NARA Biofuels Production Emissions

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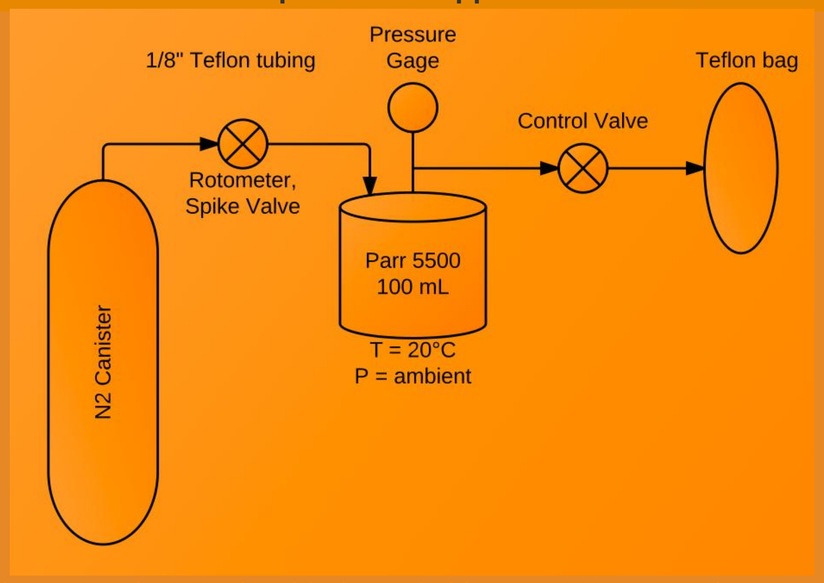
Introduction:
The Northwest Advanced Renewables Alliance (NARA) is an organization that aims to create a sustainable aviation biofuels production industry in the Northwest United States. One of NARA's goals is to develop a production process with fewer environmental burdens than conventional petroleum-fuels production processes. This research aims to determine the atmospheric emissions and emission sources that may be released from proposed NARA biofuels production processes. One of the critical steps for biological conversion of lignocellulosic biomass to biofuels is the pretreatment operation. Pretreatment is aimed at decreasing the chemical recalcitrance of lignocellulose, and effective pretreatment results in an improved accessibility of the carbohydrate polymers for hydrolysis to fermentable sugars. One of the key pretreatment processes currently under study is Sulfite Pretreatment to Overcome Recalcitrance of Lignocellulose (SPORL), a process modeled after the bisulfite pulping process. In order to develop initial air emissions estimates, historical emissions testing data from the Georgia Pacific sulfite pulping mill in Bellingham, WA, will be analyzed. This data is the closest existing representative of what emissions might be from a biofuels production facility due to the similarities between the pulping process used at the Georgia Pacific mill and the SPORL process, and the existence of an alcohol production plant at the mill.

Methods:
Emissions data from the Georgia Pacific sulfite pulp mill were used to form preliminary estimates of what the emissions and emissions sources might be in a NARA biofuels production plant. In order to begin to verify these estimates, a small scale laboratory SPORL experiment was constructed. The off-gas from the experiments was diluted and captured by flowing gaseous nitrogen through the reaction vessel into a Teflon bag. Characterization of the captured gas stream was conducted using Gas Chromotography-Mass Spectrometry (GC-MS) and Proton Transfer Reaction-Mass Spectrometry (PTR-MS).

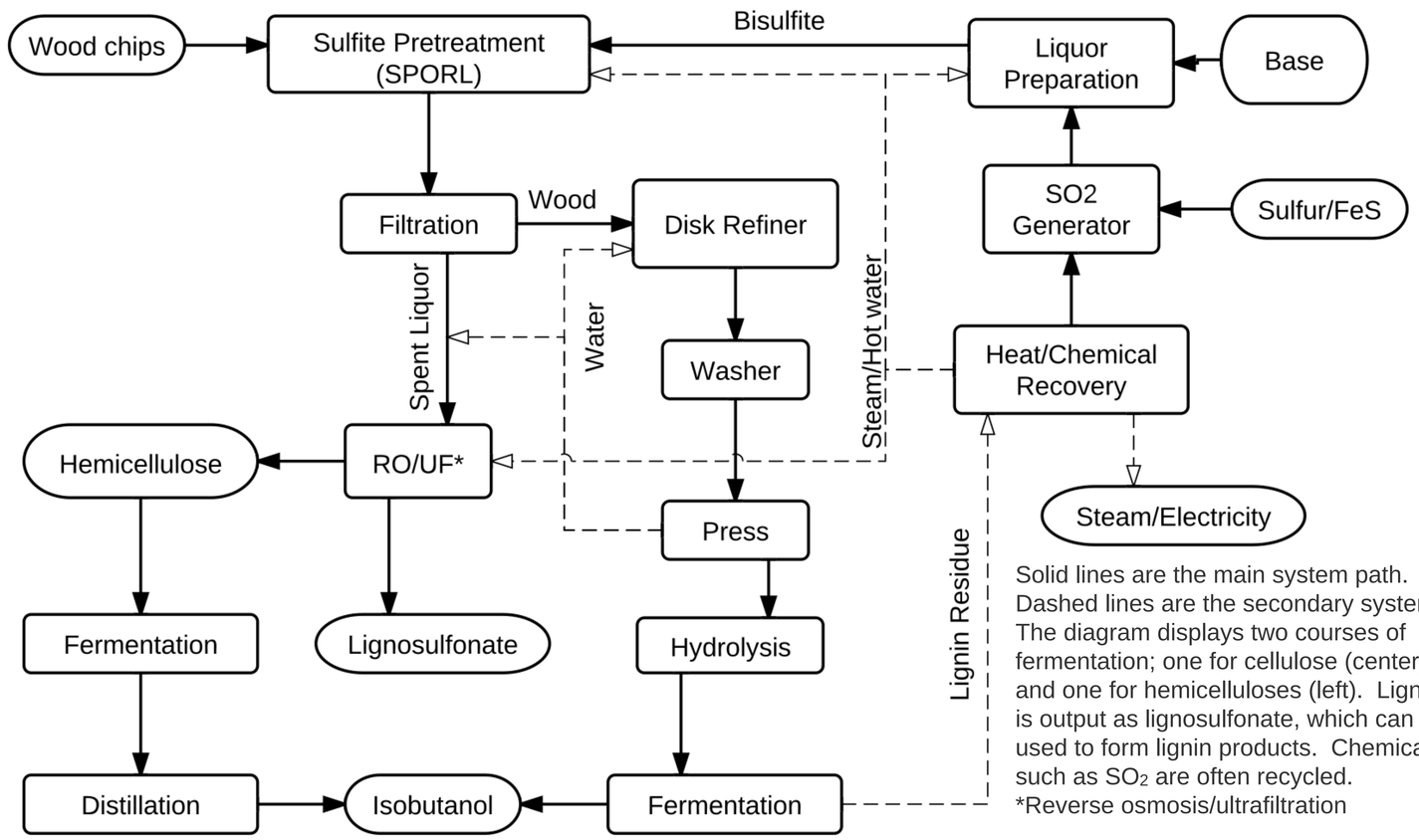
Experimental Apparatus:



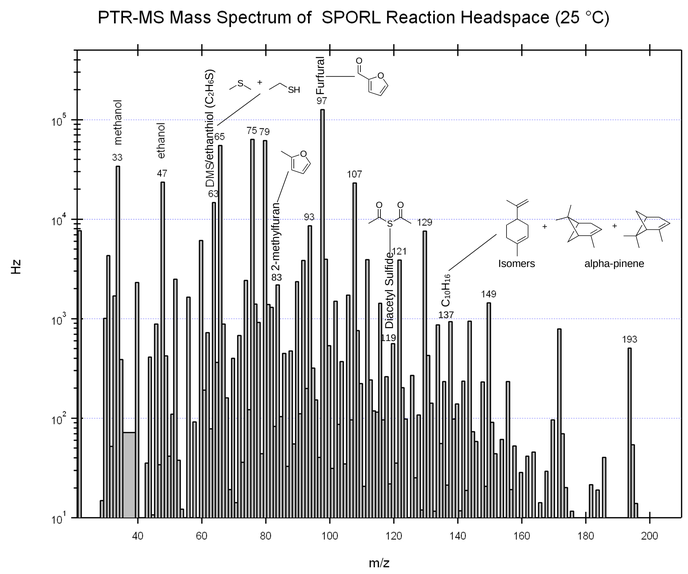
Procedure: 8g of ~0.5" shredded wood chips at 100% saturation were added to ~4 mL of 2% w/w Na_2SO_3. The mixture was placed into a 100mL Parr reactor, stirred, and heated to 180°C. The mixture was held at 180°C for 10 minutes, then allowed to cool to room temperature. N_2 was flushed through the reactor and slurry at ~200cc/min, pushing the off-gas into a ~10L teflon bag, as well as diluting it. When the bag was full, scans of the contents were taken on the PTR-MS and GC-MS. Due to the high concentration of the bag sample, N_2 was used to further dilute the sample by a factor of ~300. The data from both mass spectrometers was compared to find compounds that were likely present in the off-gas (see PTR-MS Mass Spectrum of SPORL Reaction Headspace).

This work, as part of the Northwest Advanced Renewables Alliance (NARA), was funded by the Agriculture and Food Research Initiative Competitive Grant no. 2011-68005-30416 from the USDA National Institute of Food and Agriculture.

Diagram of the Biofuel Production Process (SPORL - Alcohol Production):



Solid lines are the main system path. Dashed lines are the secondary system. The diagram displays two courses of fermentation; one for cellulose (center), and one for hemicelluloses (left). Lignin is output as lignosulfonate, which can be used to form lignin products. Chemicals such as SO_2 are often recycled.
*Reverse osmosis/ultrafiltration



PTR-MS Spectra of the off-gas from the SPORL process (left). The x-axis shows the mass-to-charge ratio for each compound. The y-axis shows the abundance of each ion in counts per second. The numbers labeling some peaks are the molar masses of the compounds that the peaks represent, plus one for the attached proton. For example, the peak at mass-to-charge ratio 33 is most likely to be methanol, which has a molar mass of 32g. Some peaks may represent fragments of emitted compounds, making it difficult to identify all of the compounds that part of the SPORL off-gas. Also, since there are many compounds of each molecular weight, some compounds may only be identified with limited certainty. This data was compared to data from a GC-MS scan of the same sample to help identify the labeled compounds.

Results:
When examining the emission inventory data from the Georgia Pacific mill, the main emission sources were determined to be: (1) the steam production plant, (2) alcohol plant, (3) digester blow pit, (4) acid production tower and scrubbers, and (5) aerated stabilization basin. Compilation of these data sets indicated that the primary emissions from these sources are formaldehyde, acetaldehyde, acetone, methanol, benzene, diethyl ether, and chloroform and other chlorinated organics. Results of laboratory-scale SPORL experiments indicated that furfural, methanol, ethanol, DMS/ethanthiol, 2-methylfuran,$C_{10}H_{16}$, and diacetyl sulfide were most likely part of the off-gas.

Future Work:
Future experiments will include comparisons of SPORL emissions under different conditions (temperature and pH differences), as well as more detailed identification and quantification of SPORL off-gases. Similar testing will take place for analyzing the off-gas from saccharification and fermentation experiments.

References:
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