration is commonly used for the separation of suspended solids and high-molecular weight solutes in wastewater treatment and food processing industries. While the operational costs may be lower for microfiltration compared to centrifugation, the filtration medium often needs to be replaced on a much more frequent basis [9,10].

Clarification is complicated when small low density particulate matter and colloidal materials are suspended in solution (as is the case with many lignocellulosic biomass processes). However, processes such as sedimentation, centrifugation, and filtration can be greatly improved through the use of flocculating agents. Flocculating agents are high-molecular weight polymers that come in a variety of chemical compositions, concentrations, and charges; they are commonly used in the water treatment, biopharmaceutical, and paper mill industries [11–15]. Generally these polymers are water soluble and are broadly characterized by their ionic nature: cationic, anionic, or non-ionic (neutral), and are referred to as polyelectrolytes [16]. By agglomerating suspended solids the flocculation process not only increases the size of the solids (making them more easily removed from solution), but also serves to scavenge very small particles that would normally be extremely difficult to remove [17–19].

Following efficient pretreatment and enzymatic hydrolysis steps, the slurry contains suspended solids that have a high percentage of lignin, in addition to a complex mixture of soluble compounds. Though complex and undefined, the lignin structure of lignocellulosic biomass is highly branched and includes many exposed weak acid groups that are negatively charged [23]. It is hypothesized that these exposed charges will readily interact with charged surfaces of polyelectrolytes, causing flocculation and rapid removal of solids from solution, very similar to mechanisms of flocculation within other industries [11–15] and discussed in more detail in the Theory Section below. In addition, residual cellulose and/or hemicellulose solids will also contain exposed hydroxyl groups that could also interact with flocculants. For this project the primary goal was to evaluate and understand polyelectrolyte flocculation as a technique to improve the solid–liquid clarification of Ponderosa Pine hydrolyzate

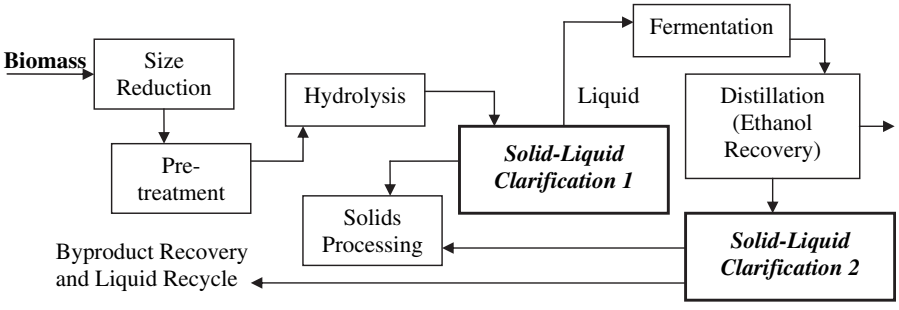


**Fig. 1 – Schematic of separate hydrolysis and fermentation process for the conversion of lignocellulosic biomass into ethanol.**