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COMPARATIVE STUDY ON THE SODA-ETHANOL AND SODA-BUTANOL PULPING OF *Nypa fruticans* PETIOLES

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Abstracts

This work investigates the effect of cooking liquor (soda-ethanol and soda-butanol) on the pulp yield, kappa number and residual lignin of *Nypa fruticans* petioles pulp. This comparative study was done at two temperatures (120°C and 150°C) and four cooking time (30, 60, 90, and 120min.) each. At both temperatures, soda-butanol gave higher pulp yield with low kappa number and residual lignin. It was found that increase in temperature and time led to decrease in pulp yield, kappa number and residual lignin of *Nypa fruticans* petiole pulp for both soda-ethanol and soda-butanol liquor. Hence soda-butanol has high selectivity on the delignification of *Nypa fruticans* petioles with minimal rate of cellulose degradation.

Key words: Soda-ethanol, Soda-butanol, *Nypa fruticans*, Pulp yield, Kappa number and Residual lignin

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Introduction

Conventional pulping processes produces large amounts of highly polluting waste water, especially sulphite and sulphate based processes and also give lower pulp yield with higher amount of residual lignin. These reasons have raised the need for new processes such as organosolvent (organosolv) processes that reduce the unpleasant effects. Organosolv pulping is a chemical pulping method in which delignification of the biomass (wood or non-wood) is done in an organic solvent or in organic solvent-water mixture system [1]. However, the advantages of organosolv pulping is lower kappa number of the resultant pulp and has low impacts of environmental problems (as known to be an environmentally friendly than other pulping process), and the silica of raw material does not accumulate in the system but retained in the pulp [2].

As compared with conventional methods, organosolv cooking delignifies hardwoods and non-wood materials more easily than softwoods. This is because hardwood lignin is more reactive and is present in smaller amounts than softwood lignin [3].

In general, organosolv pulping has low effect on carbohydrate degradation and has good selectivity in the delignification reaction. By protic solvents, such as alcohols, in the absence of acids and bases the main reactions occurred in the pulping process are hydrolysis and to a lower extent solvolysis [4].

In conventional cooking and organosolv cooking, the lignin structure is broken into smaller parts before it dissolves in the cooking liquor. Process variables such as cooking time and temperature also affect the reactions in the same way as in conventional cooking. The cleavage of ether bonds in the lignin structure is a key to delignification reaction [1]. The reactions taking place during alkaline organosolv cooking are similar to those in the corresponding conventional processes (Kraft, soda, and alkaline sulphite). Organosolv processes have been applied with varying success to hard and soft woods and also, to a lesser extent, to non-wood materials [4].

However, in alcohol pulping, the pulp quality can be improved by adding alkali to the system. Although Koll and co-workers [5] have treated birch with several organic solvents in the supercritical state. In the temperature range 523-553K (250°C – 280°C), at pressures around 10 MPa, alcohols showed the highest delignifying capability.

Alkaline-ethanol pulping has been investigated [6]. Soda and soda-ethanol pulping of *Nypa fruticans* petiole has been reported [7]. Ethanol-based pulping from *Cynaracardunculus* L. was examined by Oliet and his co-workers [8]. This non-conventional pulping process based on the delignification of cardoon (*Cynara cardunculus* L) in ethanol–water mixtures was studied to evaluate its pulping potential and to establish the optimum pulping conditions for this lignocellulosic material.

Ethanol/water pulps from sugar cane straw and their bio-bleaching with *Xylanase* from *Bacillus pumilus* was examined. The influence of independent variables (temperature and time) on the cooking of sugar cane straw with ethanol/water mixtures was studied to determine operating conditions of obtaining pulp with high cellulose content but low residual lignin [9]. Base-catalyzed organosolv pulping of jute has been investigated [10]. In its research, Jute fibres were pulped using a caustic soda, and ethanol alkali (EtOH–NaOH) pulping process with the aim of minimizing problems associated with conventional chemical pulping.

Cellulosic pulp from *Leucaena diversifolia* by soda–ethanol pulping process was investigated. In this work the anthraquinone–soda–ethanol was selected attending to its documented effect in increasing the degree of delignification, the yield and the process selectivity in alkaline cooking [11].

Muurinen and co-workers [12] have made a preliminary comparison between 27 organosolv methods. When the comparison criteria were cooking conditions, pulp quality, solvent properties etc., alkali ethanol- anthraquinone pulping of spruce [13], [14] was found out to be a very promising new pulping method.

Methanol and ethanol are the most popular alcohols used in pulping. However, several other alcohols have also been proposed to be used as pulping chemicals. Propanol, butanol and glycols appear in several papers which are therefore referred to here. Other alcohols proposed are benzyl alcohol [15], tetrahydrofurfuryl alcohol [16], [17], glycerol [18] and chloroethanol [19].

As with many other alcohols, butanol was originally used as a solvent to decompose wood in order to study lignin. Bailey [20] has patented a process producing pure cellulose from wood by treating it with an aqueous mono-hydroxy alcohol having at least four carbon atoms. At least three of the carbon atoms have to be in a straight chain. The alcohol has to be

substantially insoluble in water at temperatures below 373K (100°C), but soluble therein at temperatures above 373K (100°C). An inorganic alkali is also added to the pulping liquor in amounts from 2 % to 10 %. Pulping is carried out at 373-473K (100°C- 200°C). If the butanol pulping liquor is made alkaline by adding sodium hydroxide, the spent liquor is separated into two layers upon cooling. The lignin is concentrated in the lower aqueous layer. The upper alcoholic layer can be directly used in the preparation of pulping liquor [20]. Aqueous n-butanol (50 v-%) can be used to effectively delignify southern yellow pine meal. At 478 K and 2.2 MPa the original lignin content of wood (30.2 w-%) can be reduced to 16.1 % when the residence time is 12 hours [21]. McGee and April [22] have compared aqueous ethanol and aqueous 1-butanol pulping of pine. They found that butanol pulping produced significantly higher delignification levels than ethanol pulping. Rice straw has been delignified with aqueous butanol in the presence of catalysts. Acid-catalyzed treatment with aqueous butanol (50 %) at 443 K for one hour resulted in almost complete (> 90 %) lignin removal. Ghose and co-workers [23] have compared butanol and ethanol in pulping of rice straw. Both alcohols are effective delignifying agents for agricultural residues. Influence of cooking variable on the Soda and soda-ethanol pulping had been investigated in our previous work [7]. It was found that soda liquor gave lower pulp yield with high kappa number while soda-ethanol liquor gave higher pulp yield with low kappa number (high rate of delignification).

Hence the aim of this work is to investigate the effect of the cooking liquor (soda-ethanol and soda-butanol) on the pulp yield, kappa number and residual lignin of *Nypa fruticans* petioles in order to ascertain the organic solvent (alcohol) that is more suitable for the delignification of *Nypa fruticans* petioles.

Material and Methods

Sample Preparation

The air dried chips of *Nypa fruticans* petiole (of known moisture content) was used for the pulping studies.

Cooking Liquor

The cooking liquors were prepared as follows:

(i) Soda Liquor

Concentrated solution of sodium hydroxide was prepared by pouring some sodium hydroxide pellet into a 10L plastic container containing about 500ml of water. 20ml of this

solution was placed in 500ml standard flask and diluted with 100ml of distilled water. The diluted solution was titrated against a standard solution of H₂SO₄. The result of the titration was used to determine the concentration of the stock solution. The concentration of sodium hydroxide used this experiment was prepared from this stock solution.

(ii) Alcohol Solutions

(a) Preparation of alcohol solution

60% ethanol was prepared by measuring 60ml of 99% ethanol in the measuring cylinder and diluted it with distilled water to 100ml. This gives 60% ethanol and 40% water. The same procedure was used for the preparation of 60% butanol.

(b) Soda-Alcohol Solution

Soda-ethanol solution was prepared using 50ml of 8% sodium hydroxide and 50ml of 60% /40% ethanol-water solution. This gives (1:1 v/v) of soda-ethanol solution. The same procedure was used for the preparation of soda-butanol solution.

Pulping Procedure

Pulping studies were carried out on *Nypa fruticans* petiole chips. These samples were subjected to soda-ethanol and soda-butanol pulping. The pulping was done at two different temperatures (12°C and 150°C) at 30, 60, 90 and 120min respectively at each temperature. The cooking of the sample was done in a 10L autoclave digester. The pulping experiment was carried out on 10g of the air dried chips. The chips were put into each cup and 10ml of the cooking liquor was added. These cups were placed inside the inner jacket of the digester so that they can be pulped under the same conditions. One litre of water was put into the digester and the inner jacket was then fitted into the digester. After pulping, the digester was kept for 10min before opening. The spent liquor was immediately separated from the pulp by filtering in order to avoid lignin precipitation. The resultant pulp was then characterised. Pulp yield was determined gravimetrically

Characterization of Pulp

Pulp characteristics signify the effect of the cooking variables and the potential of the pulp in paper making. The following properties of the pulp were determined.

Determination of Kappa Number

Kappa number is used to describe the relative hardness, the degree of delignification obtained in a chemical pulping process, the bleachability or whitening aptitude of a pulp. It is defined as the volume (in milliliters) of 0.1N (0.02M) potassium permanganate solution

consumed by one gram of moisture-free pulp. The results are corrected to 50% consumption of the permanganate added. Kappa number was determined using TAPPI standard, [24].

About 0.5g of the oven dried pulp was disintegrated in 100ml of distilled water until free of fibre clots. Disintegration was done using magnetic stirrer. Disintegrated pulp was then transferred into 500ml reaction beaker, 100ml distilled water was added to bring the total volume to 200ml. The beaker was placed on a magnetic stirrer with continuously stirring. 25 ml of 2M (4N) sulphuric acid solution was measured and 25ml of 0.02M (0.1N) potassium permanganate solution was pipetted, they were added to the disintegrated test specimen simultaneously, starting a stopwatch. At the end of exactly 10.0 min, reaction was stopped with the addition of 5ml of 1M (1N) potassium iodide solution. Immediately after mixing, but without filtering out the fibres, it was titrated with 0.2M (0.2N) sodium thiosulphate solution, few drops of the starch indicator was added toward the end of the reaction.

The blank determination using exactly the same method as above but omitting the pulp was carried out.

Kappa number was calculated as follows:

$$K = \frac{p \times f}{w}$$

$$p = \frac{(b-a)}{0.1} N$$

Where:

K = kappa number

f = factor for correction to a 50% permanganate consumption,

w = weight of moisture-free pulp in the specimen, g

p = amount of 0.1N permanganate actually consumed by the test specimen, mL

b = amount of the thiosulfate consumed in the blank determination, mL

a = amount of the thiosulfate consumed by the test specimen, mL

N = normality of the thiosulfate

Determination of Residual Klason Lignin

Residual Klason lignin was calculated from kappa number according to the following relation;

% Residual Klason Lignin (RKL) = Kappa number x 0.13 [24].

Result and Discussion

Effect of Pulping Liquor on the Pulp Yield of *Nypa fruticans* Petioles

Pulping Liquor exert greater effect on the pulp yield of *Nypa fruticans* petioles, this is presented in Fig.1 and 3. However, organo-solvent pulping has low effect on carbohydrate degradation and has good selectivity in the delignification reaction. Higher pulp yield was obtained with soda-butanol with shorter pulping time (30minutes) at both temperatures. At the same pulping conditions, soda-ethanol pulping gave lower pulp yield. The lower pulp yield of soda-ethanol pulping is due to the high rate of degradation of cellulose. Soda-butanol has lowest effect on carbohydrate degradation [25], hence higher pulp yield. Also, higher pulp yield obtained for soda-butanol is due to the higher boiling point of butanol (117.7°C) compared to ethanol (78°C). Ethanol evaporate at higher temperature thereby resulting in the increase in the concentration of soda liquor, this result in the increase in the rate of degradation of carbohydrate hence decrease in the pulp yield. During pulping both lignin and cellulose are dissolved at different rates, this rate is much accelerated by increasing the temperature and time [26]. For both pulping liquors, the higher pulp yield was obtained at the pulping temperature of 120°C. And the lower pulp yield was obtained at the pulping temperature of 150°C. This implies that higher rate of degradation of cellulose occurs at elevated temperature and longer pulping time [27], [28] and [7].

Effect of Pulping Liquor on the Kappa Number and Residual Klason Lignin of the *Nypa fruticans* pulp

Kappa number entails the amount of residual klason lignin of the pulp. Residual klason lignin indicates the amount of bleaching agent that will be needed to bleach the pulp. As presented in fig.2 and 4, at all temperatures soda-ethanol liquor gave higher value of kappa number and residual lignin which implies low rate of delignification whereas at the same conditions, soda-butanol liquor gave lower value of kappa number and residual lignin, this in turns implies higher rate of delignification. This is because organic solvent reduces the surface tension of the pulping liquor, thereby promoting the penetration of the alkali into the chips and the diffusion of the breakdown products of lignin from the chips to the liquor. However, soda-butanol degrades lignin and prevents it from condensing since the solubility of n-butyl alcohol in water is 8 – 9 parts per 100 hence the pulping liquor is made up of organic layer and aqueous layer hence the lignin will remain in aqueous layer this prevent precipitation of lignin on the pulp and this in turns result in the low residual lignin. [4].

Table 1: Pulping at 120°C

| Pulping Liquor | Time to Temp. (Min.) | Time at Temp. (Min.) | Pulp Yield (%) | Kappa Number | Residual Klason Lignin (%) |
|-----------------------|-----------------------------|-----------------------------|-----------------------|---------------------|-----------------------------------|
| Soda-ethanol | 22 | 30 | 49.02 | 35.4 | 4.6 |
| | 19 | 60 | 47.92 | 32.3 | 4.2 |
| | 24 | 90 | 47.06 | 31.2 | 4.1 |
| | 24 | 120 | 46.40 | 22.7 | 3.0 |
| Soda-butanol | 22 | 30 | 52.58 | 26.2 | 3.4 |
| | 19 | 60 | 51.91 | 26.6 | 3.5 |
| | 24 | 90 | 51.91 | 23.4 | 3.0 |
| | 24 | 120 | 48.28 | 22.5 | 2.9 |

Table2: Pulping at 150°C

| Pulping Liquor | Time to Temp. (Min.) | Time at Temp. (Min.) | Pulp Yield (%) | Kappa Number | Residual klason Lignin (%) |
|-----------------------|-----------------------------|-----------------------------|-----------------------|---------------------|-----------------------------------|
| Soda-ethanol | 32 | 30 | 32.83 | 18.1 | 2.4 |
| | 35 | 60 | 31.08 | 14.1 | 1.8 |
| | 33 | 90 | 29.95 | 12.4 | 1.6 |
| | 38 | 120 | 27.50 | 10.5 | 1.4 |
| Soda-butanol | 32 | 30 | 40.00 | 17.8 | 2.3 |
| | 35 | 60 | 38.87 | 13.2 | 1.9 |
| | 33 | 90 | 37.41 | 11.6 | 1.5 |
| | 38 | 120 | 33.59 | 9.5 | 1.2 |

The spent liquor is separated into two layers upon cooling. The lignin is concentrated in the lower aqueous layer. The upper alcoholic layer can be directly used in the preparation of pulping liquor [20].

Also, higher rate of delignification of soda-butanol at higher temperature is due to high boiling point of butanol since much of the solvents will remain at higher temperature, this in

turns enhances higher rate of delignification. Ethanol (boiling point less than 100°C), at higher temperature, most of the solvent will evaporate out and this decreases the rate of delignification. Polarity of butanol is the major contributive factor to its high rate of delignification [4], [22].

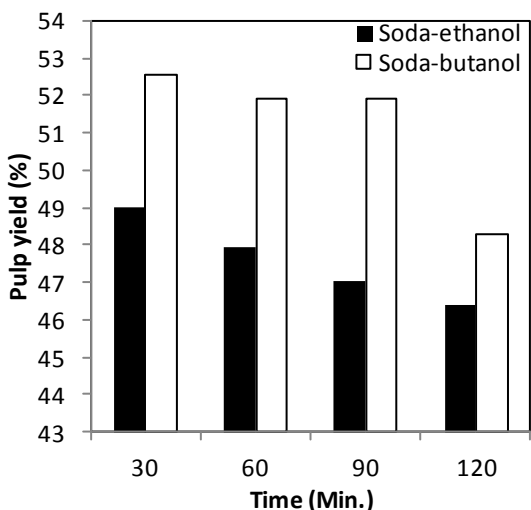


Fig.1: Bar chart showing effect of cooking liquor on pulp yield of *Nypa fruticans* petioles at 120°C

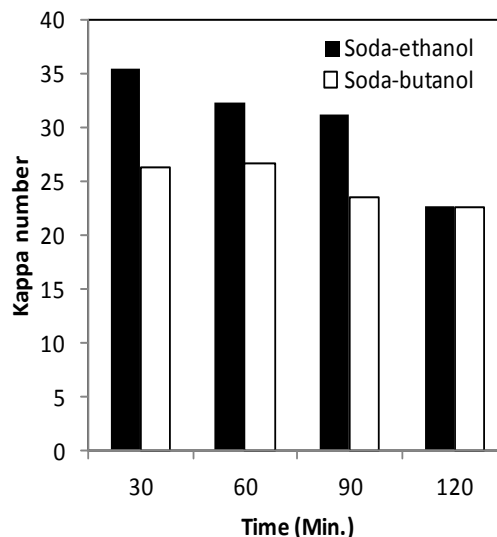


Fig.2: Bar chart showing effect of cooking liquor on kappa number of *Nypa fruticans* petioles at 120°C

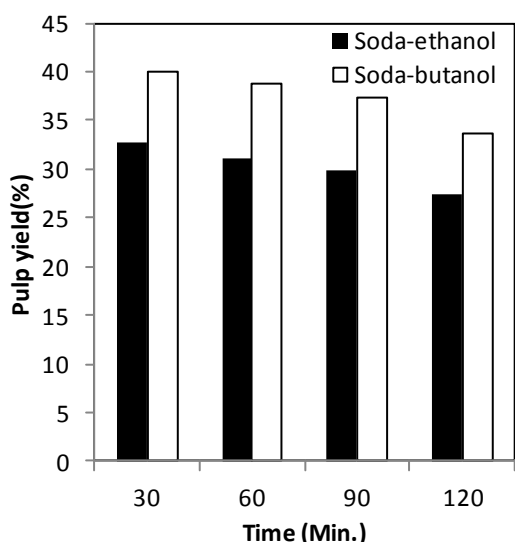


Fig. 3: Effect of cooking liquor on pulp yield of *Nypa fruticans* petioles at 150°C

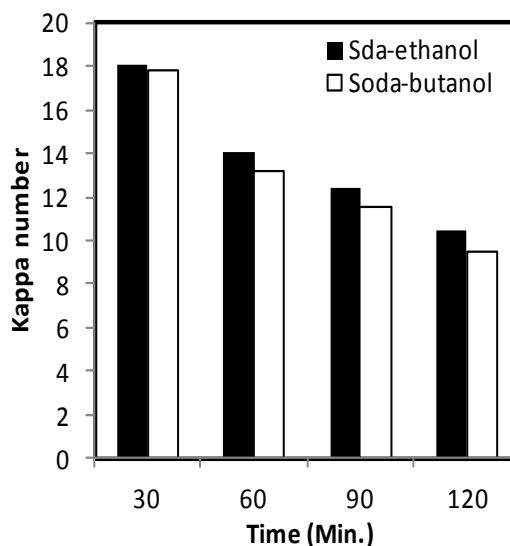


Fig. 4: Effect of cooking liquor on the kappa number of *Nypa fruticans* petioles at 150°C

Conclusion

In this work, pulp was produced from the petiole of *Nypa fruticans* under soda-ethanol and soda-butanol pulping liquor at 120°C and 150°C. Soda-butanol gave higher pulp yield with lower kappa number and residual lignin while soda-ethanol gave the lower pulp yield with higher kappa number and residual lignin at both temperatures. Moreover, higher pulp yield for each cooking liquor was obtained at the shorter pulping time (30 minute). It has been observed that soda-ethanol pulping led to higher rate of cellulose degradation and high residual lignin; hence to obtained higher pulp yield with minimal cellulose degradation and higher rate of delignification, soda-butanol should be employed.

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