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ORGANOSOLV PRETREATMENT

Stuart Black, D. K. Johnson, and Helena L. Chum
Chemical Conversion Research Branch
Solar Energy Research Institute
1617 Cole Blvd.
Golden, Colorado 80401

ABSTRACT

The objective of this task is to explore organosolv pretreatment as an option for fractionation of all biomass components for the conversion of biomass into liquid fuels. Conditions optimal for pulp production differ substantially from those needed to produce digestible cellulosic materials. This report summarizes work carried out in collaboration with several researchers. The areas addressed are: (1) Evaluation of enzyme hydrolysis of organosolv cellulosic residues produced in a batch mode. This work was carried out in collaboration with Prof. H. A. Schroeder and Ms. K. Wallace (Colorado State University), Prof. K. V. Sarkanen (sabbatical leave 1986 at SERI, University of Washington), and with the Biotechnology Research Branch (J. Baker and K. Grohmann). These studies indicated that the cellulosic residues need to contain less than 13% xylan for high digestibility to be realized; similar trends have been observed with dilute acid hydrolysis and steam explosion. This content corresponds roughly to removal of 50% of the original xylan. The kinetics of enzyme hydrolysis is described phenomenologically as composed of two simultaneous pseudo-first order reactions in which fast and slow hydrolyses of cellulose occur. The ratio of fast to slow rate constants is roughly 10. The higher severity pretreatments produced a higher amount of fast hydrolyzable cellulosic residues. (2) Construction and testing of a flow-through delignification reactor for comparative studies between batch and semi-continuous mode of operation and kinetic studies. (3) The evaluation of sulfur dioxide as catalyst for organosolv pretreatment. These studies are being carried out in collaboration with Dr. Vincent Chiang (Michigan Technological University) and his students. Mr. G. Moffitt and Ms. R. Puumala spent one month at SERI to perform experiments in the flow-through reactor with SERI researchers. An empirical model of the effects of process conditions on total hexosan retention, pentosan and lignin removal has been made for birch. Experimental work will continue with Populus species, and other feedstocks of interest to the short-rotation production program managed by ORNL.

ORGANOSOLV PRETREATMENT

INTRODUCTION

Organosolv delignification was originally studied by Kleinert and Tayenthal (1932) and Kleinert (1967, 1972, 1974a, 1974b, and 1977) as a novel method for producing chemical pulps for paper manufacture. Compared to conventional kraft pulping processes, the advantages included substantial reduction in capital costs and higher pulp yields for the same level of delignification. The two broad categories of organosolv processes are catalyzed and uncatalyzed. The catalysts can be acids or salts; base can also be added (see Sarkanen 1980, Aziz 1987 and Paszner 1987 for reviews). Pilot-plant-scale studies are underway using catalyzed and uncatalyzed aqueous ethanol solutions (Lora and Aziz 1985). The ALCELL™ process, formerly of the Biological Energy Corp., will be demonstrated in a 36 ton/day pulp mill by Repap Technologies. Repap Enterprises Inc. of Montreal will build this demonstration mill and start up is expected in 1988 (Pye et al. 1987).

Major efforts are ongoing in Europe, principally Germany, to develop alkaline organosolv pulping technologies (Patt et al. 1987, Feckl and Edel 1987, Nimz 1987). Pilot-scale efforts are in progress in Germany on at least two of the alkaline processes. These demonstration efforts are needed because key issues determinant of the feasibility of these processes are solvent recovery and their complete mass and energy balances. Though bench- and pilot-scale data exist for pulping, they are not sufficient to extrapolate to operating mills. There are still uncertainties as to whether these processes can be applied to a large variety of species. Softwoods are more difficult to pulp than hardwoods by this process.

The ability of the organic/aqueous solvent to selectively extract high yields of the lignin fraction or a combination of lignin and hemicellulosic fractions, principally for hardwoods, the species of main interest to the DOE program, suggests that potentially these processes could be used as a pretreatment for the production of relatively high purity cellulosic substrates for enzyme hydrolysis. Removal of most of the lignin and xylan fractions would facilitate operation of simultaneous saccharification and fermentation digestors because these inert materials would not occupy 30%-40% of the digester capacity; in addition, lignins are potentially capable of affecting the downstream enzyme recycle by adsorption of enzyme components (Himmel et al. in press, Sutcliffe and Saddler 1987).

Initial studies by Holzapple and Humphrey (1984) demonstrated that the ultimate yield of fermentable hexoses after organosolv pretreatment varied over wide limits depending on the acid, salts, and bases used as catalysts. The digestibility of the organosolv cellulosic residues appeared to depend on the content of residual lignin and hemicellulose in the pulps. A systematic study of organosolv delignification kinetics in batch and flow systems has been carried out by Sarkanen and coworkers (Tirtowidjojo et al. in press, Sarkanen 1987, Tirtowidjojo 1984) in the temperature range of 130-210°C using 0-0.05 M sulfuric acid as catalyst. These authors find that the bulk delignification phase follows a pseudo-first order kinetics with a 19 kcal/mol activation energy, suggesting that the cleavage of benzyl ether

linkages is the rate determining step. The rate constant for the flow-through reactor is about twice that in the batch reactor (10:1 liquor-to-wood ratio) because of higher solubilization of organosolv lignins.

In the previous contractor report, we have shown that for organosolv cellulosic residues, the digestibility is enhanced markedly if the xylan content of the cellulosic materials is less than 13%; this number implies that there is a need to remove at least 50% of the original xylan from the hardwood. A similar trend had been previously observed for steam explosion (Brownell 1985, Mackie et al. 1985, Puls et al. 1985) and for dilute acid hydrolysis (Grohmann et al. 1985, Grethlein 1985).

We will report a systematic study of the enzyme hydrolysis rates of organosolv cellulosic materials as a function of severity of the pretreatment in batch reactors (4:1 liquor-to-wood ratio). These results are in the process of publication (Chum et al. in press) and have been presented, along with our initial results using the flow through reactor, at national and international meetings (Chum et al. 1987a, Chum et al. 1987b, Chum et al. 1987c). In addition, we will report on the construction and operation of the flow-through delignification reactor (200-300 g of wood) and the activities on sulfur dioxide catalyzed organosolv pretreatment, carried out in collaboration with Dr. Vincent Chiang and graduate students, G. Moffitt and R. Puumala. Each part will contain a brief description of results and discussion.

RESULTS

Evaluation of Enzyme Hydrolysis Rates of Organosolv Cellulosic Residues as a Function of Pretreatment Severity

Chum, H. L., D. K. Johnson, S. Black, J. Baker, K. Grohmann, K. V. Sarkanen (sabbatical leave at SERI, summer 1986, University of Washington) and K. Wallace and H. A. Schroeder (Colorado State University).

A number of organosolv delignification reactions were carried out with varying amounts of catalysts and reaction times. The ability of the reaction conditions to remove the various polymer components of aspen (Populus tremuloides) is shown in Fig. 1 for representative 2.5 h experiments. Representative plots of the logarithms of the residual unhydrolyzed glucan in enzymatic hydrolysis are shown in Fig. 2. There are two types of behavior distinguishable. The release of glucose from organosolv fibers containing more than 13% residual xylan (<51% removal from original) follows a pseudo-first order reaction (see topmost line from a sample containing 18% residual xylan or in which 31% of the original xylan was removed); this behavior is exhibited by all uncatalyzed residues produced, which had nearly quantitative retention of xylan (see Fig. 1). Similar pseudo-first order behavior was observed by Philipp et al. (1981) for some cellulosic samples with a rate constant of 0.0045 h^{-1} , which doubled upon base treatment. The rate constant calculated for the organosolv samples was 0.0090 h^{-1} (no catalyst, 2.5 h); 0.011 h^{-1} (no catalyst, 7.5 h) and 0.010 h^{-1} (pH 3.2, 2.5 h).

All other curves in Fig. 2, using samples with lower residual xylan concentration, including α -cellulose, the reference material used in these studies, display a kinetic pattern consisting of both a slow and a fast

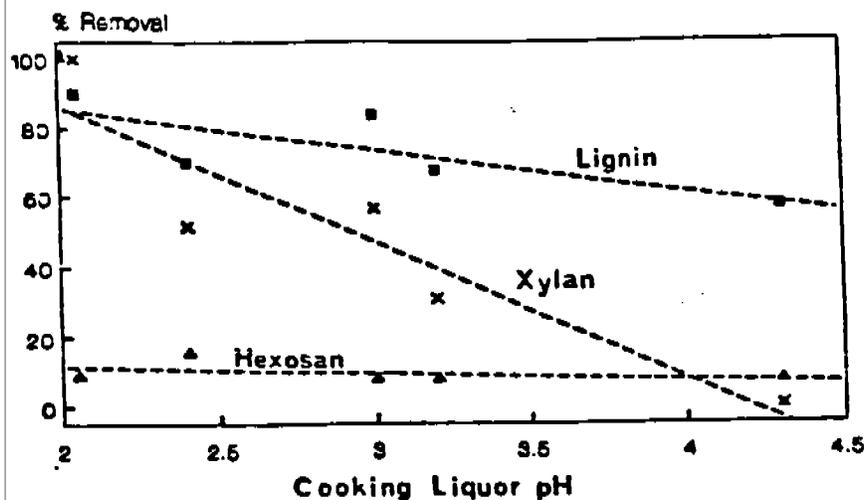


Figure 1. Removal of Hexosan, Xylan, and Lignin in Organosolv Pretreatment of Aspen as a Function of the Cooking Liquor pH at 165°C. Solvent: methanol:water (70:30% by volume).

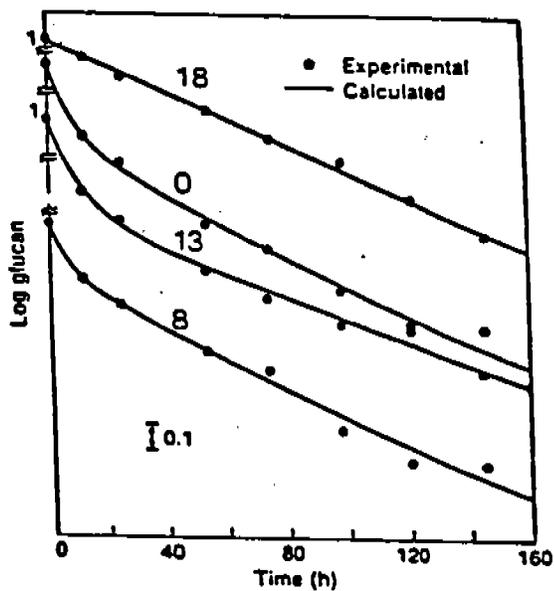


Figure 2. Enzyme Hydrolysis of Aspen Organosolv Pulps Prepared in the Presence of Acidic Catalysts and Compared to α -Cellulose Reference Material. Logarithms of Residual Glucan Concentration are Plotted as a Function of Time. Points are some of experimental data; lines or curves are calculated. Residual pulp xylan content is indicated by numbers on the curves.

phase of hydrolysis. The curves of Fig. 2 were calculated assuming two simultaneous pseudo-first order reactions using the Simplex Algorithm (Caceci and Cachieris 1984). The fast hydrolysis rate constant is about $.2 \text{ h}^{-1}$. The fraction of fast hydrolyzable material varies between 20% and 45% (samples with residual xylan concentration lower than 13%; otherwise, the fraction of fast hydrolyzable cellulose is zero). The more severe the pretreatment conditions, the higher is the amount of fast hydrolyzed material. There is also an increase of the rate of slow hydrolysis as the severity increases. For instance, in the series shown in Fig. 2, with pH 2.05, the fast hydrolysis fraction is 45% of total and the rate of slow hydrolysis is 0.017 h^{-1} ; this number is somewhat higher than the rates of slow hydrolysis above. Plotting the fraction of fast hydrolyzable material as a function of residual pulp xylan one obtains a sigmoidal-shaped curve, similar to that shown by the digestibility plots as a function of residual pulp xylan content. Above 13% residual xylan, the fast hydrolyzable fraction approaches 45%, and at 18%-29% residual xylan the fraction is zero.

It is interesting to note the similarities and differences between cellulose enzymatic and heterogeneous acid hydrolysis. Similar phenomenological equations describe both hydrolyses. While in the cellulose heterogeneous acid hydrolysis case (Saeman 1945) the fraction of fast hydrolyzable material is about 10%-15% and corresponds roughly to the accessible amorphous cellulose, the fraction of fast hydrolyzable material varies between 0% and 45%, depending on the pretreatment severity in the cellulose enzymatic hydrolysis. In the heterogeneous acid hydrolysis of cellulose, the rate constant for fast hydrolysis is about 100 times the rate constant for the slow phase. In cellulose enzymatic hydrolysis, the ratio between fast and slow rates of hydrolysis is about ten. Rates constants of the slow phase of hydrolysis vary by a factor of 15, depending on the cellulose sample preparation in the acid hydrolysis case. In the organosolv samples investigated, only about a factor of two difference is seen in the rate constant for the slow hydrolysis.

Many other samples have been analyzed, and the complete set of data is in press (Chum et al.). This kinetic analysis is very simple and it could be used to guide pretreatment optimization.

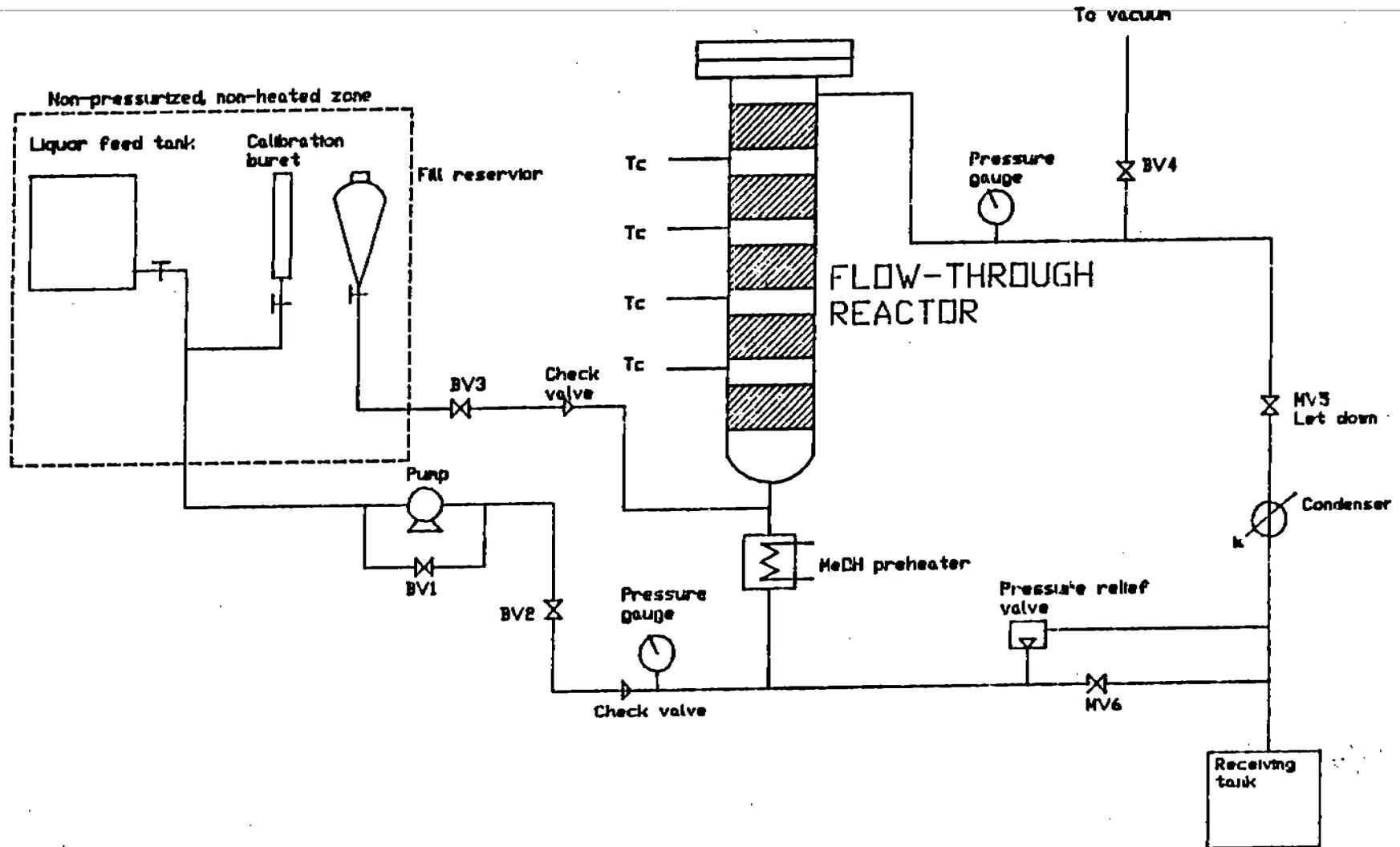
Construction and Testing of a Flow-Through Delignification Reactor for Comparative Studies Between Batch and Semicontinuous Mode of Operation and Kinetic Studies

S. Black, D. K. Johnson, and H. L. Chum with the cooperation in the design phase of P. Bergeron (Biotechnology Research Branch).

The schematic of the single pass flow-through delignification reactor which was assembled and tested during this period is shown in Fig. 3. Wood chips (180 g OD equivalent) were placed in a stainless steel mesh basket, loaded into the reactor, and thermocouples were inserted into the chip bed. The lowest thermocouple (Tc 4) was inserted into a bed of stainless steel nuts used as a chip bed support and liquid distribution bed. After the reactor was sealed, the vessel was evacuated for 30 min, after which the reactor was filled with cold liquor and the heaters were turned on. Heatup time for the reactor from 20°C to pulping temperature (165°C) was 45 min. Pressure in the reactor was allowed to rise to 380 psi which was regulated by a spring-loaded relief valve.

Figure 3. Schematic of Flow-Through Delignification Reactor

SEMI-CONTINUOUS ORGANOSOLV SYSTEM



During batch experiments, the reactor was kept sealed during the pulping time. For continuous experiments, a metering valve (MV⁴) was opened and the pressure regulated to 300 psi. The liquor was pumped through the chip bed by means of a piston pump at a flow rate that allowed for a liquid residence time of 40-70 min. Washes for both types of operations were made by flowing liquor, without catalyst, through the chip bed so it would also have a residence time of about 40-70 min. During the wash, all heaters were turned off with the exception of the methanol preheater and the bottom-most band heater. At the end of the wash, the liquor was drained off through MVS and collected in the receiving tank. The reactor was cooled to near ambient temperature, the chips removed, fiberized in a blender, filtered, and air dried.

A number of organosolv pulping experiments were carried out on aspen (Populus tremuloides) to test the reactor behavior in either batch mode with continuous wash or semicontinuous mode. A 50:50 (by volume) methanol:water solution was used for pulping and wash liquors; a range of pulping temperatures of 162^o-175^oC; pulping times of 1.0 to 1.5 h, and liquor-to-wood ratios of 7:1 to 16:1. Pulps were made in both types of reactor using either no catalyst or mineral acids such as H₂SO₄ or H₃PO₄ as catalysts. Table 1 gives the pulping conditions, analyses of the pulps, and pulp yields for selected experiments.

The liquor was fractionated in the following manner. After neutralization with NaOH and volume reduction (to near dryness) under reduced pressure at temperatures of less than 40^oC, acetone was added. The carbohydrates were precipitated from acetone and collected by filtration. The acetone-soluble fraction contains lignin-carbohydrate complexes which were isolated by evaporation of the solvent and vacuum drying. Total mass balance for the continuous-mode experiments ranged from 97% to 102% of the original feedstock (pulp + acetone insoluble + acetone-soluble-derived materials). The dried acetone-soluble fraction was washed in water (5:1 liquor-to-solids ratio) overnight and frozen. After thawing, the crystalline precipitate was easily filtered and washed with approximately an equal volume of water. The yields of the water-insoluble lignins (or lignin and residual carbohydrate for H₃PO₄ experiments) are also shown in Table 1. It is more difficult to remove carbohydrates from the lignin-carbohydrate complexes from the experiments with phosphoric acid catalyst than from sulfuric acid catalyzed samples.

Table 1 illustrates the effect that batch versus continuous pulping in the flow-through reactor using 50% methanol has on lignin removal. In the case of continuous operation, lignin removal is significantly increased over batch operation, while removal of the hemicellulose remained nearly the same for both cases. This can also be observed in the no catalyst cooks at 170^o to 175^o and 1.0 to 1.5 h pulping time.

Glucan digestibility tests were performed by R. Torget (Biotechnology Research Branch) on representative samples of organosolv pulps described in Table 1. The digestibility versus organosolv cellulosic xylan content curve shows that below about 14% xylan the digestibilities are in the 90%-100% range (98 h tests). At lower levels of removal of xylan, the digestibilities are in the 50%-80% range. These data confirm those obtained in the batch mode (Chum et al. in press).

Table 1. Summary of Organosolv Experiments at 50% Methanol Concentration
(C = continuous operation; BC = batch operation and continuous wash)

Catalyst	Reactor Operation T, °C	Lignin Free Yield, % Original	Lignin Removal % Original	Pulping Liquors		Mass Balance Closure
				Isolated Acetone- Soluble, % Original (% Isolated Original Lignin) ^c	Isolated Acetone- Insoluble % Original (Carbohydrate)	
None ^a	175	53.8	72.3	18.4	18.9	97
None	162	68.8	45.5	8.4 (25)	11.1	100
None ^a	175	58	-70	ND	ND	ND
None ^b	170	61	-60	ND	ND	ND
0.01M H ₂ SO ₄ ^b	163	50.1	80.9	36 (75)	11.6	102
0.01 M H ₂ SO ₄	165	46.6	89.6	39.4 (90.7)	14.7	102
0.075M H ₃ PO ₄	165	48.8	88.9	44.4 (126)	8.83	104
0.075M H ₃ PO ₄	166	49.2	89.8	50.8 (130)	14.4	116
0.025M H ₃ PO ₄	166	51.7	86.4	38.3 (126)	15.1	108

^a1.5 h residence time. All others are 1.0 h cooks.

^bBatch cook with continuous wash.

^cNumber in parentheses is % yield of lignin present in the wood after washing in water.

This work continues with the kinetics of batch versus semicontinuous operation and the analyses of the intermediate dissolved polymers. Liquor samples have been collected as a function of time during pulping experiments and are being subjected to detailed chemical analyses. The order of polymer dissolution is an important parameter in understanding the process as well as what is the composition of these polymers as they dissolve. The detailed analyses of liquors as a function of time may identify the α -benzyl ethers that are responsible for delignification (most likely lignin-hemicellulose ether and lignin-lignin α -ether bonds). Results of Tirtowidjojo et al. (in press) seem to indicate that the molecular weights of the polymers obtained from the flow-through mode reactor are higher than the corresponding batch. Also, in the continuous operation, it is more likely that soluble carbohydrate and lignin degradation reactions can be minimized. Techniques such as high field NMR and high performance size exclusion chromatography will be investigated coupled with detailed chemical analyses using both HPLC and GC sugar determination methods, and the techniques described for lignin analyses (see Lignin Characterization - a Progress Report in this proceedings).

The Evaluation of Sulfur Dioxide as Catalyst for Organosolv Pretreatment

H. L. Chum, S. Black (SERI) and G. Moffitt, R. Puumala, and Vincent Chiang (Michigan Technological University)

Dr. Vincent Chiang (Michigan Technological University) presently has a program, funded by the State of Michigan, to develop a sulfur dioxide pulping process for hardwoods and softwoods. Last year Drs. Chiang and Chum decided to begin a collaborative effort. The original data obtained at Michigan were with pulping processes in mind; we try to derive the conditions that are best suited for the development of a fractionation scheme to produce liquid fuels. Dr. Chiang, chemical engineer, and graduate students G. Moffitt and Ms. R. Puumala have been performing experiments with the set up described above, using sulfur dioxide catalyst and varying solvents (methanol, ethanol) as well as the species under investigation (many hardwoods and softwoods). At SERI, the species investigated so far were aspen, spruce, and one run on whole-tree black locust chips.

Chiang et al. (1987) have obtained an empirical model of the effects of process conditions on pulp yield, kappa number, and pentosan content for birch and spruce. Kappa number is a measure of residual lignin in a pulp. It is determined by lignin oxidation by the excess permanganate for a fixed amount of time, followed by reduction of excess with iodide and titration of generated iodine with thiosulfate. Kappa numbers correlate with Klason lignin contents linearly with a factor that depends on species (see Lignin Characterization - a Progress Report in this Proceedings). Techniques such as linear regression modeling and response surface methodology have been employed (see Box and Wilson 1951). All data obtained at Michigan were on small-scale batch reactors, with a liquor-to-wood ratio of 6:1. The independent variables studied were temperature (proportional to X_1), time at temperature (inversely proportional to X_2), alcohol content (proportional to X_3), and SO_2 concentration (proportional to X_4). The run conditions were chosen according to a central composite experimental design (see Box and Wilson 1951, Box, Hunter and Hunter 1978). These correlations apply to a wide range of conditions: 125^o-155^oC, times at temperature of 50-135 min,

methanol concentration of 30%-75% by volume, and SO₂ concentration varying in the range of 0.3%-1.7% by weight) (Chiang et al. 1987).

For birch, the pulp yields corrected for the lignin content, the so-called lignin-free yields (LFY) can be described as:

$$\begin{aligned} \%LFY = & 47.6 - 5.6X_1 + 2.0X_2 + 2.4X_3 - 1.2X_4 + 1.3X_1^2 - \\ & -1.5X_2^2 + 0.7X_4^2 - 0.6 X_1X_2 - 1.2X_1X_3 + 0.6 X_1X_4 \end{aligned}$$

with a correlation coefficient (R²) of 0.98. The key variable determinant of yield is temperature followed by effects of alcohol, time at temperature, and catalyst concentration in decreasing order of importance. Quadratic terms and other interaction terms are somewhat important.

The residual lignin concentration measured by the kappa number generated the following model:

$$\begin{aligned} KAPPA = & 40.8 - 6.1X_1 + 4.9X_2 - 8.1X_3 - 9.0X_4 + 10.0X_1^2 + \\ & +8.9X_3^2 - 3.5X_1X_2 - 9.1X_1X_3 + 3.8X_3X_4 \end{aligned}$$

with a correlation coefficient of 0.89. The residual lignin content depends primarily on the catalyst concentration followed by alcohol concentration, temperature, and time at temperature. The two quadratic terms on temperature and alcohol concentration are important as well as the product of the interaction of the two.

At SERI, with G. Moffitt, we utilized the software Statgraphics to recalculate these data in terms that are more meaningful to producing a cellulosic residue rich in hexosans and containing less than 13% by weight of pentosans. The data were expressed in terms of total hexosans yield (THY):

$$\%THY = \text{total pulp yield} - \text{residual lignin} - \text{pulp pentosan content} - (\text{extractives and other components})$$

The model generated was:

$$\%THY = 86.7 - 7.9X_1 + 2.7X_2 + 3.8X_3 - 1.8X_4 - 3.0X_1X_3 + 1.8 X_1X_4$$

with a correlation coefficient of 0.88. The total hexosan yield depends most strongly on temperature, followed by alcohol concentration, followed by time at temperature and then SO₂ concentration; quadratic terms which were important in the previous correlations, are not important for THY but the interaction terms between temperature and alcohol concentration and time at temperature and catalyst concentration appear important.

Overplots for a few representative conditions of constant hexosan yields in the 75% to 100% range which contain less than 13% pentosan are shown in Fig. 4. From Fig. 4a, 53 min at 130°C, with 0.5% of SO₂, and at roughly 53% methanol concentration, one could reach 100% hexosan recovery with a 12% pentosan content. To reach lower levels of pentosan levels, the temperature could be increased, but substantial hexosan losses would result.

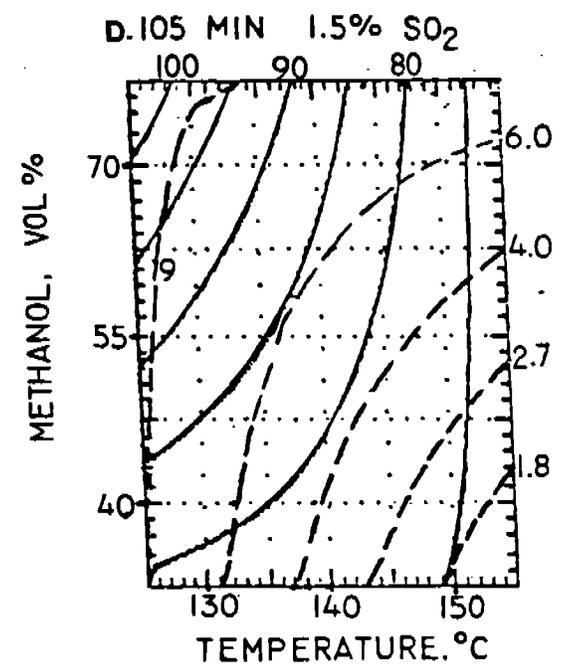
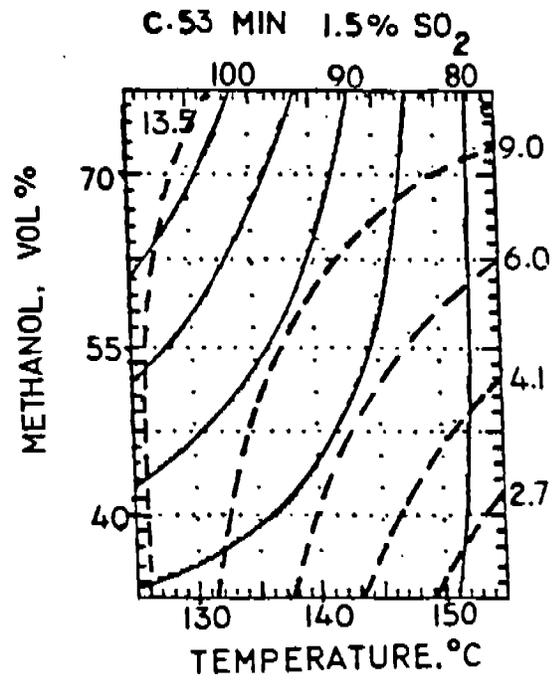
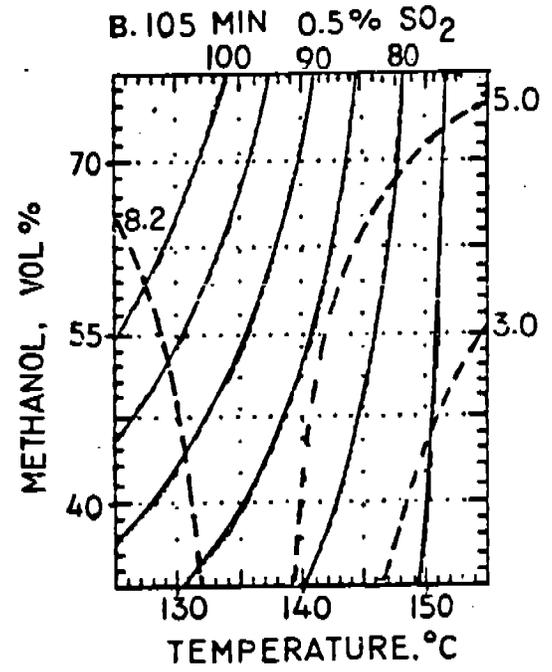
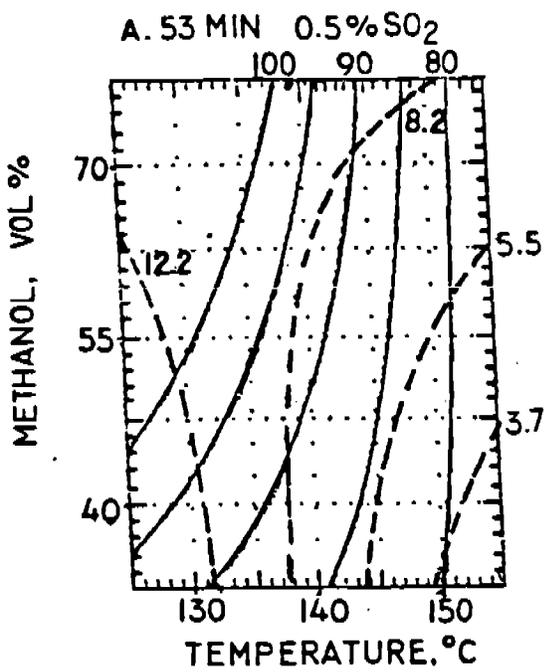


Figure 4. Birch Organosolv Pretreatment as a Function of Temperature, Time at Temperature, Alcohol Concentration, and Sulfur Dioxide Catalyst. ——— represents total hexosan yield in the 75-100% range. - - - represents wt % of pentosan remaining in the pulp.

The lines should be viewed as having about $\pm 5\%$ error. A 3-fold increase in catalyst concentration would reach the desired conditions of total hexosan recovery with under 13% pentosan at about 126°C and 62% alcohol (Fig. 4b) in 53 min. Again, the same trend observed before can be seen. In order to increase removal of pentosan, the hexosan losses become more substantial. If time at temperature is increased by a factor of 3 at 0.5% catalyst, the resulting contour plots are shown in Fig. 4c. The conditions for best hexosan yield at 8% pentosan are 58% alcohol and near 130°C in temperature. As in the previous plots, substantial losses of hexosans can occur in order to reduce the level of pentosans, in agreement with the data in Fig. 1. Higher catalyst concentration (Fig. 4d) does not improve achieving both high hexosan and low pentosan yields without substantial loss of hexosan.

We are continuing to analyze this type of information with canonical analyses (Box, Hunter and Hunter 1978) to define better the optimum operating conditions, and select values of the independent variables which are going to be used in the experimental work.

A total of six experiments were carried out using the flow-through reactor with aspen and sulfur dioxide catalyst, beginning the experimental design described above. These runs continue to be performed by SERI staff. In addition, ten experiments were performed with spruce, completing a part of a central composite experimental design which will be continued in January, when G. Moffitt and R. Puumala will return to SERI to complete the experimentation on spruce and perform more data analyses. Table 2 shows the type of experimental results generated with sulfur dioxide catalyst.

An important accomplishment was the development of an amperometric method of SO_2 concentration determination in the presence of methanol. Direct titration using starch indicators does not work in the alcoholic medium because of changes in the association constant responsible for the iodine-starch color. The method employed is an amperometric titration using two platinum electrodes to which a 50 mV potential is applied. Addition of the titrant iodate leads to no current changes until all the sulfur dioxide has been reacted. At this point, there is a major current increase and the titration is stopped (a dead-stop titration). The titration can also be used to determine the concentration of sulfur dioxide in the pulping liquors in the presence of lignins. Because of the low applied potentials, lignins do not interfere with the determination.

FUTURE WORK

Organosolv pretreatment will continue to be investigated. Emphasis will be given to sulfur dioxide as catalyst as well as to the understanding of the delignification reactions in the flow-through reactor. We will continue to obtain mass balances for typical conditions of the process, and work on the isolated fractions and their characterization. The nature of the complexes between lignin and carbohydrates generated in these processes will be investigated and the kinetics of the process. Experimental designs such as the composite previously employed will be used on a well defined clone of Populus species, to be selected by ORNL. This clone will be used in most of the ORNL hybridization studies with other poplars.

Table 2. Summary of Experimental Conditions and Runs Performed in the Flow-through Delignification Reactor (Liquor-to-Wood -8:1).

Run	Mode	Temp. ($^{\circ}\text{C}$)	Time (min)	SO ₂ (wt %)	MeOH (v %)	Kappa	LFY %
ASPEN							
1	flow	130	70	0.2	40	72.3	60.1
2	batch	130	70	0.5	40	62.9	57.8
3	flow	130	55	0.5	40	65.7	53.5
4	flow	130	70	0.5	40	56.8	50.7
5	flow	130	70	0.5	30	66.6	51.3
6	batch	130	70	0.5	30	83.3	54.7
SPRUCE							
7	flow	155	53	1.5	65	69.2	44.9
8	flow	165	105	1.5	65	26.6	41.2
9	flow	165	53	3.5	65	28.4	42.6
10	flow	165	105	3.5	65	30.7	39.4
11	flow	165	53	3.5	65	47.9	41.2
12	flow	160	70	2.5	70	27.6	40.9
13	flow	165	53	1.5	65	30.5	41.4
14	flow	155	105	3.5	65	17.6	41.9
15	flow	155	105	1.5	65	38.2	43.4
16	flow	155	53	3.5	65	20.9	44.1

ACKNOWLEDGEMENTS

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