Microemulsions for Enhanced Biomass Pretreatment

Recipient Organization: North Carolina State University
Principal Investigator: Orlando Rojas
Project Location: Raleigh, North Carolina

Reporting Period: October 1, 2012 – December 31, 2012
Date of Report: January 29, 2013
Written by: Orlando J. Rojas

1. Planned Activities:
   • Determine the effect of biomass pretreatment via microemulsion system on the energy consumption to deconstruct cellulose fibers into smaller units
   • Evaluate the impact of the lignin content in the microemulsion-pretreated biomass in deconstructed fibers

2. Actual Accomplishments:
   Oil in water microemulsions were used as vehicles to deliver chemicals to pretreated cellulotic pulps for deconstruction (size reduction). Two chemicals additives were used in the microemulsion system to pretreat the pulps: urea and ethylenediamine. Their effect in the degree of fibrillation and the energy consumption were evaluated. The impact of lignin content of the pulps in the final characteristics of the obtained fibrils was investigated, as well as the effect in energy consumption during processing.

Effect of the type of chemical:
Fully bleached Birch pulp was treated for 12 hours with two different microemulsions. The first one contained urea as the active chemical for pretreatment and the second one included ethylenediamine. After the pretreatment, the pulp was centrifuged and then washed with a mixture of ethanol and water (1:4 by volume). After washing, the pretreated pulp was centrifuged again and two more washing steps with distilled water were carried out. The pretreated and washed pulp was homogenized with an ultraturrax at 20,000 rpm for 20 minutes. After homogenization, the pulp was defibrillated in the microfluidizer at 2000 bar for 7 passes. Samples were taken after each pass and analyzed. A control sample was also prepared treating the pulp with an aqueous solution of the active chemical with the same concentration than the microemulsions, following the same procedure. The water retention value (WRV) of the produced fibrils was measured and used as a quantification of the degree of fibrillation. The WRV results in these experiments are presented in figure 1.
It can be observed (Figure 1) that the WRV values of the fibrils obtained after using the chemicals in the microemulsion are higher than the values for the pretreatment using the aqueous solution of the same chemical. In the case of urea, the WRV using the microemulsions is about 20% higher than the values for samples after using the aqueous solution. For the pretreatment using ethylenediamine the trend is the same but the respective difference in WRV values is about 18%. These observations indicate that compared to the aqueous solutions the microemulsions enhance the delivery of the chemicals to the pulp. This is explained by their ability to impregnate more effectively the porous substrates as was demonstrated in our previous results with wood samples. Therefore, it is possible to reduce the energy consumption using these microemulsions, since the same degree of fibrillation can be obtained using a smaller amount of energy in the microfluidizer. In the case of urea, the WRV’s are higher compared to the values obtained for the fibrils obtained after using ethylenediamine, indicating that urea is a more effective agent as hydrogen bond breaker to reduce the energy consumption deconstruction when compared to ethylenediamine. Atomic force microscopy was used to observe possible differences in the physical characteristics of the defibrillated pulps obtained by the different methods. Figure 2 include AFM images of the different fibrils obtained. As the number of passes through the microfluidizer increases, the fiber diameter is reduced, as expected. However, it can be observed that the increment is more notorious for fibrils that were obtained after processing pulps with microemulsions with added urea, confirming the results obtained from WRV measurements.
Effect of the presence of lignin in the raw material:
Eucalyptus pulp with a kappa number of 27 was used as a raw material to compare with the fully bleached pulp used in the previous part. The pretreatment was performed using the urea microemulsion since this was the chemical that showed the better performance. The procedure for obtaining the fibrils was identical to the procedure explained in the previous section. The WRV values were measured as an indication of the degree of fibrillation of the pulp and the results are presented in figure 3.

The eucalyptus pulp treated with the urea microemulsion, presents WRV 55% larger compared to the same treatment using the aqueous solution of urea. The difference in the WRV between the pulps treated with the microemulsion and with the aqueous solution is larger when the raw material has lignin as can be observed by comparison of these results with those presented above. However, the WRV of the fibrils with lignin are lower compared to the fully bleached pulp. Therefore, the presence of lignin reduces the effectiveness of the microemulsions to deliver the chemicals for pretreatment. This could be due to the fact that when lignin is present, the existence of hydrophobic domains presents a barrier for the aqueous solution systems but it is reduced when microemulsions are applied. Overall, the presence of lignin leads to lower degrees of fibrillation for deconstruction of lignin-loaded biomass compared to fully bleached pulp.
Figure 3. Differences in the WRV for the pulp with lignin and without lignin.

These results are being used to understand the role of lignin in impregnation and deconstruction of biomass by microemulsion systems, especially when the emulsions are loaded with hydrogen breaking molecules that are expected to make the cell wall components more accessible to enzymes and other systems in bioprocessing.

3. Explanation of Variance:
Below we present a summary of work tasks in the project:

<table>
<thead>
<tr>
<th>Work Tasks</th>
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<tbody>
<tr>
<td>1. Development of SOW systems</td>
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<td>2. Application against biomass samples and measurements</td>
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<td>3. Evaluate effects of microemulsion treatments on the capillary nature and swelling of cellulosic substrates</td>
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<td>4. Analysis of biomass crystallinity and pore volume before and after the impregnation</td>
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<td>5. Analysis of change in lignin content and structure (as a function of amine agents)</td>
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<td>6. Study of effect of variables (pH, osmolality, temperature) on the penetration profile</td>
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<td>7. Study of penetration and lignin/extractive solubilization in microemulsion systems with biomass substrates</td>
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<tr>
<td>8. Analysis of penetration into biomass substrates using microemulsion systems</td>
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<tr>
<td>9. Investigate emulsion inversion and phase separation for component recovery and recycling.</td>
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<tr>
<td>10. Measure energy consumption in disk defibrator to process biomass after</td>
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Task 1-5, 7 and 8 have been completed. One variation is that we have concentrated in 5 different wood species and still need to evaluate switchgrass briquettes. This report concerns task number 10, which was conducted during this quarter as we took advantage of access we were given to defibrillation devices to study biomass deconstruction. Tasks 9, 11-13 are still pending and will be completed in the next quarters, provided we are approved a requested no cost extension by SunGrant.

4. Plans for Next Quarter:
   • Investigate emulsion inversion and phase separation for component recovery and recycling.
   • Measure energy consumption in disk defibrator to process biomass after microemulsion impregnation (if needed)
   • Test activity and turnover rate of cellulases against biomass as a function of a variety of microemulsion conditions
   • Explore the effect of microemulsion in reducing enzyme inhibition.
   • Test optimal enzyme and conditions. Comparison against benchmarks and economic analyses.

5. Budget:
   a. Funds Expended to Date (End of Reporting Period): 85,061
   b. Remaining Balance of Funds: 93,048

6. Patents: N/A

7. Publications / Presentations:
4. Rojas, O.J., New technologies for wood pretreatment within the concept of the biorefinery and novel uses of cell wall components, Frontiers in Biorefining, St. Simmons Island, GA, November 2, 2012

8. Name of Students Funded on Project, including Department, Institution, Thesis/Dissertation Title (if applicable), Degree Obtained (if applicable), and Program Area:

<table>
<thead>
<tr>
<th>Student Name</th>
<th>Department</th>
<th>Institution</th>
<th>Thesis/Dissertation Title</th>
<th>Degree Obtained/Date</th>
<th>Program Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carlos A. Carrillo</td>
<td>Forest Biomaterials</td>
<td>North Carolina State University</td>
<td>Biomass pretreatment with novel microemulsions system</td>
<td>Degree to be obtained in 2014</td>
<td>Forest Biomaterial</td>
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