

Automated Biomass Pretreatment Analysis using an Accelerated Solvent Extractor

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Introduction:

The ability to screen feedstocks for their relative structural recalcitrance is an important tool in the development of advanced cellulosic biofuels. Methods are needed which can be reproducibly repeated across a variety of laboratories so that comparisons between data sets can be meaningful. While such methods have been developed for enzymatic Saccharification and fermentation (ref), no similar standard method has emerged for evaluating a feedstock's response to pretreatment (the process by which the biomass structure is altered to aid in the enzymatic Saccharification of the biomass). One reason why this has not developed is the variety of pretreatment reactors in use on the bench scale. While some reactors have been applied in a variety of labs, (Parr reactors, modified sand bath and tube apparatus', etc.) these reactors require significant operator knowledge and have not conclusively proven to provide similar results under similar conditions. As well, they lack the capacity to effectively screen a large amount of feedstocks. It is desirable to develop a standard pretreatment platform which is easy to use, automated, can provide reproducible results, and relies on commercially available and multifunctional equipment. In this study, we present data showing the use of an Automated Solvent Extractor (ASE 350, Dionex corp.) to conduct dilute acid pretreatments of corn stover. We evaluate the ability of the equipment to effectively pretreat the corn stover and its ability to provide meaningful information for feedstock analysis.



Why use the ASE 350?

- Fully automated system, can run 24 samples sequentially
 - Can do solid liquid separation; usually a time consuming step
 - Acid resistant construction, so compatible with dilute acid pretreatment
 - Capable of handling high temperatures and pressures
 - Commercially available system, making standard methods possible
 - Equipment has other laboratory uses, extractions, etc.
 - Sample size large enough for in depth analysis
- ### Drawbacks
- Slow heat up time for high temps (7-9 minutes)
 - Limited reaction temperature range (maximum 200°C)
 - Not able to change solvents quickly, difficult to quench reactions

Research Goals:

- Determine whether biomass can be effectively pretreated in ASE 350.
- Determine whether the ASE350 can perform consistently in desired ranges
- Identify an operating range which can provide sufficient xylan hydrolysis for comparing feedstocks while minimizing degradation products

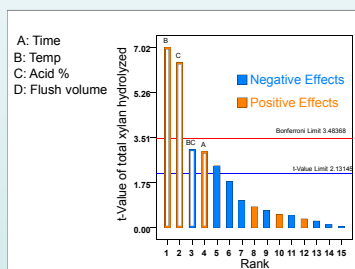
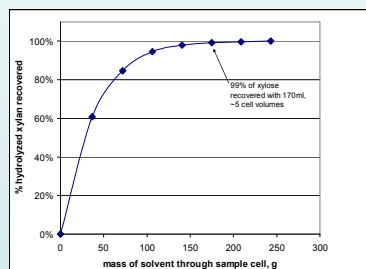
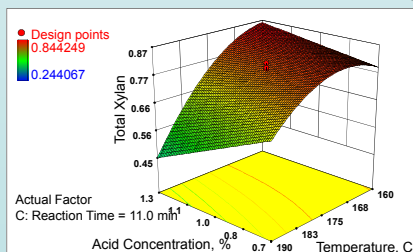


Figure 1: Fraction of hydrolyzed xylose recovered in successive washes. ASE has the ability to wash pretreated biomass and effectively recover xylan hydrolyzed during pretreatment.

Figure 2: Pareto chart showing the main effects on total xylan hydrolysis in the ASE350. Standard reaction variables show a normal effect on xylan hydrolysis as opposed to equipment operating parameters.



Conclusions

•ASE 350 is capable of pretreating biomass and achieving high levels of xylan hydrolysis. The system was easy to use and exhibited good reproducibility

•The ASE 350 shows similar pretreatment trends to other bench scale reactor systems.

•Large amounts of degradation were observed at higher severities, suggesting the need to operate at lower severities. This may be due to the long heat up times

•The system needs to be evaluated further to determine the optimal operating conditions for feedstock comparisons. An evaluation of different feedstocks is also necessary.

Figure 3: Surface response model for total xylan hydrolysis. ASE 350 is capable of a range of xylan yields and can effectively remove ~87% of total xylan. Better xylan yields were seen at lower temperatures due to xylose degradation (figure 4).

Experiments

- Full factorial design to determine the impacts of reaction time (2-6 minutes), reaction temperature (150-190°C), acid concentration (0.3-1% w/w), and solvent flush volume (50-100% reactor volume).
- Central composite surface response design to determine region with ~80% total xylan hydrolysis with minimal furfural production. factors: reaction time (5-17 minutes), Reaction temperature (160-190°C), and acid concentration (0.7-1.3% w/w)
- Verification study to determine reproducibility and sensitivity around one possible reaction coordinate for comparing feedstocks along with coordinate points to assess sensitivity.
- Equipment shutdown to determine adequate operating conditions such as flush volume, purge time, etc.

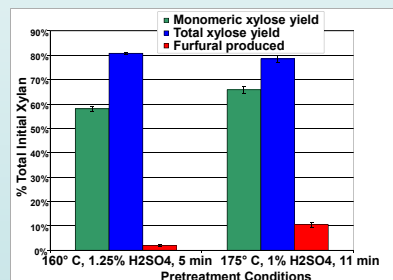


Figure 5: Xylan yields for two selected replicated conditions, n=5. The ASE shows good reproducibility between samples and run days.

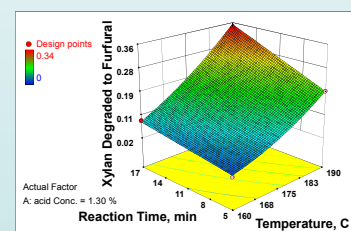


Figure 4: Furfural produced in pretreatment as a fraction of initial xylan. The ASE produced excessive amounts of furfural at higher temperatures and times. Similar trends held at lower acid concentrations. This suggests the ASE needs to be run at lower severities

Methods and Equipment

Equipment and materials: The ASE 350 (figure 1) was purchased from Dionex corporation. For this study we used Dionium® cells, which are manufactured to be resistant to corrosion by dilute acid. Sulfuric acid was used as the catalyst and was diluted to a working solution of either 1% (w/w) or 2% (w/w). Corn stover was used as the model feedstock. The stover was Pioneer variety 33A14, (from the Kramer farm, Wray, CO) harvested in 2002, and was knife-milled to pass either a 6mm round rejection screen. The material was then sieved using a 20 mesh sieve and the top fraction (+20) was used for the analysis. The composition has previously been reported in the literature (2).

Standard Pretreatment methods: Between 11 and 13 grams of air dried corn stover was packed into a 66ml Dionium cell using a packing rod. The cell was brought on the carousel into the oven which was already at the reaction temperature. Room temperature acid solution was pumped into the cell and allowed to come up to temperature and pressure. We used the solvent saver pressure mode, which maintained a constant pressure of 1500psi in the cell. The cell was then held at static temperature and pressure for the desired reaction time, and then evacuated into the 250ml collection vial. The cell was flushed with one reactor volume of the acid solution and then purged with nitrogen for 30 seconds. The samples were then flushed in the cells with four reactor volumes of DI water to remove any excess hydrolyzed sugars in the cell, quench the hydrolysis reaction and bring down the temperature of the biomass in the cell.

Analytical Methods: All analytical methods used followed standard NREL Laboratory Analytical Procedures, which can be accessed at http://www1.eere.energy.gov/biomass/analytical_procedures.html

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