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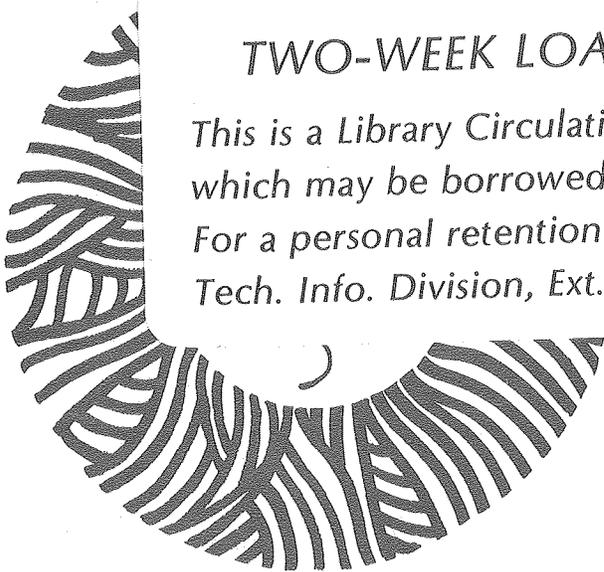
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PRETREATMENT OF BIOMASS PRIOR
TO LIQUEFACTION

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ABSTRACT

The hydrolytic pretreatment of wood flour (prepared at Albany from Douglas Fir chips) using 500 ppm sulfuric acid is sometimes ineffective because neutralization of acid occurs during the reaction. This phenomenon has been investigated and is tentatively ascribed to the presence of base-forming impurities. The problem can be overcome by using higher concentrations of acid, e.g., 1000 ppm. The final concentration of insoluble solids in a pretreated wood slurry prepared from a 1-to-4 mixture of wood-to-water is about 15%. The solids in these pretreated slurries settle at rates on the order of 10^{-2} ft/sec. These slurries are therefore still unsuitable for pumping in a slow, laminar flow system such as the one at Albany. However, two options for retarding settling appear promising. In the first, the pretreated slurry is homogenized by blending with air using a high speed mixer. In the second, a pretreated slurry prepared from chips is passed through a conventional disc refiner. This report focusses on the problem of pH control.

BACKGROUND

The technical feasibility of pumping concentrated slurries of wood flour in carrier oil at the Albany, Oregon, wastewood-to-oil facility remains in question. Therefore, the investigation of wood pretreatment options for the purpose of providing pumpable slurries has been continued. Previous work showed that acid prehydrolysis might be feasible as an alternative to the costly drying and grinding operations required to produce wood flour. This quarter's work proceeded on two main fronts: (1) control of pH during the course of acid-catalyzed hydrolysis; (2) correlation of the bulk properties of prehydrolysis slurries with the behavior of such slurries under actual pumping conditions. Pumpability studies are at a preliminary stage--these findings will be discussed in a companion report.

The conditions specified by LBL for prehydrolysis were as follows: a 23% slurry of wood chips (o.d. basis) in aqueous sulfuric acid (500 ppm; pH 2.0) is heated at 180°C for 45 minutes with vigorous agitation. This should result in extensive size degradation and fiber scission. Those wood chips not disintegrated become friable, readily crumbled between the fingers.

In early August, Rust Engineering at Albany, reported that they had been unable to reproduce our results. We inspected a sample which they made available and confirmed that the reaction conducted in their 350-gal. pretreater had been incomplete. Some size degradation had occurred, but the mass of chips showed little discoloration or structural weakness.

In probing possible causes for the difference in results, we noted that the final pH of the aqueous phase of the sample provided by Rust was on the order of 3.0. That is, the final hydrogen ion concentration was an order of magnitude smaller than that required. Since the rates of hydrolysis of hemicellulose and cellulose are first order in hydrogen ion concentration, it seemed clear that the difficulty was connected with control of pH.

RESULTS

A series of hydrolysis experiments were conducted using wood flour (OF) and wood chips (OC) received from Albany in late 1978 and wood flour (NF) received in August, 1979. All wood flour had been prepared at the Albany facility from Douglas Fir wood chips. The first set of experiments used aqueous sulfuric acid, pH 1.98, taken from a common source. Results are shown in Table I.

Table I

Hydrolysis of Douglas Fir in Dilute Aqueous Sulfuric
Acid at an Initial pH of 1.98

<u>Rx</u>	<u>Feedstock</u>	<u>Heatup Time, min</u>	<u>Final pH</u>
HP-12	NF	60	2.39
HP-13	NF	60	3.38
HP-14	NF	23	2.43
HP-15	OF	23	2.38
HP-16	NF	23	2.45
HP-18	OC	38	2.17

Initial conditions: 20% solids, pH 1.98. Reaction
conditions: 45 min at 180°C. Feedstock: NF = wood flour
(1979), OF = wood flour (1978), OC = wood chips (1978).

These results indicate that the pH of the hydrolyzate increased in every case.
The degree of neutralization of the original acid ranged from 35-96%.

A second series of experiments was conducted in which the initial pH was varied
from 1.02 to 1.98. These results appear in Table II.

Table II

Hydrolysis of Douglas Fir Wood Flour at
Various Concentrations of Dilute Sulfuric Acid

<u>Rx</u>	<u>Initial pH</u>	<u>Final pH</u>	<u>Equiv's of Acid Neutralized per Liter</u>	<u>% Solids Recovered</u>
HP-23	1.02	1.17	.028	67
HP-19	1.20	1.22	.003	71
HP-20	1.37	1.44	.006	73
HP-21	1.60	1.68	.006	77
HP-22	1.79	2.01	.006	82
HP-16	1.98	2.45	.007	83

Initial conditions: 20% solids (NF). Heatup times, 23-25 min. Reaction conditions: 45 min at 180°C. Reactor: 250-ml Parr bomb.

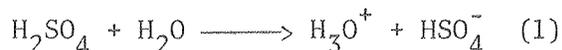
Based on these results, it appears that for the particular batch of wood flour tested, an initial pH of 1.8 suffices to give the desired degree of pretreatment. It was also found that the amount of reducing sugars in the aqueous phase of HP-23 was half that found in HP-16. Thus extensive sugar degradation occurs under the more severe conditions.

DISCUSSION

No attempt has been made to identify the base produced during acid hydrolysis or even to determine its origin, whether intrinsic or extraneous. Nevertheless, several issues have been resolved as a result of this investigation.

One issue that surfaced during discussions with Rust personnel concerned the preparation of sulfuric acid solutions. LBL made up solutions to a pH of 2.0. Rust-Albany added the calculated amount of sulfuric acid (500 ppm) to water. However, the so-called calculated amount gives a hydrogen ion concentration of 8×10^{-3} moles/liter, 20% less than that of a pH 2.0 solution.

The discrepancy is small but significant. It arises, we believe, because the assumption (made by both LBL and Rust) that sulfuric acid is completely dissociated in dilute aqueous solution is incorrect. The second ionization of sulfuric acid is incomplete, having an ionization constant of 0.012. Thus:



When this is taken into account, the calculated concentration of sulfuric acid for a pH 2.0 solution, neglecting activity coefficients, becomes approximately 650 ppm.

Regarding the matter of the unexpected rise in pH during hydrolysis, we suspect the cause to be an adventitious base-forming impurity. This would explain the discrepancy in final pH values of duplicate runs HP-12 and HP-13 on the basis of unequal distribution of the extraneous substance. Also, if the rise were due to components of ash, the pH of an aqueous slurry would be expected to increase upon boiling. The opposite effect is observed and this probably is due to the hydrolysis of uronic and acetic acid-forming groups. The source of base could be a neutral substance such as urea which hydrolyzes slowly to give ammonia. However, there are other explanations which can not be eliminated at this time.

The important point here is that solutions of strong acids at pH 2.0 are so dilute that it takes very little basic impurity to increase the pH to the point where the pretreatment becomes ineffective. Thus for the general application of hydrolytic pretreatment to biomass feedstocks, higher acid concentrations are desirable.

The goal of pretreatment is the production of a concentrated, pumpable slurry. A hydrolytically pretreated wood slurry is several orders of magnitude less viscous than a slurry of untreated wood flour of the same concentration and therefore "appears" to be more "pumpable." Pumpability, however, must be referenced to the particular pumping system to be used and depends among other things on available pumping flow rates. Specifically the velocity of an upward flow system must be sufficient to keep the particles of a slurry in suspension, that is, to overcome settling due to gravity.

The settling rates of several pretreated wood slurries have been measured and found to be on the order of 10^{-2} ft/sec. Since settling rate varies only as the square root of particle diameter and since the rates measured are still much too high to be accommodated by the flow capability at Albany, it appears that further reduction of particle size will not solve the problem. Therefore we are starting to investigate several options involving additional processing.

DISC REFINING

Pretreatment under the comparatively mild conditions specified above leaves a significant fraction of particles which are too large to pass a 40-mesh screw. These larger particles could be screened and returned to the hydrolyzer in a batch operation. An alternative scheme, which lends itself to a continuous process mode, is to pass the entire slurry through a disc refiner of the type used in the paper industry for defibration and thermomechanical pulping.

We tested this process option using a Bauer benchscale refiner equipped with a manual feed. We found that screened, pretreated chips are readily defibrated in one pass. A second pass results in a concentrated slurry that, although fibrous, shows little tendency to settle. Several barrels of pretreated chip slurry from Albany are scheduled to arrive shortly. This will enable us to produce disc-refined slurry in sufficient quantity to permit pumpability tests.

HOMOGENIZATION

We have discovered that the vigorous mixing of pretreated wood slurries produces homogenized suspensions of solid, liquid and air that show no tendency to settle. The behavior of these systems is described in a companion report.

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