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ORGANOSOLV PULPING OF PARASERIANTHES FALCATARIA

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ORGANOSOLV PULPING
OF PARASERIANTHES FALCATARIA

by

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ABSTRACT

The potential of organosolv pulping using *Paraserianthes falcataria* as a raw material was studied. Organosolv pulping was carried out under 2 conditions of catalyst addition - 75% ethanol plus 0.05 M $CaCl_2$; and 75 % ethanol plus 0.10 M $CaCl_2$; and without catalyst - 75 % ethanol only.

The results indicated that without catalyst, organosolv pulping was incapable of reducing cooking chips into pulp. Catalyzed organosolv pulping at 0.05 M $CaCl_2$ produced pulp with screened yield of 45.31 % and 46.67 % for the 0.10 M $CaCl_2$ condition. These yields were slightly lower than the 48.56 % of kraft. The brightness of the unbleached pulps were 16.8 % and 15.9 % for organosolv pulping with 0.05 M and 0.10 M $CaCl_2$ conditions, respectively. These pulps were generally darker than the kraft pulp which had a brightness of 31.6 %. The strength properties i.e., burst, tear, tensile, stretch, and folding endurance of the two catalyzed organosolv pulps were very low compared to that of kraft pulp control. The total solids recovered from the black liquor of uncatalyzed organosolv process was 4.72 % while the catalyzed organosolv pulping were 7.0 % for 0.05 M $CaCl_2$ condition and 7.1 % for 0.10M $CaCl_2$ condition.

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INTRODUCTION

The chemical pulping processes in use today have evolved over the years and generally speaking have satisfactorily fulfilled the needs of paper and paperboard manufactures. Nevertheless, there is a growing interest in radically different pulping methods that are based on the use of organic solvents as pulping agents. These methods are referred to as "organosolv" pulping processes (Aziz and Sarkanen, 1989).

Organosolv processes are techniques which use organic solvents to separate lignin and the carbohydrate portions of the wood. Lately, organosolv pulping has been generating headlines (Pulp and Paper Canada, 1984) and several industrial processes have been patented.

In 1985, a session of pulping conference held in Atlanta was devoted to this subject and the topic was also discussed in recent seminars conducted in Hamburg, Federal Republic of Germany and Appleton, Wisconsin. The developments in the field of alcohol pulping were presented at the Appleton seminar.

Organosolv pulping is based on the use of organic solvents such as methanol, ethanol and higher alcohols as pulping liquor. Basically, this is different from the conventional processes because it does not make use of sulphur containing chemicals that causes emissions of foul odors. It is claimed to be pollution-free. Moreover, alcohol, as well as other pulping by-products such as, lignin, sugars and volatile components can be recovered easily (Williamson, 1987). This means cost savings, additional income and less hazards for both people and environment.

Indeed, some organosolv processes are reaching the stage of realistic industrial applications as auxiliary methods for adding incremental hardwood capacity to the existing pulp mills (Aziz, 1989). Eventually, large scale production units may evolve for pulping uniform raw materials from fast growing plantation species. No study has been carried out on the pulping of tropical hardwoods or fast growing plantation species by this process, as far as can be determined.

OBJECTIVES

The specific objectives of this study are the following :

1) to evaluate the potential of organosolv pulping processes on Paraserianthes falcataria(batai) at 3 different pulping conditions ;

2) to analyze the black liquor for recoverable total solids; and

3) to evaluate the strength properties of batai organosolv pulps.

LITERATURE REVIEW

Ethanolysis Reactions Of Lignin

The prolonged heating of lignified materials with ethanol or some other alcohol plus hydrochloric acid results in "ethanolysis" or "alcoholysis" reaction of lignin (Schubert, 1965).

Brauns (1952) noted that during the alcoholysis of lignin, three reactions may take place simultaneously namely, (a) condensation of part of the lignin with the alcohol, resulting in a soluble "alcohol Lignin," (b) condensation of part of lignin with itself resulting in a product of lesser reactivity, and (c) an "alcoholytic cleavage" of part of the lignin resulting in its depolymerization to smaller lignin building units which may be followed by the condensation of some of these units with the reacting alcohol.

In recent years, alcoholysis and especially ethanolysis, has found use as an important analytical tool in helping to establish whether an isolated product is really derived from lignin. Thus, on treating "protolignin" with absolute alcohol in the presence of catalytic amounts of hydrochloric acid, Hibbert and his co-workers ( ) obtained a series of monomeric phenylpropane derivatives. The reaction is now often used as a "test" for lignin preparations. Kratzl and Klein ( ) have applied the reactions to charactererize and identify certain lignin preparations.

Organosolv Pulping

Organosolv pulping process is the technique which uses organic solvents to separate the lignin from the carbohydrate portion of the wood.

Organosolv pulping has been classified into :

1) uncatalyzed process, and
2) catalyzed process, which is further subdivided into :
    a) acid catalyzed, and
    b) alkaline catalyzed.

Pazner and Cho (1989) divided solvent pulping into two categories, namely : uncatalyzed and catalyzed processes. The catalyzed process was further subdivided by Aziz and Sarkanen (1989) into acid and alkaline catalyzed processes.

The uncatalyzed process is done without any catalyst. Aranovsky and Gortner (1936) found that primary alcohols are more selective delignifying agents than secondary or tertiary alcohols. Recently, it has been suggested that monovalent and polyvalent alcohols have higher pulping efficiencies in the presence of water, although anhydrous alcohols have been found to be more selective delignifying agents than their aqueous counterparts.

The catalyzed process uses small amounts of alkali or acid as catalysts. Kleinert and Tayenthal (1932) recommend a broad range of acid reacting salts. Orth and Orth (US Patent 4,017,642) patented the use of aluminum chloride ($AlCl_3.6H_2O$) as the prefered catalyst for solvents of aqueous glycol or glycol ether. They further indicated that organic acids such as formic, acetic, propionic, oxalic, malic, citric or pthalic acids are suitable catalysts. Pazner and Chang (US patent,1983) patented sodium hydroxide, ammonium sulphide, sulphite anthraquinone, anthraquinone ammonium sulphide and neutral alkali earth metals (NAEM) such as calcium chloride and magnesium chloride, as suitable catalysts for organosolv pulping.

Organic solvents with pH values lower than 4.75 are also used and it has been shown that such organic acids are better than mineral acids for the pulping of softwoods. None of these catalysts, however, has satisfied the general expectations of producing pulps of high strength and viscosity at low residual kappa number (Pazner and Cho, 1989).

Pazner has patented the salts of alkaline earth metals, (calcium chloride and magnesium chloride) as catalysts in organosolv liquors with high methanol and ethanol contents (Canadian Patent, 1981).

Acid - catalyzed processes are often operated without an acid catalyst, since the acetic acid released from the wood during pulping provides the alcohol with the needed acidity. In such cases, the temperature of reaction is in the range of 185-210°C. Acid catalyst may be used to lower reactor temperature and pressure. On the other hand, alkaline organosolv processes commonly make use of NaOH or Na_2SO_3. The role of organic solvents is simply to promote the dissolution of lignin.

The Organosolv Processes

There are 3 existing recognized organosolv pulping processes (Aziz and Sarkanen, 1989) namely, (1) Kleinert (2) ALCELL and (3) MD .

Kleinert Organosolv Process

Figure 1 shows a simplified description of the process.

Pulping occurs in a counter current reactor. The pulping temperature is approximately 195°C. Pre-steamed chips enter at the top of the reactor, while the pulping liquor without any catalyst, pre-heated to 100 - 110°C, enters at the bottom. The liquor flows upward, extracting dissolved materials from the chips.

The spent liquor leaves the digester through a strainer ring located at the top of the digester and enters a quintuple evaporator. The combined condensates from the evaporator are collected for alcohol recovery. The heavier, viscous lignin phase flows into a separation tank and is

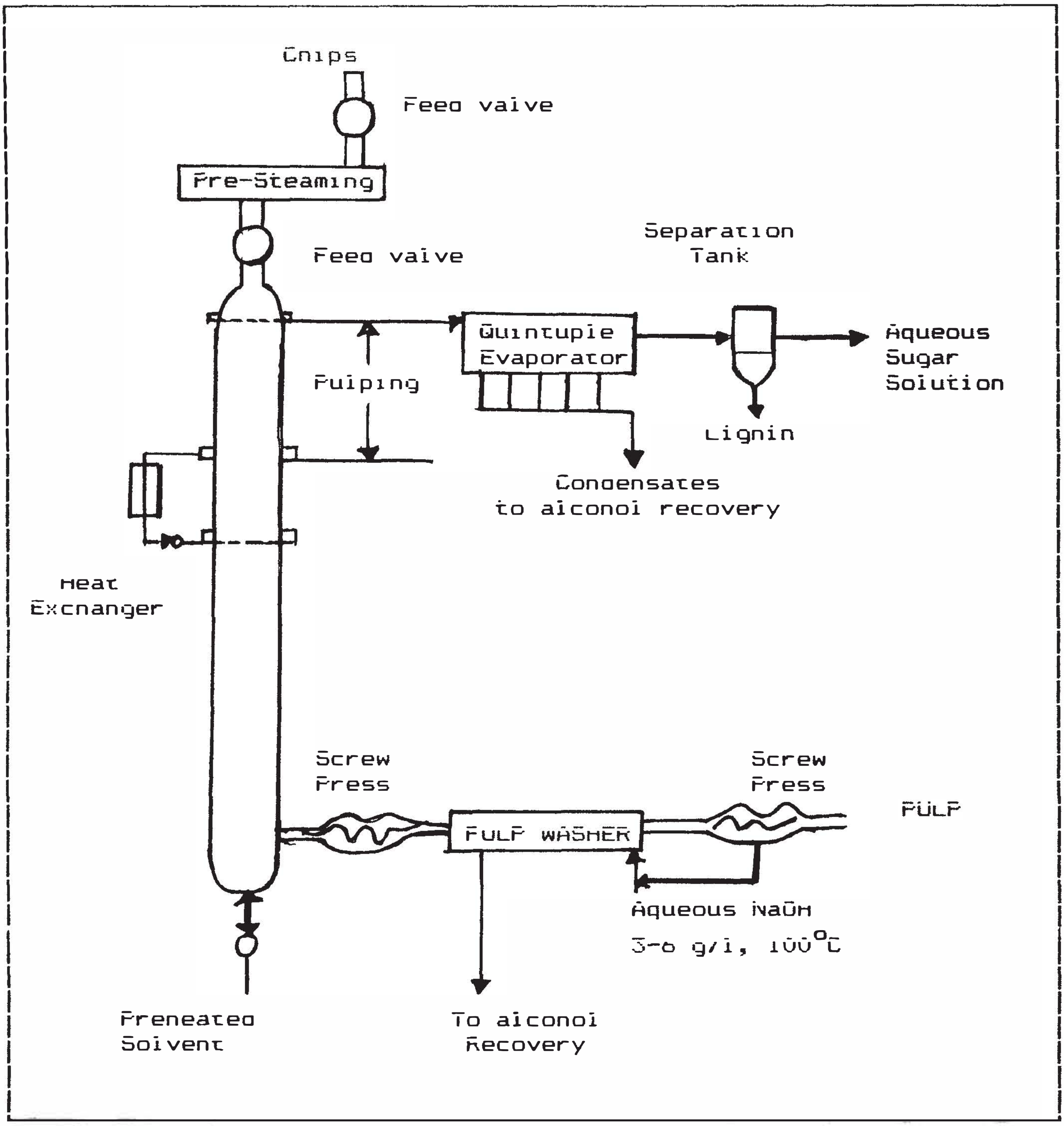

Figure 1. Flowsheet For Kleinert Organosolv System

collected from the tank bottom while an aqueous solution of hemicellulose sugars is taken off from the top.

The pulp is withdrawn from the bottom of the digester through a screw press which removes part of the organosolv liquor. The rest of the liquor is recovered from a pulp washer using aqueous NaOH as wash water. A second screw press completes the washing operation.

This process has two important limitations which are frequently overlooked. First, the production of bleachable grade pulps from softwoods proceeds smoothly to kappa number of 85 to 100 but comes to a virtual standstill at this point. The strength properties of these pulps are satisfactory, but, can hardly be expected to successfully compete with conventional kraft process in the manufacture of linerboard and bagpulps. The second limitation is in the pulping properties of hardwood species which are somewhat variable. These characteristics can cause problems and in the worst case, require segregation of species in the wood yard.

ALCELL Organosolv Process

This process evolved and was developed by Repap Technologies out of the ideas and studies made by Katzen et. al. (1981) to refine and improve the application of organosolv pulping in batch systems. Their idea was to apply the principle of gradual displacement of the pulping liquor in the digester with hot organosolv wash liquors. The process flow chart is shown in **Figure 2.**

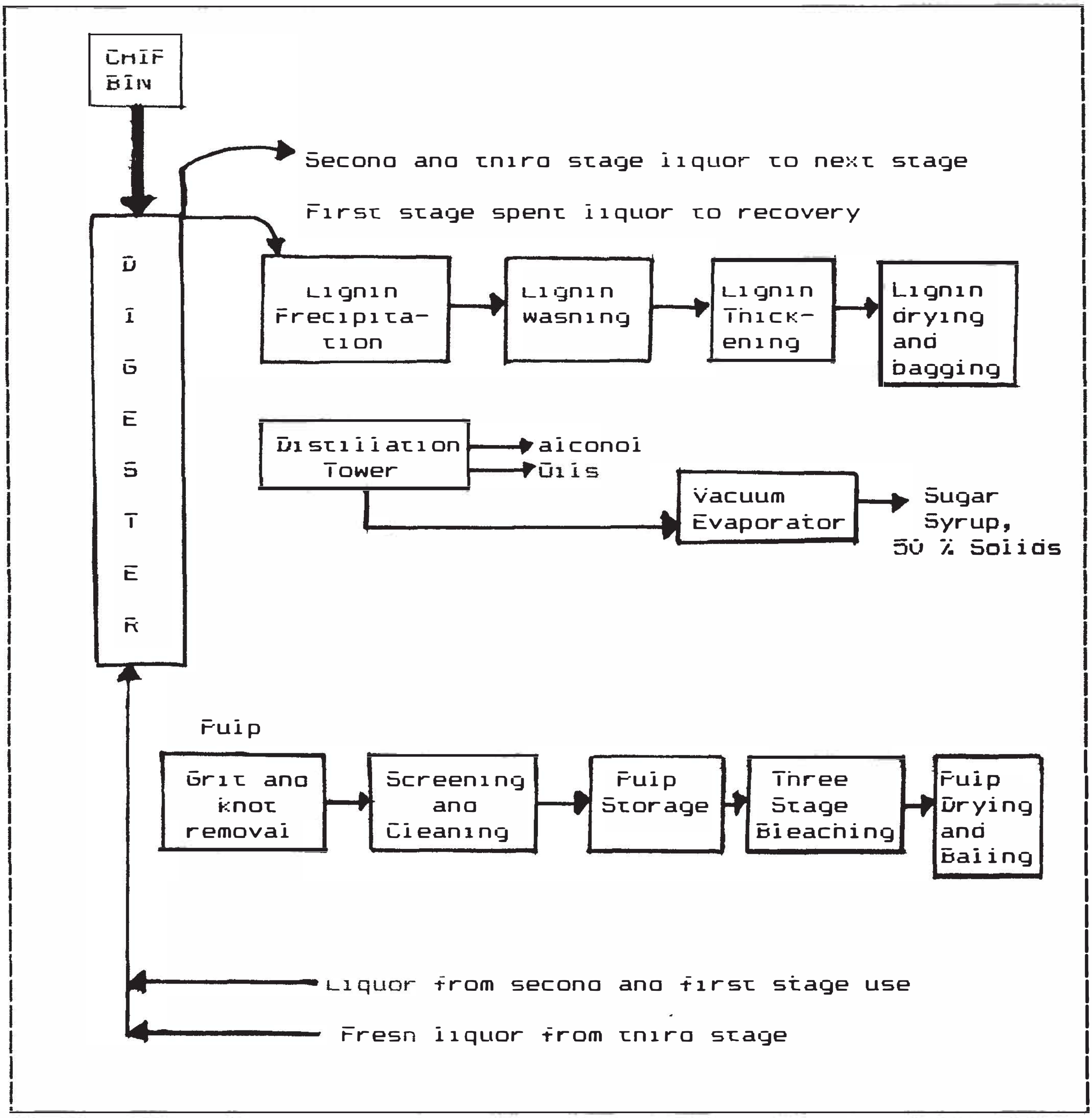

Figure 2. Flowsheet For ALCELL Pulping Process And Subsequent Recovery Of By Product Chemicals

Preheated chips (80°C) are packed in the digester using steam. The purpose of steaming is to displace air from the chips. Preheated solvent that has been previously used as a wash liquor from two earlier batches is pumped into the digester and the temperature rapidly raised to between 190° C and 210°C, corresponding to an operational pressure of 500 psi. The liquor is circulated continuously in the digester during the pulping period. At the end of this period, the liquor in the digester is displaced by wash liquor that was used in the second washing stage of the previous batch. The displaced liquor from the digester flows to the lignin and sugar recovery system. The third stage wash liquor is displaced by fresh liquor and flows into an intermediate storage tank for use in the second stage. The second stage wash liquor is drained into another storage tank for use in the digester.

At this point, the digester contains soaked, delignified chips and alcohol water vapor at pulping temperature and pressure. The pressure is released and the vapor is condensed for reuse as fresh pulping liquor. Finally, the alcohol remaining in the digester is driven off by steaming . The pulp is diluted with water and pumped out of the digester for cleaning and bleaching treatments. The first stage spent liquor entering the by-product recovery system is first splashed and then diluted with process water to precipitate the dissolved lignin. After settling, the solid lignin is separated by centrifugation, washed and dried.

The filtrate enters a distillation tower, where alcohols and some acetic acid and furfural are recovered. Finally, the remaining aqueous liquor is further evaporated to a sugar syrup.

MD Organocell Process

This process is a modification of the Kleinert process for the purpose of producing bleachable grade pulps from softwoods. The system is shown in **Figure 3.**

Softwood chips are impregnated with methanol-water before entering the first stage continuous reactor. The first stage is operated under a 40 bar pressure at 195°C. Approximately 20 % of the lignin and a major part of the hemicellulose is removed from the chips.

The chips are then transported to the second stage digester, which is operated at 170°C under alkaline conditions. The combined residence time in both reactors is only 45 minutes. The strength properties of the pulp produced are only slightly lower than those of corresponding kraft pulps. Organics and NaOH are recovered from the second stage liquor. After the methanol is recovered, the remaining liquor enters an electrolytic cell which separates NaOH and precipitates lignin in a filterable form.

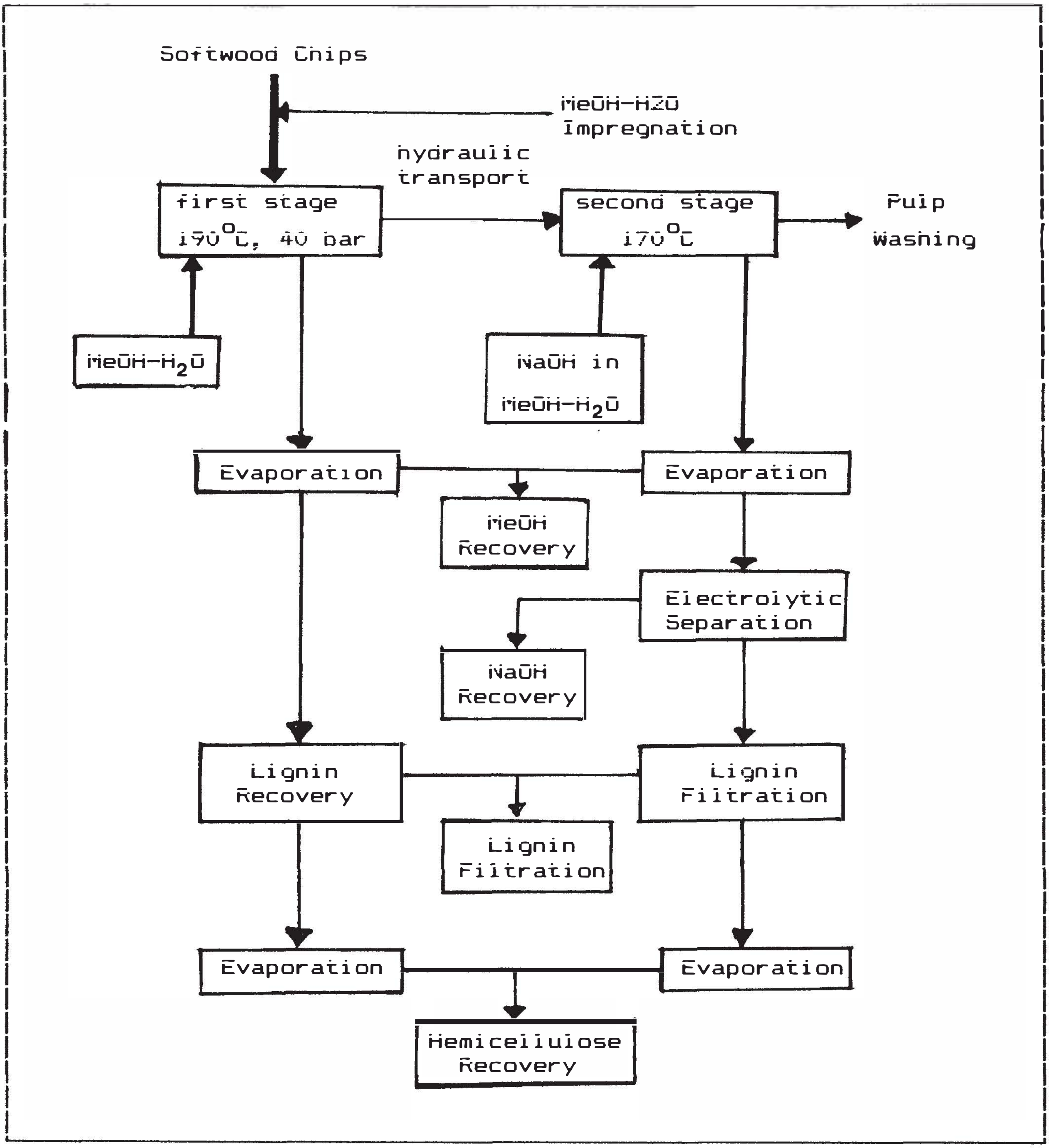

Figure 3. Flowsheet of MD Organocell Pulping System

Mechanisms Involved In Organosolv Processes

Pazner and Cho (1989) stated that the mechanisms involved in solvent pulping have not been investigated in detail, and that opinions as to the selectivity of solvents during delignification vary greatly.

Aranovsky and Gortner (1936) suggested that the pulping efficiency of solvents is related to the zeta potential of the cellulose solvent interface. On the other hand, Kleinert (1975) suggests that lignin depolymerization is a free radical process and that solubilization depends on pH, temperature or solvent concentration. Kleinert recommended the use of systems with near neutral pH since low pH values are also responsible for the hydrolysis of hemicellulose.

Kleinert Uncatalyzed Process

A detailed analysis of Kleinert process was undertaken by Baumeister and Edel (1980) giving particularly close attention to the conditions of solvent composition, isothermal heating and liquor flow. They concluded that the rate and degree of delignification are controlled by opposing mechanisms, i. e., hydrolysis of the lignin macrogel and condensation of the solvolysis products, respectively. Both of these reactions are catalyzed by protons, which are modified by the alcohol concentration in the liquor. Evidently, lignin dissolution is considerably retarded at alcohol concentrations greater than 50%.

There is a high initial topochemical effect resulting in the formation of fissures, caused by partial delignification in the middle lamella. Fiber liberation, however, does not occur until a later stage of the cooking. High temperature cooking leads to a rapid increase in the acids concentration of the hemicellulose rich regions (P, S1, S2) of the cell wall and causes in situ condensation and precipitation of the solvolysis lignin products. The removal of the condensed lignin from the cell wall is not possible until substantial amounts of the hemicelluloses are solubilized and the cell wall is opened up through the creation of macropores. As such, long cooking times could lead to rapid degradation of the cellulose, resulting in low viscosity.

With open structured hardwoods, cell wall accessibility is a lesser problem. However, the combined effects of high temperature, long cooking times and uncontrolled low pH could result in dark pulps of unacceptably low viscosity and unacceptably high (up to 10%) rejects content. Baumeister and Edel (1980) concluded that the isothermal reaction conditions (uncatalyzed 30 to 50% alcohol) of the Kleinert process are unsuitable for the production of paper grade pulp from most woods except aspen and the poplars.

Neutral Alkali Earth Metal (NAEM) Catalyzed Solvent Pulping

The mechanisms of catalysis by neutral alkali earth metal (NAEM) salts in methanol pulping has not yet been investigated in detail (Pazner and Cho, 1989). However, the metal ion sequestering properties of wood and lignin have been known for sometime. In all probability , the primary step in the catalysis adsorption of divalent ions on the wood is through the carboxylic acid groups **(Figure 4).** This causes a rapid drop of pH in the pulping liquor even before cooking commences. The divalent ions apparently stabilizes the carboxylic acid groups of carbohydrates while reducing the extent of acetic acid formation upon high temperature splitting of O-acetyl moieties from the hemicellulose. The formation of Ca^{-2} and Mg^{-2} acetates by reactions of the catalyst with the liberated acetic acid contributes further to the excellent pH control in the NAEM catalyzed solvent system.

The solvent effect of the NAEM ion catalyses is to protect the cellulose from hydrolytic degradation and to arrest the deacetylation of the hemicellulose by preventing the excessive drop in cooking liquor pH.