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PRETREATMENT OF BIOMASS PRIOR TO LIQUEFACTION

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ABSTRACT

Pretreatment of biomass prior to liquefaction was proposed by the Bureau of Mines as an optional procedure for injecting biomass into high pressure vessels. In the Bureau of Mines process the purpose of pretreatment was to change the rheological properties of biomass so that biomass flour/oil slurries containing up to 50 percent treated biomass could be injected into high pressure vessels. Lawrence Berkeley Laboratory researchers investigated the rheological and chemical changes occurring upon pretreatment of wood and conceptualized a process scheme in which wood chips are hydrolyzed under mild conditions to obtain a concentrated aqueous slurry that can be directly injected into the liquefaction system without a carrier oil.

This presentation deals with the results of the LBL studies on pretreatment of biomass prior to liquefaction and the process conceptualized at LBL.

BACKGROUND

In the Bureau of Mines-Albany biomass liquefaction scheme, wood is converted to oil by treating with carbon monoxide and aqueous sodium carbonate catalyst at elevated temperatures and pressures. Some of the major developmental difficulties encountered at the Albany 3 TPD facility have arisen in connection with the front end of the process where wood chips must be reduced to a form capable of being pumped into the reaction system. This paper describes the current status of research directed toward the development of chemical alternatives to drying-and-grinding for the purpose of wood preparation.

The original process design called for green wood chips to be dried, milled to a -50 mesh flour and then slurried with vehicle oil at a solids concentration of 30%. However it has proved impossible to pump a 30% slurry. Slurries of 20% solids have been pumped with some difficulty but most of the development work at Albany has been restricted to concentrations of 10%. The question is critical since the economic feasibility of the process hinges on being able to inject solids at the 30% level. It is clear that the lower the concentration of biomass in the feed to the reaction system, the larger the plant size for a given production rate.

In addition to difficulties encountered in pumping concentrated slurries of wood flour, there is also the expense involved in drying and grinding. An

economic analysis showed that 22% of the cost of product oil would be attributable to these operations.

That the potential for such problems existed had been recognized early. One option considered by the Bureau of Mines was chemical pretreatment. The basic idea was to subject wood chips to partial carbonization in order to increase their bulk density and thereby favorably alter the rheological properties of the slurry feed. It was hoped that, after drying and grinding, the resulting powder could be slurried at concentrations as high as 50%. An engineering data base for pretreatment was prepared by BOM and two pretreatment reactors were designed and installed at Albany.

In the BOM pretreatment technique wood chips and water (30/70)* are heated to 500°F and 700 psig for 60 minutes. After cooling, the solids are separated by vacuum filtration, dried and pulverized to -50 mesh, mixed with recycle oil and injected into the liquefaction loop.

The results of four pretreater test runs conducted at Albany were generally unsatisfactory. First, the filtering system in the plant was underdesigned and did not perform properly. Product solids proved unexpectedly difficult to dewater; drying and grinding presented additional difficulties. It appeared that new approaches to the problem were needed.

LBL PROCESS DEVELOPMENT

Several pretreatment runs were conducted by LBL on a small scale, duplicating the conditions used at Albany. Significantly, it was found that the carbohydrate fraction of the wood was almost entirely destroyed under these conditions; the product analyzed as a dehydrated char. In our view this was a serious shortcoming since carbohydrates have been shown to liquefy readily under BOM/Albany conditions, whereas chars typically are intractable.

On the other hand we noted that extensive size degradation occurred in the course of pretreatment, and we reasoned that it might therefore be possible to eliminate filtration, drying and grinding

*Plant practice established 23% solids as a more manageable concentration.

altogether. Thus a new goal for the development of a pretreatment process was established: to produce, with no sacrifice of the original heating value, a concentrated slurry of biomass capable of being pumped directly into the liquefaction system. A five-point process development plan was formulated for the purpose of guiding the overall research effort:

1. research chemical pretreatment methods
2. research
 - a. size degradation efficiency
 - b. rheological properties of solids
3. research liquefaction of treated biomass
4. obtain data base for large scale test run at Albany
5. conceptualize a process.

CHEMISTRY OF PRETREATMENT

Initial guidance as to research direction was provided by an examination of the chemical composition of Douglas Fir (*Pseudotsuga menziesii*), the predominant species in the Albany area (Table 1).

Table 1. Composition of Douglas Fir (moisture free)

Cellulose	41%
Hemicellulose	26
Lignin	28
Uronic anhydride	3
Ether-soluble extractives	1.0
Acetyl	0.6
Ash	0.3
	99.9

Cellulose and hemicellulose, comprising the carbohydrate fractions, should be preserved, either as such, or in the form of their constituent sugars which are liberated upon hydrolysis. Lignin, a three-dimensional matrix of oxygenated phenylpropane units, accounts for most of the remainder.

The conditions specified by the Bureau of Mines are apparently too severe since they result in charring and destruction of carbohydrate. Milder conditions require the use of a catalyst. Obvious catalysts are acids or bases. In aqueous media the polysaccharides undergo hydrolysis catalyzed specifically by hydrogen ion. Mild acid conditions, for example 0.05% sulfuric acid at 140-180°C, suffice to hydrolyze hemicellulose to give (in the case of Douglas Fir) mannose, glucose, xylose, galactose and arabinose in the ratio of about 10:4:2:2:1. More severe acid conditions promote the liberation of glucose from cellulose but simultaneously cause the degradation of the more readily liberated hemicellulose sugars [1]. Cooking with strong aqueous sodium hydroxide, on the other hand, results in the partial solubilization of lignin as in the well-known but antiquated "soda process" for the manufacture of wood pulp. Thus either acid or base might conceivably be used to chemically disrupt the

structural integrity of wood chips in order to realize the objectives of pretreatment.

RESULTS OF CATALYTIC PRETREATMENT

Sodium Hydroxide

It would be desirable to effect pretreatment under basic conditions since subsequent liquefaction also requires basic catalysts. Furthermore the effect of concentrated base is to break down and solubilize the ligneous fraction. This might be important because there is evidence to indicate that native lignin is resistant to the conditions of liquefaction.

It was found that treatment with 20% sodium hydroxide at 356°F for 60 minutes, conditions somewhat more severe than those used in the pulp and paper industry, leave the fibers of cellulose intact and give rise to viscous slurries characteristic of wood pulp. Since these slurries appeared unsuited for liquefaction, further research on basic pretreatment has been suspended.

Dilute Aqueous Mineral Acid

More promising results are obtained in the case of mild acid hydrolysis accompanied by vigorous agitation. Conditions have been found which result in complete hydrolysis of the hemicellulose with little loss of carbohydrate values (Table 2). Under these conditions the remainder of the wood undergoes extensive size reduction, forming spherical rather than fibrous particles. The resulting slurries have been shown to possess superior rheological characteristics.

Table 2. Data Base for Hydrolysis

Wood/Water Ratio	23/77
Heat-up Time	12 min
Temperature	180°C (356°F)
Acid (pH)	0.05% H ₂ SO ₄ (2.0)
Retention Time	45 min

Approximately one dozen hydrolysis experiments have now been conducted in autoclaves ranging in size from 400 ml to 400 gallons (i.e., a test run at Albany) with essentially identical results. Material, carbon, hydrogen and energy balances are typically 0.85 or better.

The success of hydrolytic pretreatment in reducing wood chips to fine particles is probably due to a combination of chemical and physical action. Most of our experiments have been conducted in a 10-gallon digester equipped with a hydraulic agitator which is run at 900 rpm. The shaft contains three pitched-blade turbine impellers and a two-piece baffle assembly. Using this unit we find that about half of a 4.0 kg charge of dry wood chips, nominally 1¼" in length, is reduced to -20 mesh or finer under the conditions specified above.

Those particles larger than -20 mesh can for the most part be crumbled between the fingers.

PROCESS DEVELOPMENT CONSIDERATIONS

Several experiments designed to test the suitability of pretreated wood slurries for liquefaction have been performed. Under identical conditions prehydrolyzed wood gives slightly higher yields of oil than wood flour.

In order to adapt the acid pretreatment technique to the Albany process, neutralization with calcium hydroxide and separation of precipitated calcium sulfate sludge would be required. This is an obvious disadvantage which could be avoided if (a) a basic pretreatment or (b) an acidic liquefac-

tion method could be developed. Active research in this area is under way. Several promising acid catalysts for liquefaction have been discovered but have not yet been fully evaluated.

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References

- [1] Saeman, J.F., "Kinetics of Wood Saccharification," Ind. Eng. Chem. 37, 43 (1945).

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