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PREPARATION OF CELLULOSE FROM OIL PALM EMPTY FRUIT BUNCHES VIA ETHANOL DIGESTION: EFFECT OF ACID AND ALKALI CATALYSTS

ASTIMAR ABDUL AZIZ*; MOHAMAD HUSIN* and ANIS MOKHTAR*

ABSTRACT

Ethanol digestion of oil palm empty fruit bunches (OPEFB) fibres at a temperature between 165ºC - 180ºC for 2 hr and at a solid-to-liquid ratio of 10:1, ethanol-to-water ratio of 1:1, and with or without 10% 1 N HCl and 1.25 M NaOH as catalysts was studied in order to prepare cellulose via ethanol pulping. The pulp produced was studied for yield, moisture content, solubility in cold/hot water and 1% NaOH, lignin, holocellulose and α-cellulose content.

The highest yield of pulp (57%, oven dried weight basis) was from OPEFB fibres digested at 170ºC for 2 hr without addition of catalyst, whereas OPEFB fibres digested at 175ºC for 2 hr with acid catalyst gave the lowest yield of 45% (oven dried weight basis) pulp. Higher cooking temperature gave lower yield of pulp since the reaction hydrolyzed out the hemicellulose, lignin and part of the cellulose. The reactions at 165ºC, 170ºC and 175ºC with acid catalyst produced 56%, 50% and 45% of pulp yield, respectively. It was found that a temperature of 180ºC with or without catalyst was too high for pulping because it totally digested the fibre into a viscous soluble pulp.

On the effect of catalysts, acid catalyst was found to enhance the pulping of OPEFB fibres. Without the acid catalyst, at temperature of 165ºC, the fibres could not be fully cooked and would still be in the fibrous form. Reactions at 170ºC and 175ºC without catalyst gave 57% and 55% yield of pulp, respectively whereas with acid catalyst gave 50% and 45% yield of pulp respectively. The base catalyst could only fully pulp the OPEFB fibres at a temperature of 175ºC, but the fibres dissolved at temperature 180ºC.

Pulp produced at 175ºC for 2 hr with 10% 1.25 M NaOH gave the best quality pulp, which contained lowest lignin and highest holocellulose at 8.2% and 91.8% (based on the dry weight of pulp), respectively. The maximum yield of α-cellulose (isolated from the pulp) also was obtained from OPEFB digested with alkali catalyst at 175ºC for 2 hr (64.3% based from dry weight of pulp; 34.1% based on dry weight of OPEFB).

Keywords: cellulose, alcohol pulping, oil palm empty fruit bunches.

INTRODUCTION

OPEFB contains about 77.7% holocellulose which consists of 44.2% and 33.5% α-cellulose and hemicellulose, respectively, and 20.4% lignin (Basiron and Husin, 1996). An attempt was made to extract pulp or cellulose using an environmental friendly method. If successful, this will add value to OPEFB.

Lignin, as a highly branched polymer attached with polysaccharides, is composed of phenyl propane-based monomeric units linked together by several types of ether linkages and also various kinds of carbon-carbon bonds (Goheen, 1978). Many

* Malaysian Palm Oil Board, P.O. Box 10620, 50720 Kuala Lumpur, Malaysia.

products can be made from lignin, *e.g.,* cresols, phenol, catechols and vanillin from fragmentation process; dispersants and emulsion stabilizers from macromolecules in solution systems process; thermosetting resin, polyblends, antioxidant and rubber reinforce by macromolecules in material systems and energy as well (Krinqstad, 1978).

Cellulose is a linear polymer of anhydroglucose units linked together with β-1,4-glucosidic bonds. Two adjacent glucose units are linked by elimination of one molecule of water between their hydroxylic groups at carbon 1 and carbon 4. Cellulose contains crystalline (50%-90%) and amorphous regions (Fengel and Wegener, 1989a). These structural features of cellulose determine its chemical characteristics including (1) the degree of swelling by water, (2) crystallinity, (3) presence of specific functional groups, and (4) accessibility to cellulolytic enzymes. Several physical or chemical processes, including pulping have been identified to extract cellulose from lignocellulosic materials.

Two common methods for the preparation of holocellulose are (a) chlorination including alternating extraction with hot alcoholic solutions of organic bases, and (b) delignification with an acidified solution of sodium chlorite (Fengel and Wegener, 1989b). The important criteria can be defined for holocellulose:

- low residual lignin content;
- minimal loss of polysaccharides; and
- minimal oxidation and hydrolytic degradation of cellulose.

Alcohol pulping or digestion has been the recent focus of the pulping process since it generates pulp in higher yields than the chemical process and with properties similar to those of bisulphite pulps and with the advantage of recovery of valuable chemical by-products (Paszner and Cho, 1989; Asiz and Sarkanen, 1989). This process is a green-pulping process since it involves no hazardous chemicals. Furthermore, the organosolv process was found feasible for fractionation of lignocellulosic material into three major components - hemicellulose sugars, cellulosic pulp and low molecular weight lignin (Sarkanen and Tillman, 1980).

Alcohol delignification is a complex process involving the breakdown of the lignin-carbohydrate complex, solvation of the breakdown products, and repolymerization and/or redeposition of the breakdown products on the solids. It has been suggested that the organic solvent swells the wood structure where the extent of swelling increases with the polarity of the solvent and acts as a solvent for the lignin (Kleinert, 1974). This ensures that the lignin can be extracted without extensive modification of its stucture. Addition of acid or alkali catalysts is believed to enhance the pulp yield and reduce the reaction time and temperature needed. Acidic catalysts increase the extent of pentosan removal whereas basic catalysts prevent or reduce the pentosan removal/hydrolysis (Kleinert, 1974; McDonough, 1993).

Since most of the cellulose produced is used in the food and pharmaceuticals industries, alcohol digestion is one of the suitable processes because it is an environmental friendly process and does not use dangerous chemicals. Unfortunately since it involves lignin-to-carbohydrate bond hydrolytic cleavage, it requires a very high digestion temperature and an acid catalyst. The objective was to study the effect of acid and alkali catalysts in alcohol digestion and to optimize the parameters to produce cellulose.

MATERIALS AND METHODS

Alcohol Pulping

The OPEFB fibres used in this study were obtained from Sabutek Sdn. Bhd., Teluk Intan, Perak, Malaysia. Alcohol pulping of OPEFB fibres was done using a MK Pulp Digester (10 litres vessel) in which 300 g (oven dried) fibres were digested for 2 hr in ethanol-water solution with the ratio of 1:10 (solid: solution) and whereas the ethanol to water ratio was 1:1. The cooking temperatures studied were 165ºC - 175ºC. An acid catalyst, 10% 1 N HCl, and base catalyst, 1.25 M NaOH, were used.

Pulp Recovery and Analysis

When the pulping process was completed, the digested fibres (known as pulp) was separated from the black liquor and washed. The pulp was then obtained by screening the residual fibers after beating with Pulp Disintegrator in water suspension at 3000 rpm for 20 min. The pulp was then air dried before further analysis for moisture content, cold water solubility, hot water solubility, 1% NaOH solubility, Klason lignin, holocellulose, pentosan and α-cellulose content based on methods as follows:

- moisture content of pulp - TAPPI Method T208 om-84 (Anon., 1984a);
- water solubility of pulp - TAPPI Method T207 om-81 (Anon., 1981);
- one percent sodium hydroxide solubility of pulp - TAPPI Method T212 om-83 (Anon., 1983a);
- pentosan content of pulp - TAPPI Method T223 hm-84 (Anon., 1984b);
- Klason lignin of pulp - TAPPI Method T222 om-83 (Anon., 1983b);

- holocellulose content of pulp was based on the method by Browning (1967); and

- α-Cellulose content of pulp - TAPPI Method T203 om-83 (Anon., 1983c).

RESULTS AND DISCUSSION

The physical appearances of the resulted pulp and the black liquor produced from each digestion are shown in *Table 1*.

The undigested fibres (NC1, BC1 and BC2) were not considered as pulp and therefore were not further analysed. It was also found that digesting at 180°C with/without catalyst was too extreme as it dissolved the OPEFB fibres.

The results in *Table 2* show that the temperature of digestion and catalysts used affected the yield of pulp and the chemical characteristics of the pulp. The highest yield of pulp was from OPEFB fibres digested at 170°C for 2 hr without any catalyst (NC2, 57.0%); whereas the lowest yield (45.0%) was from OPEFB digested at 175°C for 2 hr with 10% 1 N HCl catalyst (AC3) (*Table 2*).

Cooking at higher temperature gave a lower yield of pulp since the reaction hydrolyzed the hemicellulose, lignin and part of the cellulose (*Figure 1*). Cooking at the temperatures of 165°C, 170°C and 175°C with acid catalyst gave 56%, 50% and 45% yield of pulp, respectively. It was found that the cooking temperature of 180°C with or without catalyst was too high for pulping because it totally digested the fibres into viscous soluble pulp. This was due to the fact that at high temperature (>180°C), more homolytic and hydrolytic reactions occurred between the lignin and cellulose, hence more cellulose could be isolated from the fibres (Bryce, 1980).

During solvent pulping, lignin-to-carbohydrate bonds are cleaved either homolytically during the high temperature cooking or hydrolytically with the addition of hydrochloric acid or alkali. Simultaneously, the acetyl groups, which are mainly linked to

TABLE 1. PULP AND BLACK LIQUOR PRODUCED FROM THE DIGESTION OF OIL PALM EMPTY FRUIT BUNCHES FIBRES UNDER DIFFERENT COOKING PARAMETERS

Parameters	Sample	Physical appearance of pulp	pH of black liquor
Without catalyst			
- 165°C	NC1	Intact fibres - dark brown (undigested)	4.32
- 170°C	NC2	Pulped fibres - dark brown	4.26
- 175°C	NC3	Pulped fibres - dark brown	3.89
With acid catalyst			
- 165°C	AC1	Pulped fibres - reddish brown	3.99
- 170°C	AC2	Pulped fibres - reddish brown	3.61
- 175°C	AC3	Pulped fibres - reddish brown	3.26
With base catalyst			
- 165°C	BC1	Intact fibres - light brown (undigested)	6.00
- 170°C	BC2	Intact fibres - light brown (undigested)	5.42
- 175°C	BC3	Pulped fibres - light brown	4.48

TABLE 2. CHEMICAL PROPERTIES OF PULP PRODUCED UNDER DIFFERENT DIGESTION PARAMETERS OF OIL PALM EMPTY FRUIT BUNCHES FIBRES (based on the dry weight of the pulp)

	NC2	NC3	AC1	AC2	AC3	BC3
Yield of pulp (%)	57.0	55.0	56.0	50.0	45.0	53.0
Moisture content (%)	1.9	1.5	2.1	1.5	1.1	3.6
Cold water solubility (%)	5.3	5.2	5.5	5.5	5.0	4.2
Hot water solubility (%)	5.1	4.6	5.6	5.2	4.0	5.0
1% NaOH Solubility (%)	27.0	22.4	23.5	25.3	24.8	18.3
Lignin content (%)	14.7	13.2	12.8	12.5	12.6	8.2
Holocellulose content (%)	85.3	86.8	87.2	87.5	87.4	91.8
α-Cellulose content (%)	47.8	51.2	49.7	52.5	55.1	64.3
α-Cellulose content (%) *	27.2	28.2	27.8	26.2	24.8	34.1

Note: * based on the dry weight of oil palm empty fruit bunches.

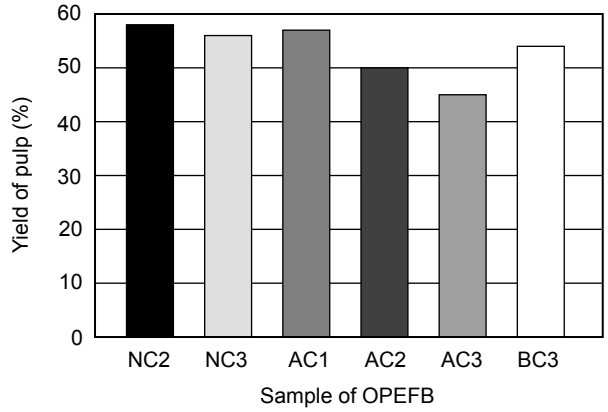

Figure 1. Yield (%, based on the dry weight of the oil palm empty fruit bunches) of pulp from different parameters of ethanol digestion of oil palm empty fruit bunches.

the hemicellulose portion, are unstable to alkali and are cleaved at a very early stage of the cooking (Glasser, 1980; Bryce, 1980). This was shown by the decrease in pH of the resulting black liquor during the pulping of OPEFB fibres, with/without catalyst, either acid or base.

The affinity of cellulose towards water that is shown as its moisture content is dependent on its capillary structure and surface area and may affect adversely the reactivity of the cellulose to subsequent reaction systems (Green, 1963). These structural changes can be achieved by chemical reaction or swelling agents as shown by the moisture content of OPEFB pulp from different catalysts. Pulp from OPEFB fibres digested with alkali catalyst (BC3) showed the highest moisture content of 3.6%, whereas the one from acid catalyst at 175ºC (AC3)

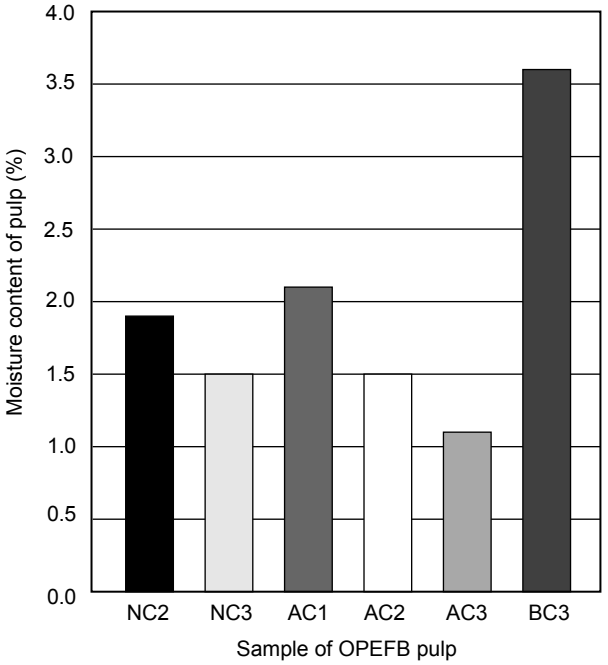

Figure 2. Moisture content of pulp extracted from different parameters of ethanol digestion of oil palm empty fruit bunches.

gave the lowest moisture content of 1.1% (*Figure 2*). Sodium hydroxide causes swelling, leading to an increase in the internal surface area, decrease in the degree of polymerization, decrease in crystallinity and to certain extent, it can separate the structural linkages between lignin and carbohydrates and causes disruption of the lignin structure (Fan *et al.,* 1987). The same explanation also applies to the lowest lignin content of the BC3 sample (8.2%, based on the dry weight of the pulp).

Alkali catalysts, which act as a swelling agent for cellulose, known as intracrystalline swelling, penetrate and swell both the accessible amorphous and crystalline region of the cellulose (McGinnis and Shafizadeh, 1980).

The acid treatment of OPEFB fibres also showed a reduction in moisture content of the pulp to 2.1%, 1.5% and 1.1% by increasing the temperature from 165ºC, 170ºC and 175ºC as shown in samples AC1, AC2 and AC3, respectively (*Table 2*). This indicates that the pulp had become more water resistant. This was due to the fact that the acid catalyst for ethanol pulping of OPEFB fibres ruptured the capillary structure of the cellulose which subsequently reduced its reactivity and adsorption capability (Mann and Sharples, 1963).

The pulp from acid catalyst pulping showed slightly higher in 1% NaOH solubility compared to that of without catalyst and with alkali catalyst. This may be due to the affinity of the acid catalyst pulp towards alkali. The pulp from the alkali catalyst pulping at 175ºC shows the lowest 1% NaOH solubility at 18.3%. This is also similar to the moisture content (*Figure 3*) which indicates the hydrophobic criterion as discussed earlier. As expected, NaOH reacts as delignification agent which is shown by the lowest lignin content of BC3 (8.2%, based on dry weight of pulp) as shown in *Figure 4.*

The highest holocellulose extractable was also from the BC3 sample at 91.8% (based on the dry weight of pulp) as shown in *Figure 5.* As a comparison to that prepared from the chlorite bleaching method, the yield based on the weight of initial OPEFB fibres was slightly higher at 77.7% (Basiron and Husin, 1996) than the BC3 sample at 48.7% (*Table 2*). The higher holocellulose extracted from the raw OPEFB fibres via chlorite bleaching (*Figure 6*) may be explained by the possible of existence of intact hemicellulose and traces of lignin within the fibres since this procedure only involved the oxidation and discoloration of lignin (Wise *et al.*, 1946), whereas those components had almost been extracted during the alcohol pulping (Kleinert, 1974; Paszner and Cho, 1989).

On the preparation of α-cellulose, the highest yield was also from the BC3 sample at 64.3% based on the dry weight of the pulp (34.1% based on dry weight of OPEFB).

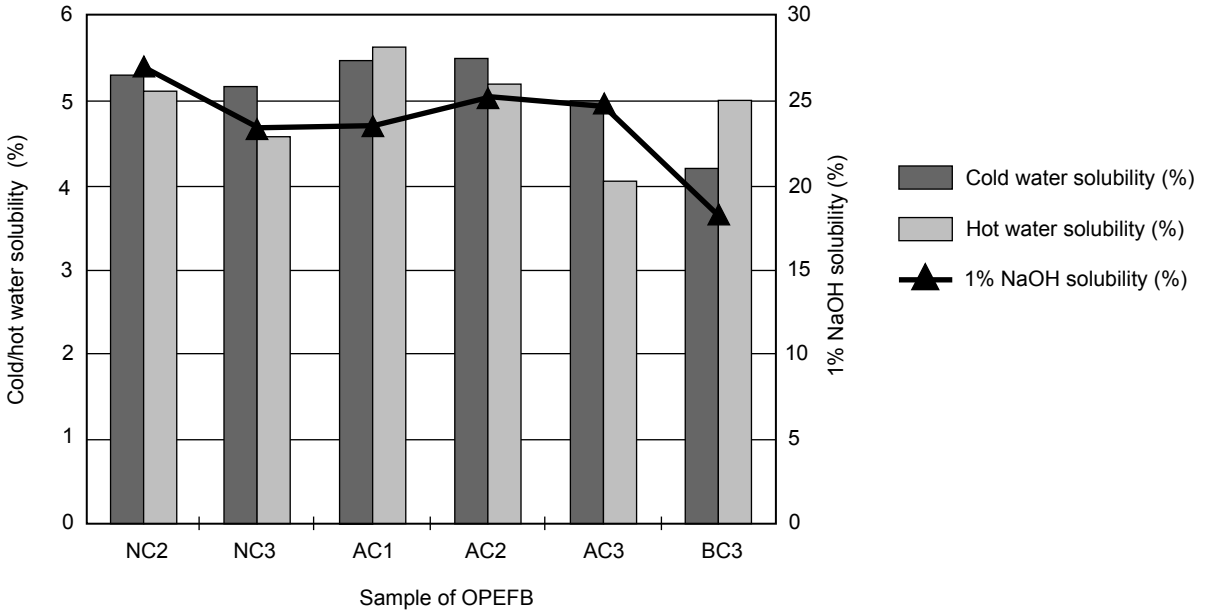

Figure 3. Solubility of pulp extracted from different parameters of ethanol digestion of oil palm empty fruit bunches.

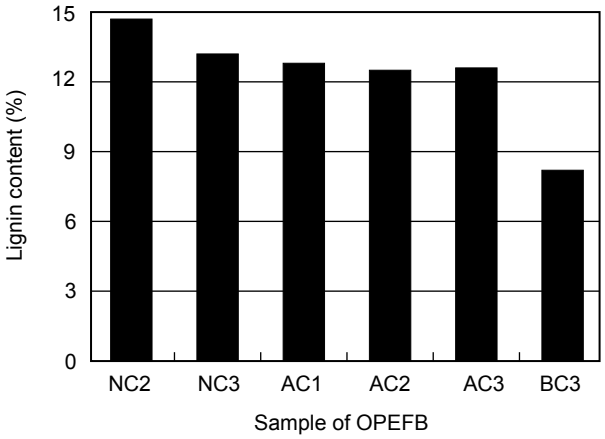

Figure 4. Lignin content of pulp extracted from different parameters of ethanol digestion of oil palm empty fruit bunches.

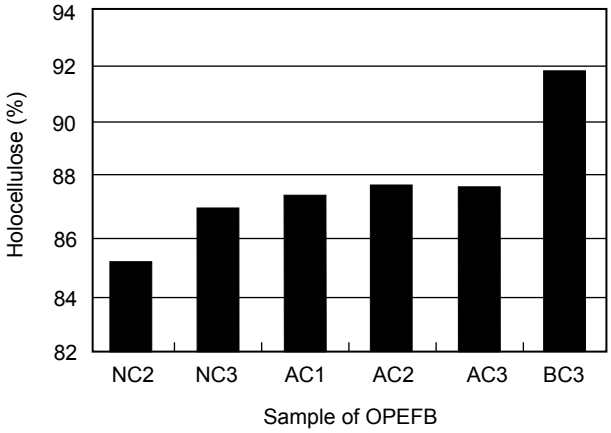

Figure 5. Holocellulose content of pulps extracted from different parameters of ethanol digestion of oil palm empty fruit bunches.

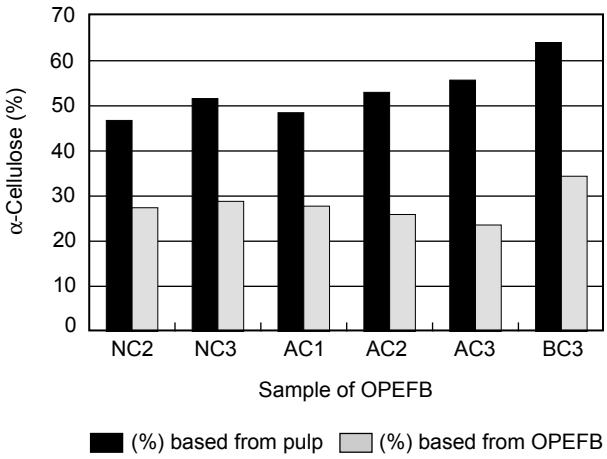

Figure 6. α-Cellulose contents of pulp extracted from different parameters of ethanol digestion of oil palm empty fruit bunches.

CONCLUSION

It is shown that OPEFB fibres pulped at a temperature of 175½C for 2 hr and at a solid-to-liquid ratio of 10:1, ethanol to water ratio of 1:1, and with 10% 1.25 M NaOH as catalyst produced the highest α-cellulose at 64.3% based on the dry weight of the pulp (34.1% based on the dry weight of the OPEFB).

Although acid catalyst ethanol pulping of the OPEFB gave the higher yield of pulp, proximate chemical analysis of the pulp showed an inferior quality with high lignin content and lower holocellulose and α-cellulose yield.

Proximate chemical analysis showed the basic chemical characteristics of the pulp produced, but further detailed studies would have to be carried out to determine the quality of the cellulose produced.

The crystallinity/amorphous structure (X-ray diffraction method), degree of polymerization and

functional group analysis have further to be analysed to ensure the reactivity as well as the edibility of the cellulose.

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