International Journal of Chemical Science
www.chemicaljournals.com
Online ISSN: 2523-2843, Print ISSN: 2523-6075
Received: 25-03-2022, Accepted: 10-04-2022, Published: 25-04-2022
Volume 6, Issue 1, 2022, Page No. 22-29

Proton generating NAEM-catalyzed organo-solv pulping of seven (7) Nigeria savanah timbers: A potential replacement for the kraft process

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Abstract

The use of a proton generating NAEM-catalyst salts in aqueous alcohol is a critical determinant in obtaining pulp that can match the strength properties of Kraft pulps. Use of catalyst in cooking liquor of about 70-80% aqueous ethanol concentration is required to effectively solubilize lignin and liberate fibre up to 50 to 65 % yield and has a remarkable impact on pulp production capability in the alcohol organosolv pulping of lingo-cellulosic biomass. The use of aqueous alcohol in the pulping of ligno-cellulosic biomass in the absence of a suitable catalyst would not effectively liberate fibre from the lignin matrix. The use of small doses of neutral alkaline earth metals (NAEM) salts acts as catalyst and buffers the solution, maintaining pH at 4.8. Under this favorable condition, destruction of hemicellulose is less severe and this is responsible for the high yield and strength properties of NAEM-catalyzed organo-solv pulp. In this research study, it was observed that divalent metal ions are very effective, whereas monovalent cations were incapable of fiber liberation and trivalent cations were found to be too aggressive causing extensive damage to the fibers. Under the specified pulping conditions, the organosolv pulping process catalyzed by the divalent metal ion was capable of producing about 60-65% pulp screened yield.
Successful chemical pulp production by the NAEM (Neutral Alkali Earth Metal) catalyzed organosolv pulping process opens access to bio-refining and provides value recovery both from the pulp and also from the dissolved wood components from the spent pulping liquor. With less dehydration, pulp of very good flexibility and high viscosity is very promising. While the yields of organosolv pulps were as high as 60%, the highest yields for Kraft pulp average 45%. It is believed that this approach will produce vigorous data and analyses which will serve as a foundation for commercial innovation with the ultimate goal of contributing to the development of new improved process and paper products.

Keywords: organo-solv pulp, sulphidity, kraft pulp, ligno–cellulose, bio-refining, NAEM-catalyst salts

Introduction

Organosolv is derived from two words viz (organic and solvent). It is a new pulping process under study whereby wood delignification to obtain cellulose pulp is achieved by the use of organic solvents. By this extraction process, non-cellulosic wood materials like lignin, resins, fats, albumins, pentosans, hexosans and other wood extractives are dissolve out with little or no degradation. The idea of organosolv pulping was first mooted out by kleinert and tayenthal, who in 1930 proposed the use of aqueous ethanol for the removal of lignin from wood. This has always been ignored because the dominance of the Kraft process is anchored on its versatility to pulp almost any wood material successfully with excellent pulp quality and well established efficient system for the recovery of cooking chemicals [1].

Nevertheless, the Kraft process has serious disadvantages. Prominent are the emission of mercaptans and other foul-smelling pollutants to the environment and the need for a very elaborate and efficient bleaching system which releases chlorinated toxic effluents into potable water systems. Subsequently, in the recovery systems, so much energy is spent in concentrating the spent liquors. Thus, the high cost of capital and technical considerations dictate the economic size of the recovery boiler. Lastly, during the pulping and recovery operations, lignin and other useful wood extractives are destroyed [2]. These known pitfall can no longer be ignored in a world where environmental friendliness is a law.

The catalyst investigated in this research study are salts of magnesium, calcium and barium having chloride as anions. High yield pulping is expected by cooking a ligno-cellulosic materials at an elevated temperature in an alcohol-water mixture of ethanol in volume ratio of 40 to 60 parts up to substantially anhydrous alcohol and only a trace amount of water, employing as primary catalyst a dissolved salt which is selected from calcium, magnesium or barium salts such that calcium, magnesium or barium cations (ions) from the salt are present in the mixture as 0.005 moles per liter of a magnesium, calcium or barium equivalent to less than 30 kg per tonne of wood cooked, far higher concentrations also being effective [3, 8].

The objectives in an ideal process for cooking lignocellulosic biomass are met when virtually all the lignin becomes solubilized in a short cooking time, with minimum use of chemical concentration, with fibre yielding almost equal to the total content of cellulose and hemicellulose. Such efficient cooking would minimize the energy required in mechanical dispersion of the fibers after cooking and also minimize bleach chemical consumption. A further object of this research study is to provide an improved process for rapid and extensive delignification of ligno-cellulosic material employing an alcohol-water solvent mixture of very high alcohol-water volume ratio allowing use of elevated process temperatures without the consequence of lignin condensation and agglomeration encountered in previous organosolv cooking experiments.

Experimental

Materials

Seven species of Nigeria savannah timbers were used to investigate the potentials of Proton generating NAEM-Catalyzed Organo-solv pulping method: Pinus Carribea, Ficus Exasperata, Ceiba pentandra, Hibiscus Cannabinus, Adansonia Digitata, Mitragyna ciliate, and Gmelina Arborea. These qood materials were obtained from different geogtaphical locations in Nigeria. The preferred alcohol is Ethanol in aqueous mixture of alcohol-water volume ratio ranging from nearly equal moles, e.g. 70 volumes of Ethanol to 30 volumes of water, but preferably higher alcohol-water ratios for example 95 volumes of ethanol to 5 volumes of water are considered more effective for rapid delignification. At the highest ratios it is necessary to calculate the amount of water contributed by the moisture content of lignocellulosic material such as wood chips, and to proportion the mixture using anhydrous alcohol stock [4, 9].

Methods

Organosolv Pulping Operation.

To investigate the effectiveness of delignification and yield of fiber when using the novel salt-catalyzed ethanol-water solvent mixtures in comparison with the kraft process, a number of cooks were carried out in a laboratory scale stainless steel rotating type wood digester. Wood chips in both air-dry and green condition were brought to uniform moisture content prior to cooking. Batch quantities of wood chips amounting to or equivalent to 2kg oven-dry (O.D) weight were loaded into the digester followed by the addition of prepared solvent mixture of about 100 g to 120 g of predetermined quantities of catalyst compounds in biomass/liquor ratio of 1/4. The void volume of the chamber was about 15 to 20 cm3. The lowest pressure produced was about 15 atmospheres at 170° C. for a 70:30 alcohol-water mixture. The highest pressure was above 40 to 48 atmospheres for virtually anhydrous alcohol at various temperatures.

In the organo-solv process, the main organic solvent used was 50% proof ethanol of about 0.93 specific gravity. The initial pH of the organic solvent was recorded at 6.2. The digester was loaded with wood chips along with the required cooking liquor at a liquor to wood ratio of 4 to 1. In the cook, the bottom outlet valve of the digester was tightly closed (firmly bolted) against any leakage. Time to reach the maximum cooking temperature was about 63minutes while the time at reaction temperature was varied for each wood specie depending upon the respective lignin content of each wood. The various changes in these parameters were carefully recorded. At the first signs of emission of gases, degassing was effected usually around 110oC – 120oC. A constant appearance of blackness in the emitted black liquor signaled the cessation of pulping operation.

Following the cessation of pulping, the digester was allowed to cool to 60oC and the contents blown down. It took about 90 to 120 minutes before the organo-solv pulping operation was terminated at maximum temperature of 170oC. Some organo-solv cooks of mitragyna ciliate required a one-stage grinding to attain proper pulp defiberization. Further processing by copious washing with water, pressing and drying were applied to obtain brown pulps. Yields for the various cooks were determined.

At the end of each cook the vessel was allowed to cool to 60oC before blow down and the liquor decanted. The drained pulp was washed with water-washed sufficiently and the cleansed pulp was air-dried until constant weight was obtained. Samples were reserved for Kappa number and viscosity determinations where applicable, and the remaining cellulosic residue was analyzed for final moisture content to allow calculation of the pulp yield. For all analyses TAPPI standard test procedures were used.

The fully cooked chips were found to be readily separable into free fibers on slushing in acetone which removed the greater part of the solubilized lignin trapped within the cooked chips and fibers. Some of the fiber residues were washed first with hot or with cold catalyst-free solvent mixture; it was found that subsequent washing with water had no adverse effect on bleachability of the fibers and removed only a minor amount of colour [11].

Mechanism of Organosolv Process Chemistry [5, 10]

Ethanol and water dissociate according to the following reactions:

1. $C_2H_5OH\text{-}OC_2H_5^- + H^+$

2. $C_2H_5OH\text{-}OCH_2CH_3^- + H^+$
3. $H_2O\text{-}H^+ + OH^-$

The reaction of lignin (abietic acid) and the dissociated ions of ethanol water at high temperature and pressure can be represented as shown below:

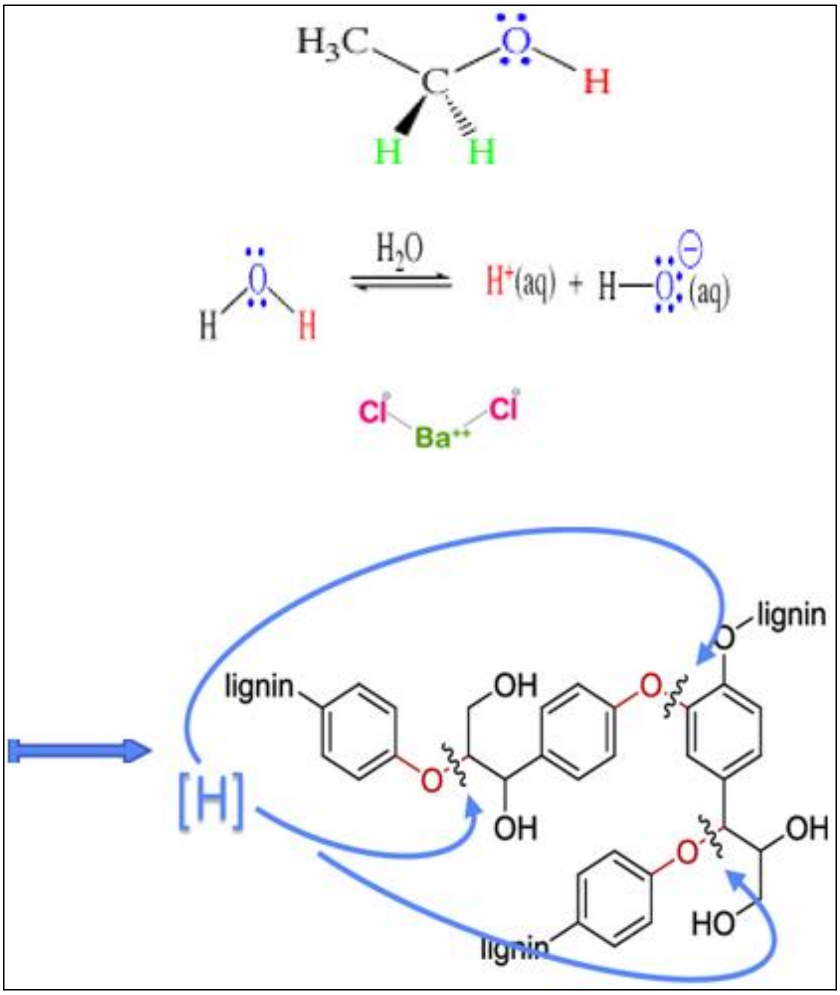

Fig 1: Mechanism of Lignin Solubilization [3, 7]

Result and Discussion

In the catalysed organosolv pulping, the PH of the cooking liquor decreased from 5.6 to 4.8 due to the high content of protons released from the dissociation of alcohol. The use of NAEM Catalysts buffered the solution and kept the PH at 4.8. Under this favorable condition destruction of hemicellulose is less severe and this is responsible for the high yield and strength properties of NAEM Catalysts Organosolv pulp. With less dehydration, pulp of very good flexibility and high viscosity was obtained. While the kraft process is associated with the emission of malodorous pollutants arising from the sulphides, mercaptans, and p-cymols.

Table 1: Summary of the Pulp Woods, Their Maturity Age, Fibre Lenght, and Sources in Nigeria.

Wood Specie	Age (Years)	Fiber Length (mm)	Sources of wood in Nigeria
Pinus Carribea	15-20	2.6	South, West, East and Middle Belt
Ficus Exasperata	10	1.75	All the states of Nigeria
Ceiba Pentandra	7	2.2	All the states of Nigeria
Hibiscus Cannabinus	4	1.3 (Stem) 2.7 (Bark)	Tropical and Rain Forest
Mitragyna Ciliata	15	2.0	Savannah Belts
Adansonia Dititata	10	3.6 (Bark) 2.7 (Stem)	Southern Nigeria Savannah
Gmelina Arboria	8	1.2	Tropical and Savannah zones

O.D =Oven dry weight basis NAEM-ORG = Non Alkaline-Earth Metal Salts, Catalysed Organosolv process

Organosolv pulping was accompanied by the emission of sweet-smelling esters and aldehydes. This emission of very high content of sulphides also explains the very dark colour of kraft pulps in contrast to the brownish colour of organosolv pulps.

Table 2: Levels of Different Parameters Investigated for Organosolv process.

Wood Specie	Cook No.	Total Yield (%)	Residual Lignin as % O.D Pulp	Kappa Number	Ash content of wood (g)	Wood Moisture content (wt %)	O.D of wood (g)	Fiber length (mm)
Pinus carribea	1	62.8	5.10	75.1	5.10	6.10	1992	2.590
Hibiscus cannabinus	2	62.0	2.40	60.2	2.20	14.1	1889	1.290(stem) 2.689(bark)
Ficus exasperata	3	62.2	4.70	52.5	3.41	12.9	1890	1.750
Ceiba pentandra	4	61.5	4.70	62.9	3.89	12.4	1655	2.189
Mitragyna ciliata	5	61.7	6.10	76.5	4.11	10.1	1799	1.999
Adansonia digitata	6	61.0	6.60	68.2	4.69	9.92	1816	3.586(bark) 2.677(stem)
Gmelina arborea	7	62.5	6.80	55.7	4.99	9.54	1892	1.2

The results presented in Table 2 are summarized for the organosolv pulping process of the seven Nigeria Savannah Wood Species as investigated in this research study.

The cooking time ranged from at least sixty (60) minutes to one twenty (120) minutes. The process yielded bright, free-fiber pulp even at residual lignin of 80 Kappa number as high as 75% of softwood and up to 70% of hardwood weight, of viscosity (TAPPI 0.5% Cu En) above 18 up to 60 centipoise. Addition of trace amounts of an acidic compound as a secondary catalyst increases the rate of delignification. Elevated pressures on the cooking solvent mixture also increases the rate of delignification.

Table 3: Levels of Different Parameters Investigated for Kraft Process.

Wood Specie	Cook No.	Total Yield (%)	Residual Lignin as % O.D Pulp	Kappa Number	Ash content (g)	Moisture content (wt %)	O.D (g)	Fiber length (mm)
Pinus carribea	1	46.5	6.50	18.5	5.10	6.10	1992	2.590
Hibiscus cannabinus	2	51.2	4.60	17.2	2.20	14.1	1889	1.290(stem) 2.689(bark)
Ficus exasperata	3	48.5	6.80	18.6	3.41	12.9	1890	1.750
Ceiba pentandra	4	41.8	6.10	16.6	3.89	12.4	1655	2.189
Mitragyna ciliata	5	47.2	7.40	23.4	4.11	10.1	1799	1.999
Adansonia digitata	6	48.5	6.90	22.1	4.69	9.92	1816	3.586(bark) 2.677(stem)
Gmelina arborea	7	42.5	6.75	19.7	4.99	9.54	1892	1.2

The results presented in Table 3 are summarized for the Kraft pulping process of the seven Nigeria Savannah Wood Species as investigated in this research study.

Ceiba Pentandra pulp recorded the lowest yield which averaged 41.8% based on dessicated wood weight as 100, this figure showing little variation with actual pulp yield. The TAPPI 0.5% CuEn viscosity (TAPPI T 230 os-76) determined on the alpha-cellulose was between 35 and 54 centipoises.

The above results confirm that the NAEM Organosolv process could be available alternative to the well-established kraft process which has so far dominated the pulp industry. The use of a proton generating NAEM Catalyst salts in aquous alcohol is a critical determinant in obtaining pulp that can match the strength properties of kraft pulps.

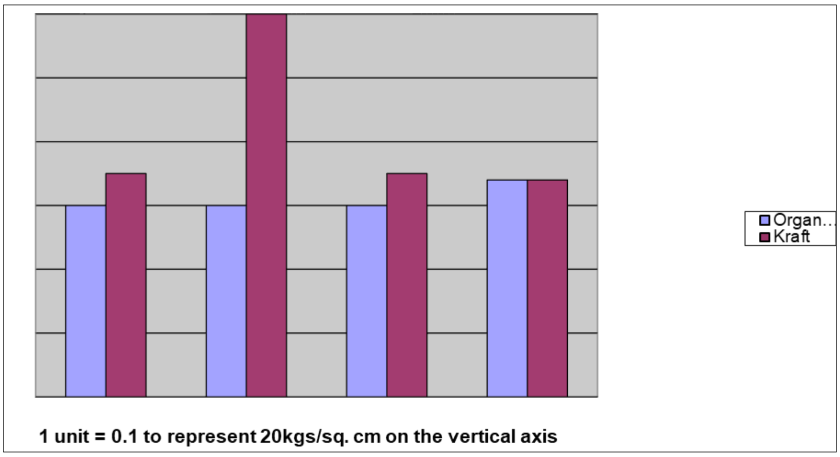

Fig 2: Burst Factor 1

Organosolv pulps can be easily bleached with hydrogen peroxide while aggressive chlorinated agents were used for bleaching of kraft pulps. While the yields of Organosolv pulps were as high as 60% the highest yields for kraft pulps averaged 45%. The strength properties with respect to tensile, burst and lean properties showed marked differences in favor of kraft pulping. However, the NAEM Catalyst Organosolv pulp produced paper of identical strength properties as kraft papers. This is evident in the results of the strength investigations carried out on the paper samples furnished from the two (organosolv and kraft) processes.

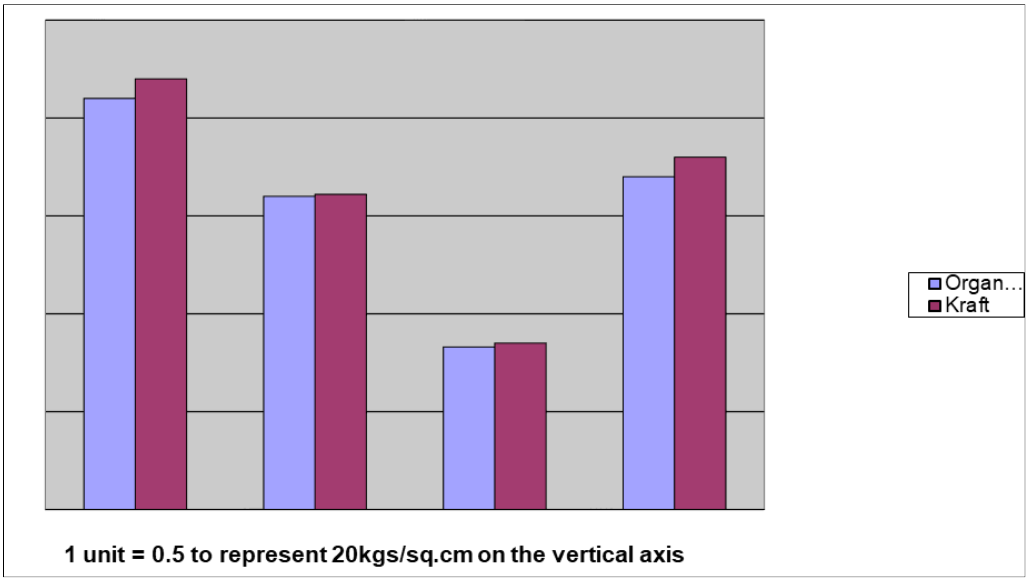

Fig 3: Burst Factor 2

Figures 2 and 3 shows the results of burst strength from paper samples of both processes which indicates that the burst strength properties are almost equal.

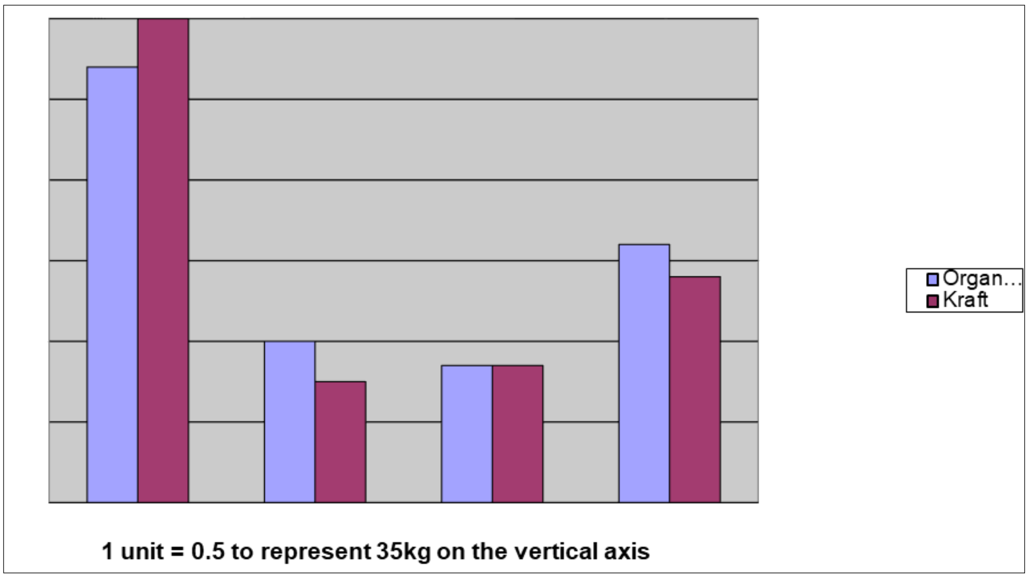

Fig 4: Tear Index 1

In figures 4 and 5, it could be clearly seen that the tear index of paper samples from both processes only show slight variation slightly favouring the kraft process. Figures 6 and 7 also show slight variation in tensile strength properties of the paper samples furnished from both processes, though in favour of the kraft process.

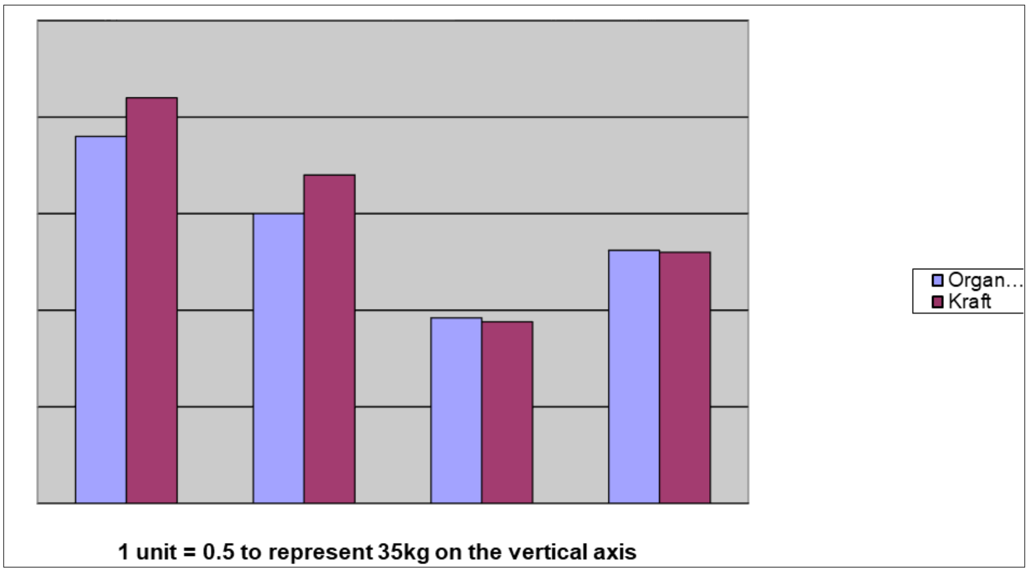

Fig 5: Tear Index 2

The pulps made were relatively bright in their unbleached state, and amounted to exceptionally high weight percentage of the wood. Several of the higher-yielding cook residues were further delignified with sodium chlorite-for 5 minutes according to TAPPI test procedure T 230-su-66 in preparation for further purification to an alpha-cellulose according to TAPPI T 429-m-48 (gravimetric) method to estimate the 17.5% NaOH-resistant fraction of the pulps.

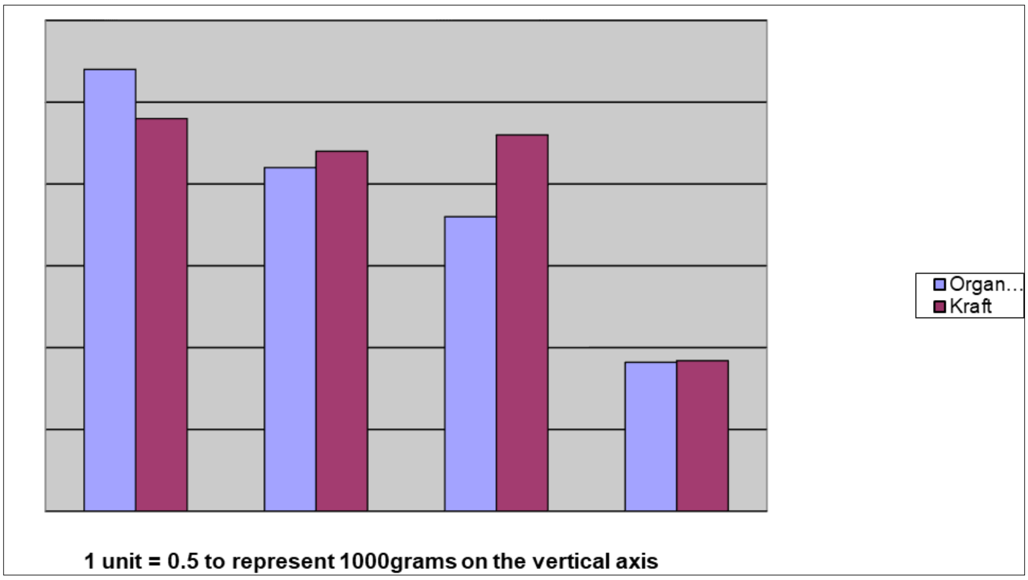

Fig 6: Tensile Strenght 1

The pulp produced is low in residual lignin content and bright in color so that bleach requirement to attain a certain brightness is much reduced. Thus the process maximizes on fiber yield and quality, mass recovery per unit weight of lignocellulose pulped and minimizes on energy required for obtaining fully liberated fibers for papermaking and dissolving pulp purposes. In some cooks where the cooking time was insufficient to allow total fiber liberation, it was found that vigorous agitation in a high speed blender rotating at 3000 RPM was effective to free the pulp fibers. The process is particularly efficient in making fibers of extremely high viscosity at high fiber yields. The spent cooking liquor is stable against lignin precipitation even after cooling to room temperature whereby pulp washing and disintegration can be done in the cooking liquor to remove trapped dissolved lignins. The combination of high alcohol concentration and high process pressures allows protection of the carbohydrates and production of pulps with superior high viscosity.

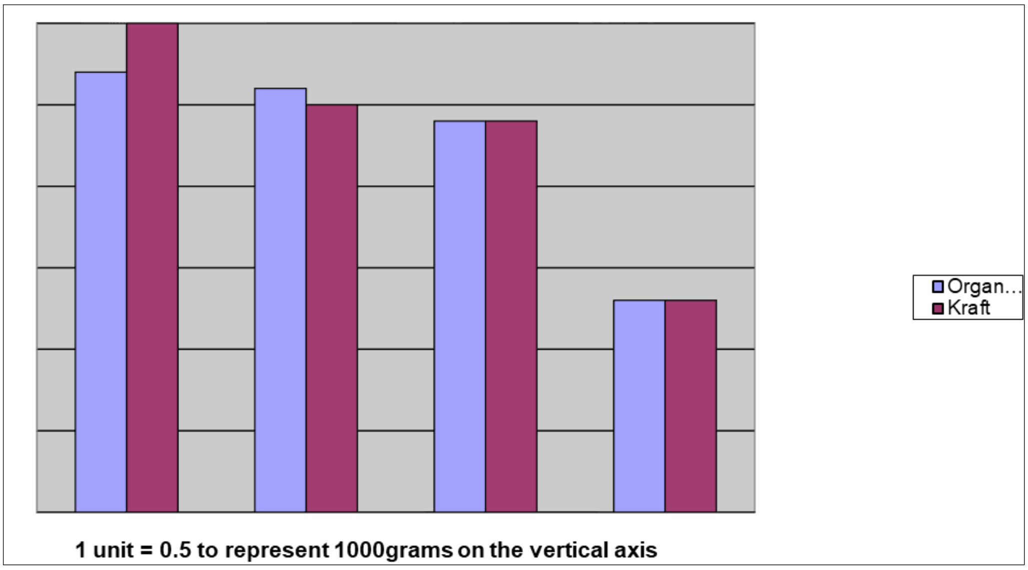

Fig 7: Tensile Strenght 2

At high alcohol-water ratios not only is delignification more complete, but carbohydrate degradation is suppressed, especially if also high pressure is used during the cooking cycle, and the resulting aqueous solution will have improved dissolving power for the lignin.

The preferred use of high process pressures allows virtually all the lignin and only a minimum of the cell wall carbohydrate materials to be removed within relatively short cooking times. Fiber yields almost equal to the total cellulose content and a substantial proportion of the hemicellulose content originally present in the wood was obtained.

Conclusion and Recommendation

The process is particularly successful in producing high yields of pulp of good quality fibers without requiring mechanical refining to liberate fibers. Such pulps have nearly theoretical alpha-cellulose content and fiber strength only slightly below the strength of natural undegraded cellulose. The process is universally effective in treating the gymnosperm and angiosperm wood species as well as lignocellulosic plant materials such as bamboo, sugarcane, cereal plants and grasses.

Delignification by use of a proton generating NAEM-catalyst salts in aqueous alcohol is an innovative, environmental friendly chemical pulping process that works without the use of sulphur compounds, with a particular benefit of simple recovery by distillation, allowing black liquor combustion to be dispensed and the dissolved lignin recovered. This process is suitable for pulping both hardwood and softwood. Compared with conventional processes, this process has the advantage of achieving a high degree of delignification through an increase in temperature during pulping without any appreciable damage to the cellulose. Proton generating NAEM-catalyst salts pulping process is none polluting compared with the soda and ktaft processes which are associated with heavy pollution load. This pulping process was selected due to its environmental and economic advantages (such as little or no emission of fowl smelling malodorous gaseous pollutants – since no sulphur compounds are used, an increase in the pulp production – as lower cooking periods are needed to obtain the same pulp quality and quantity), making the implementation of this process possible in factories situated in the vicinity of agricultural areas, since it may be adapted for low productions and may be applied to any raw wood or non-wood material. The capital outlay to build organosolv plants would certainly be less than the kraft plants due to high savings in the distillation column that would be used for recovery of spent alcohol. The process is pollutant free. Lignin and other bye-products are obtained without degradation. Thus, organosolv pulping represents an excellent process for obtaining well delignified pulp free from extractives. Such pulp can be useful in biotechnological processes of hydrolysis.

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