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Development and Optimization of a Flocculation Procedure for Improved Solid-Liquid Separation of Digested Biomass

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Abstract

One viable treatment method for conversion of lignocellulosic biomass to biofuels begins with saccharification (thermochemical pretreatment and enzymatic hydrolysis), followed by fermentation or catalytic upgrading to fuels such as ethanol, butanol, or other hydrocarbons. The post-hydrolysis slurry is typically 4-8% insoluble solids, predominantly consisting of lignin. Suspended solids are known to inhibit fermentation as well as poison catalysts and obstruct flow in catalyst beds. Thus a solid-liquid separation following enzymatic hydrolysis would be highly favorable for process economics, however the material is not easily separated by filtration or gravimetric methods. Use of a polyacrylamide flocculant to bind the suspended particles in a corn stover hydrolyzate slurry into larger flocs (≈1-2mm diameter) has been found to be extremely helpful in improving separation. Recent and ongoing research on novel pretreatment methods yields hydrolyzate material with diverse characteristics. Therefore, we need a thorough understanding of rapid and successful flocculation design in order to quickly achieve process design goals. In this study potential indicators of flocculation performance were investigated in order to develop a rapid analysis method for flocculation procedure in the context of a novel hydrolyzate material. Flocculation conditions were optimized on flocculant type and loading, pH, and mixing time. Filtration flux of the hydrolyzate slurry was improved 170-fold using a cationic polyacrylamide flocculant with a dosing of approximately 22 mg flocculant/g insoluble solids at an approximate pH of 3. With cake washing, sugar recovery exceeded 90% with asymptotic yield at 15 L wash water/kg insoluble solids.

Background

The solid particles in enzymatically hydrolyzed biomass slurries are small in size with a large size distribution (0.1-1000 µm diameter), easily deformable, buoyant, and have a negative surface charge, which causes the particles to form a colloidal dispersion. These small, deformable particles readily form an impermeable filter cake and foul filter membranes. Centrifugation and other gravimetric methods of solid-liquid separation are likewise complicated by the insignificant density difference between the particles and the suspension liquor and their small particle size. Polymer flocculants have long been successful in wastewater treatment and other processes to aid separation of suspended particles, and have also shown recent success in in biofuel production processes. Flocculation efficiency is known to vary with pH, flocculant loading, and mixing time, therefore this research focused on these variables in order to optimize a flocculation process. Corn stover undergoing an alkaline deacetylation pretreatment followed by milling in a disc refining mill has been shown to yield high sugar concentrations post-hydrolysis, while using lower enzyme loadings than previously necessary, but the resulting slurry presents increased difficulty during solid-liquid separation. This deacetylated, disk refined hydrolyzate (DDR-EH) material was selected for use in this project.

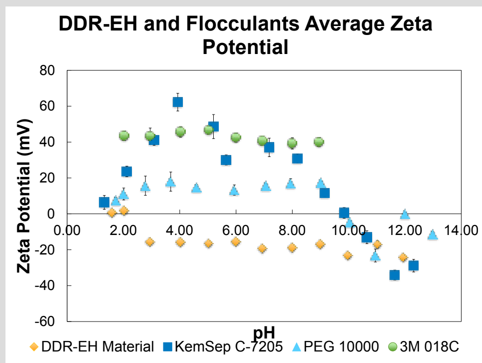

Single Disk Refiner, Andritz Inc.

Zeta Potential

Zeta Potential measurements of the hydrolyzate material and the candidate flocculants across the pH spectrum give a measure of the surface charge of the particles in solution as well as the behavior of the material at a given pH. Given the largely accepted flocculation mechanism of charge neutralization, flocculant and DDREH zeta potential values between pH 3-5 suggested favorable flocculation conditions.

Zeta Potential (mV)	Stability behavior of Colloid
0 to ±5	Rapid coagulation/flocculation
±10 to ±15	Threshold of agglomeration
±15 to ±30	Threshold of dispersion
±30 to ±40	Moderate Stability
±40 to ±60	Good stability
Greater than ±60	Excellent stability
DDR-EH Material: -15 to -25 mV	**Threshold of dispersion**

Chen, Wu. "What Is Zeta Potential?" American Filtration and Separations Society. Web. 8 July 2015.



Flocculation Optimization

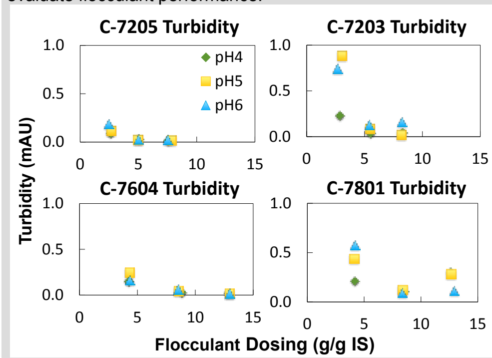
As an initial test, we screened several flocculants in a pH range of 4-5 at increasing dosages in order to observe flocculation behavior. Flocculants tested included Polyethylene glycols, 3M cationic guanylated polyethyleneimines, and KemSep cationic, nonionic, and anionic polyacrylamide flocculants. Of these flocculants, only the KemSep cationic flocculants above a threshold of flocculant molar charge successfully formed flocs.

Flocculant	% Molar Charge	Estimated Molar Weight (million)	Flocs Formed
KemSep C-7104	5	9	
KemSep C-7107	10	10	
KemSep C-7203	20	15	✓
KemSep C-7205	20	8	✓
KemSep C-7403	40	14	✓
KemSep C-7405	40	8	✓
KemSep C-7604	55	8	✓
KemSep C-7613	60	10	✓
KemSep C-7801	83	14	✓

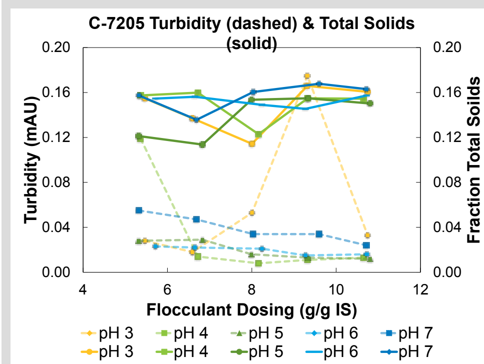
Flocculation Optimization, cont.

Further testing investigated the performance of four KemSep cationic flocculants at a range of loadings and pH values, using a shake table for mixing consistency. Slurries were centrifuged, and turbidity, total solids, and insoluble solids measurements of extracted liquors were used as metrics to evaluate flocculant performance.

		Molar Weight	
		Low	High
% Molar Charge	Low	C-7205	C-7203
	High	C-7604	C-7801



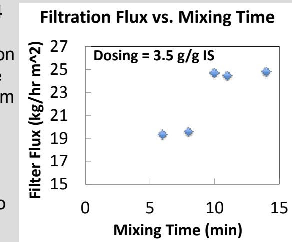
All flocculants showed significant reduction in turbidity from a baseline hydrolyzate turbidity of 1.288 mAU. Due to the low dosing of flocculant necessary to yield low values of turbidity and total solids, KemSep C-7205 was selected for further testing with an expanded range of loadings and pH values.



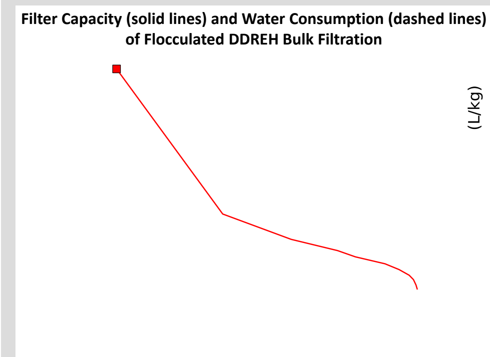
Flocculation tests performed at pH 3, 4 and 5 yielded the best results, as shown above. Increases in total solids around flocculant dosings of 7-8 g/g-insoluble-solids are thought to result from excess flocculant present in the extracted liquor, with the lowest total solids values showing an approximate optimum flocculant loading.

Vacuum Filtration

Vacuum filtrations were performed at pH 3 and 4 on a Fisherbrand glass filter with a Supelco Nylon 66 filter paper (pore size 0.2µm) at 15inHg vacuum pressure. Filtration optimization focused on flocculant loading and mixing time. Increased mixing time was found to increase filter flux.



Ideal filtration conditions of approximately 22 mg flocculant/g insoluble solids and 12 minutes of mixing were tested on a Larox Buchner Funnel with a Maro S30 filter cloth at 15 inHg vacuum pressure. A 170-fold flux improvement was seen over non-flocculated material for initial filtration. Sugar recovery exceeded 90% with asymptotic yield at 15 L wash water/kg insoluble solids.



Conclusions

Zeta Potential measurements and small scale flocculation testing using turbidity and solids measurements as metrics were found to be effective indicators of successful flocculation and optimal flocculation conditions. The success of the flocculant in binding the suspended solids into flocs is thought to be the result of charge neutralization and bridging achieved between the polymer flocculant and the solid particles.
Use of a cationic polyacrylamide flocculant was successful in increasing filter flux 170-fold at a dosing of 22 mg flocculant/g insoluble solids and yielding greater than 90% sugar recovery with cake washing.

Further studies will explore filter cloth selection as well as mixing optimization for maximum flux and sugar recovery while minimizing wash water consumption.

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