CHEMICAL FEEDSTOCKS FROM WOOD: AQUEOUS ORGANIC ALCOHOL TREATMENT

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INTRODUCTION

The current world petroleum crisis has caused renewed interest in alternative and renewable sources of fuel and feedstock chemicals. One such alternative receiving attention involves the separation of wood into its components, cellulose, hemicellulose and lignin, followed by conversion to feedstock chemicals. Treatment of wood with an aqueous organic solvent has been found to be effective in removing lignin and hemicellulose from the cellulose fibers.

Early work by Aronovsky and Gortner (1) studied the use of aqueous solutions of organic alcohols to remove lignin and produce wood pulp. They determined that aqueous n-butanol was the most effective solvent for producing a well pulped residue and for the removal of lignin.

Kleinert (2,3) found that organosolve bulk delignification occurred in two distinct psuedo-first order stages. Delignification was found to be considerably faster during the first part of the batch cook.

More recently, Katzen et al. (4) showed that a continuous alcohol pulping process using aqueous ethanol is economically feasible if the by-products (lignin and hemicellulose hydrolysis products) can be upgraded and sold. A pay out time of 3.2 years with a 22% return on investment was calculated.

This paper reviews the recent work with aqueous organic solvents conducted at The University of Alabama. Emphasis on the rate of lignin removal and the extent of pulp recovery is included. The use of the data to make preliminary process calculations regarding technical and economic feasibility is also addressed with comparisons to recent work reported in the literature.

BATCH DELIGNIFICATION STUDIES

A majority of the work reported in the literature was accomplished using batch equipment. Initial screening studies at The University of Alabama likewise followed this mode of investigation. A summary of the various conditions investigated is shown in Table 1.

Table 1 - Summary of Experimental Conditions

Wood Type	-	Southern Yellow Pine, Sweet Gum
Wood Size	-	Meal (-10 +70)
Solvent Type	-	Ethanol, Butanol, Phenol
Solvent/Water	-	50/50 by Volume
Solvent/Wood	-	15 ml Solvent/1 g Wood
Temperature	-	175-205°C
Pressure	-	1140-2180 kPa
Catalysts	-	Alum, $AlCl_3$, Anthraquinone

A summary of the results of the batch experiments is shown in Table 2.

Table 2 - Summary of Batch Results

Southern Yellow Pine			
Conditions	Time	% Residual Pulp	% Lignin Removed
Solvent: nBuOH	0.0	85.3	15.0
Temp: 175°C	0.5	74.1	36.0
Pressure: 1140 kPa	1.0	71.8	36.0
	4.0	67.5	22.0
Solvent: nBuOH	0.0	65.3	27.2
Temp: 205°C	2.0	60.7	36.0
Pressure: 2170 kPa	4.0	56.0	35.0
Solvent: Phenol	0.0	58.0	35.9
Temp: 205°C	0.5	43.0	83.1
Pressure: 1490 kPa	1.0	41.1	84.7
	1.5	39.5	87.0
	2.0	38.0	89.3
	4.0	36.2	89.7
Sweet Gum			
Conditions	Time	% Residual Pulp	% Lignin Removed
Solvent: nBuOH	0.00	90.8	17.2
Temp: 175°C	0.67	69.1	45.3
Pressure: 1140 kPa			
Solvent: nBuOH	0.0	69.2	42.2
Temp: 205°C	0.5	56.5	60.9
Pressure: 2170 kPa	1.0	50.4	78.6
	1.5	47.8	83.6
	2.0	45.7	88.8
	4.0	43.1	85.7

These data are graphically illustrated in Figures 1 & 2 in which the fractional residual pulp versus time-at-temperature is plotted on rectangular and semi-log paper, respectively. A rapid decrease in the residual pulp during the early stages of the cook is observed.

Figure 2 shows the characteristic, two stage process that has been described by Kleinert and others (5,6) by a two step, first order expression. For the systems investigated in this study the rate constants for each step were calculated to be between 5.0×10^{-3} and 2.0×10^{-2} min^{-1} for the rapid initial step and between 4.0×10^{-4} and 4.0×10^{-3} min^{-1} for the subsequent slower rate.

Figures 3 and 4 show the lignin removed versus time and the log of lignin removed versus time. The percent lignin removed reaches a maximum level in the batch studies (see Figure 3) and then decreases. This decrease in the amount of lignin removed is due to repolymerization and precipitation of removed lignin,

and/or to the decrease in solubility of lignin in the solvent as it cools to room temperature. Figure 4 shows that the removal of lignin occurs in several first order stages paralleling the results noted for residual pulp (Figure 2). Corresponding rate constants for lignin are in good agreement with those values reported for residual pulp (2×10^{-2} to 6.0×10^{-2} min^{-1} and 3.0×10^{-4} to 1×10^{-3}) indicating a common mechanism during initial stages of hydrolysis. Kleinert (2,3) reported values for the rate constants between 1.5×10^{-2} and 3.0×10^{-2} min^{-1} for times correspnding to the initial first order removal presented here.

SEMI-BATCH DELIGNIFICATION STUDIES

In order to eliminate problems of solubility and repolymerization/redeposition of lignin, and, to simulate more closely commercial delignification processing, a series of data have been collected using a semi-batch apparatus. In this scheme, the solvent phase is continuously passed over a fixed bed of wood chips. The results obtained from these runs are summarized in Table 3.

Table 3 - Semi-Batch Results

Solvent	Wood	Temp,°C	Time hrs	Flow cc/min	% Residual Pulp	% Lignin Removed	Catalyst*
EtOH	SYP	175	2.50	7.20	91.1	3.7	-
EtOH	SG	175	0.67	7.20	74.0	47.3	-
EtOH	SG	175	0.67	7.20	73.2	48.9	Anthraquinone
EtOH	SG	175	0.67	7.20	30.6	97.9	$AlCl_3$
EtOH	SYP	205	1.33	3.20	52.1	59.4	-
EtOH	SYP	205	2.50	7.20	65.4	38.9	-
EtOH	SYP	205	4.00	7.20	47.0	62.2	-
BuOH	SG	175	0.67	7.20	95.5	20.0	-
BuOH	SG	175	0.67	7.20	96.8	15.3	Alum
BuOH	SG	175	0.67	7.20	43.2	87.2	$AlCl_3$
BuOH	SG	175	0.67	7.20	74.6	37.9	Anthraquinone
BuOH	SG	200	0.67	7.20	67.8	45.2	-
BuOH	SYP	205	4.00	5.43	65.0	43.7	-
BuOH	SYP	205	4.00	6.30	69.3	43.6	-

*Catalyst concentration is 0.005 % wt

These values show that for delignification to proceed at an appreciable rate with Southern Yellow Pine, the temperature must be above 175°C. It is also seen that more lignin is removed using aqueous ethanol as a solvent (over n-BuOH) but the amount of residual pulp decreases due to increased hydrolysis of the carbohydrates.

The results show that anthraquinone has no catalytic affect in aqueous ethanol at 175°C. The use of $AlCl_3$ as a catalyst causes a severe loss of the carbohydrates. The high loss of carbohydrates makes $AlCl_3$ an undesirable catalyst for the production of wood pulp.

In aqueous nBuOH solvent at 175°C Alum has no catalytic effect. The use of anthraquinone catalyst cause the percent lignin removal to increase from 20.0% to 37.9% with a corresponding decrease in residual pulp from 95.5% to 74.6%. The use of $AlCl_3$ again leads to high lignin removals with rapid hydrolysis of the carbohydrates.

Recovery data from a four hour semi-batch extraction of Southern Yellow Pine with aqueous ethanol at 205°C are shown in Figure 5. This data was collected by sampling the effluent at 100 ml intervals. These samples were stripped of solvent using a rotary evaporator followed by analysis of the residue for lignin content. The corresponding rate of removal of the lignin was described by a first order model producing a rate constant of 1.5×10^{-2} min^{-1}; well within the rate of values calculated for batch treatment.

Using the above information and data on the physical properties of the solvents, a preliminary engineering analysis can be made evaluating commercial application of the treatment method.

Commercial applications various process schemes have been proposed for organic solvent delignification including the more recent one by Katzen (4) for aqueous ethanol extraction. Figure 6 shows a form of that process modified for n-butanol-water treatment. This process is comprised of four sections: Extraction, Solvent Separation, Solvent Recovery and Product Recovery. A fifth, pretreatment of the wood may also be included as a major section of hemicellulose recovery is considered as an option. The values shown tabulated are based on the recovery data and extraction efficiencies generated in the experimental investigation for n-butanol-water treatment.

In general, 1000 kg of wood is needed to produce 650 kg of pulp (25% lignin), 150 kg of dry extracted lignin and 200 kg of hemicellulose hydrolysis products. The pulp could be further processed for use as a paper stock or could be acid hydrolyzed to glucose. There are existing processes for converting glucose to ethanol or n-butanol, making either solvent process totally independent of petroleum sources.

Approximately 1% of the solvent would be held up by the pulp and 1% would be removed with the lignin slurry. Approximately 80-90% of this could be easily removed by steam stripping giving an overall alcohol loss of 25 kg of nBuOH per 1000 kg of wood processed. It is also estimated that 275 kcal/kg of wood processed/ extractor would be required assuming 20% energy loss. This compares quite favorably with the value of 268 kcal/kg wood given by Katzen (4) using a battery of nine extractors.

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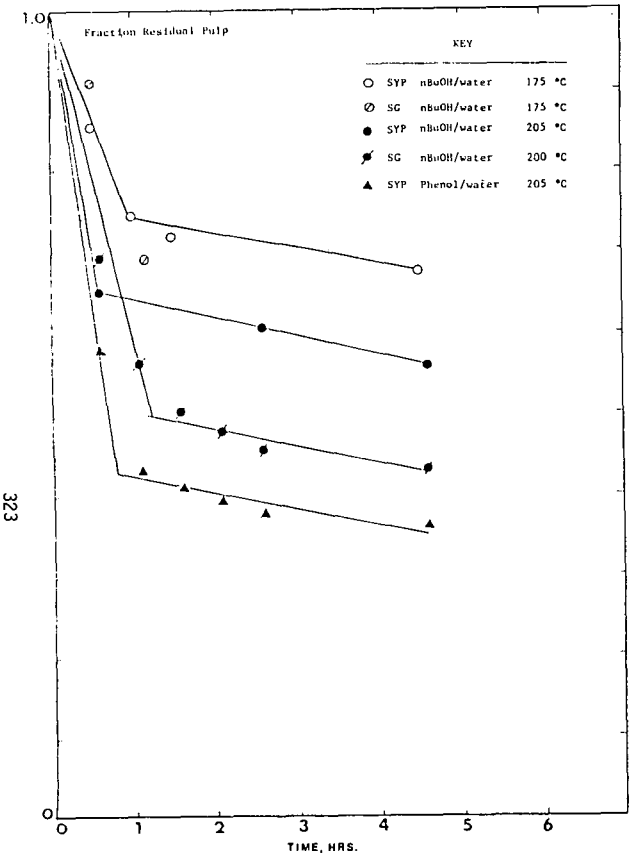


Figure 1. Fraction Residual Pulp vs. Time-at-Temperature for Aqueous Alcohol Delignification of Sweet Gum (SG) and Southern Yellow Pine (SYP).

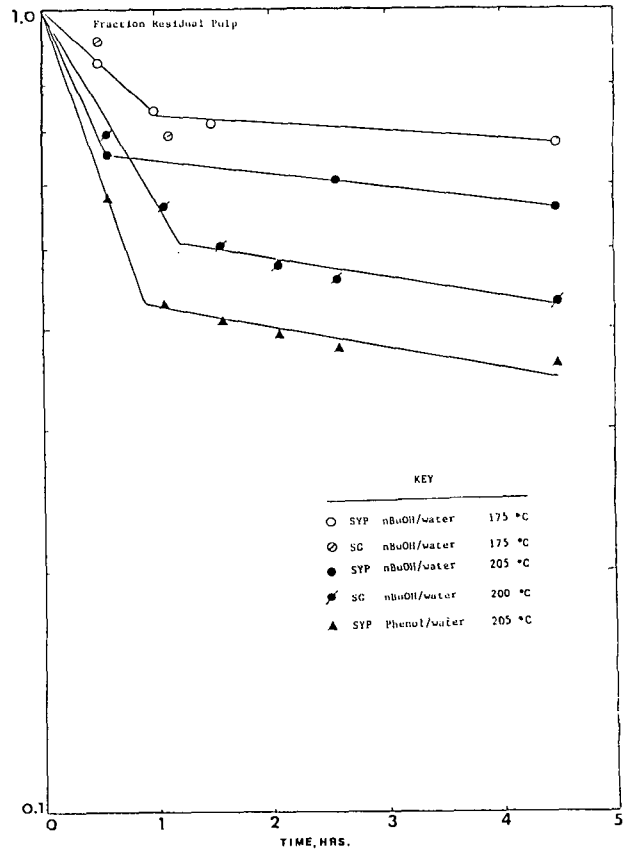


Figure 2. Fraction Residual Pulp vs. Time-at-Temperature for Aqueous Alcohol Delignification of Sweet Gum (SG) and Southern Yellow Pine (SYP).

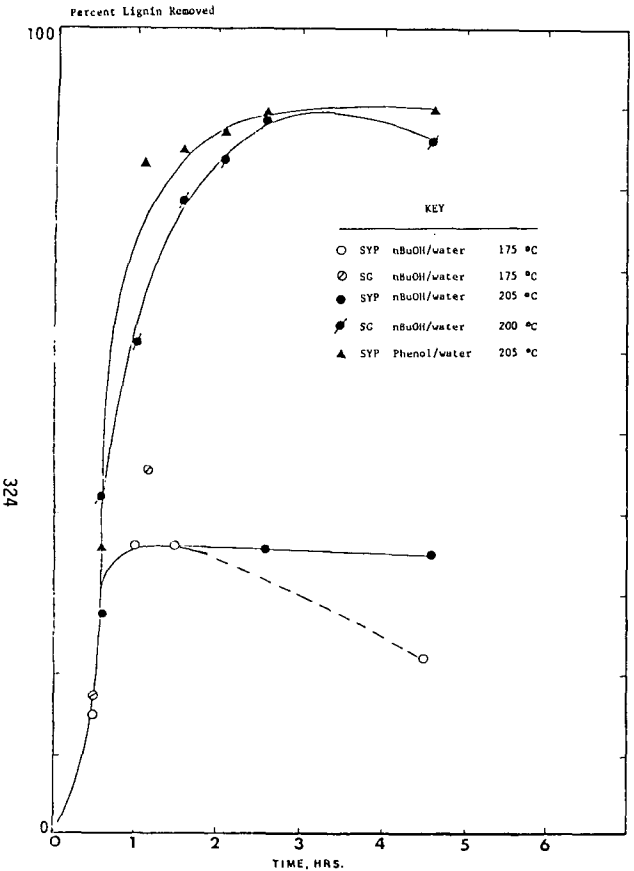


Figure 3. Percent Lignin Removed vs. Time-at-Temperature for Aqueous Alcohol Delignification of Sweet Gum (SG) and Southern Yellow Pine (SYP).

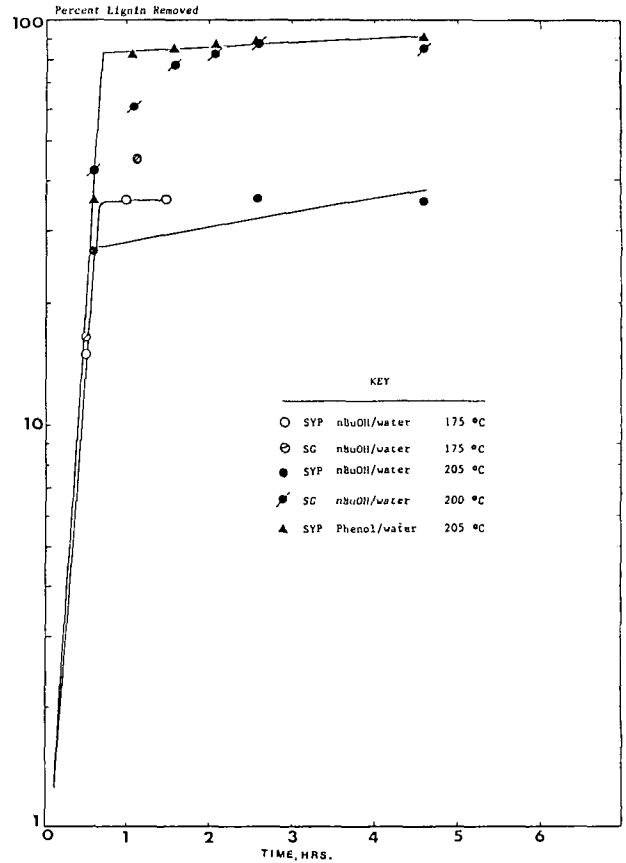


Figure 4. Percent Lignin Removed vs. Time-at-Temperature for Aqueous Alcohol Delignification of Sweet Gum (SG) and Southern Yellow Pine (SYP).

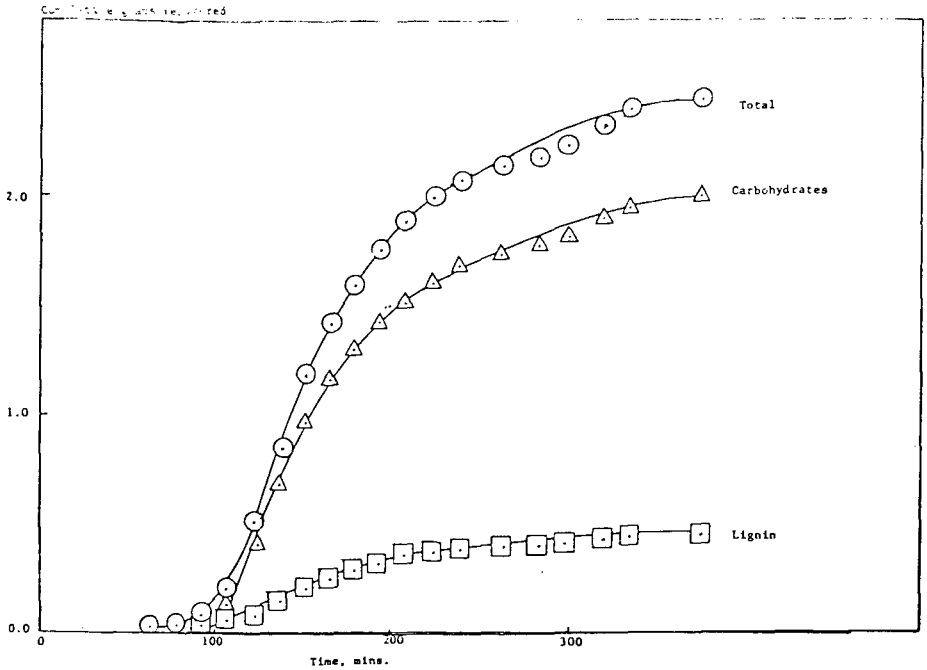
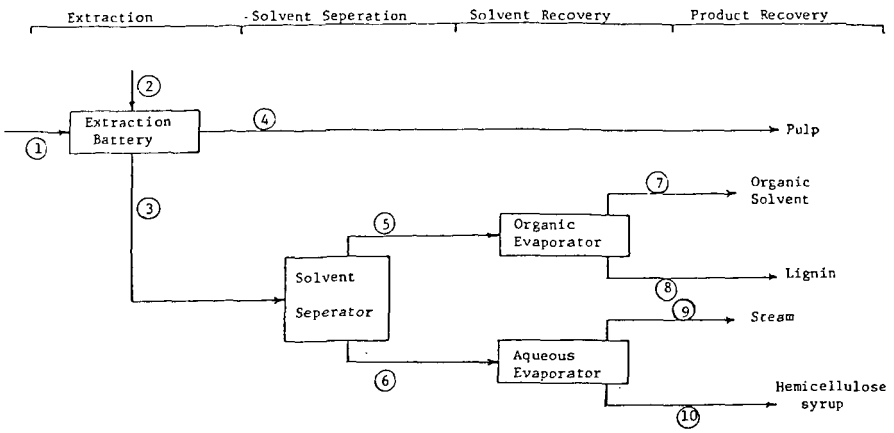


Figure 5. Cumulative Weight of Wood Components Recovered vs. Contact Time in a Semi-Batch System using Aqueous Ethanol as the Delignification Agent at 205°C.



Stream	1	2	3	4	5	6	7	8	9	10
nBuOH (kg)	-	10840	10740	90	9990	750	9910	80	750	-
H_2O (kg)	-	13470	13370	110	2720	10640	2720	-	10450	200
Cellulose (kg)	400	-	-	400	-	-	-	-	-	-
Hemicellulose (kg)	300	-	200	100	-	200	-	-	-	200
Lignin (kg)	300	-	150	150	150	-	-	150	-	-
Total Mass (kg)	1000	24310	24400	850	12860	11590	12630	230	11200	400
Temp (°C)	25	205	205	205	40	40	117	117	100	100
Q kcal x 10^6	0.005	8.89	-	-	0.518	1.064	3.411	0.005	7.144	0.014

Figure 6. Process Schematic for the Aqueous n-Butanol Delignification of Southern Yellow Pine.