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Delignification Pretreatment of Palm-Press Fibres by Chemical Method

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ABSTRAK

Daripada hasil kajian, komposisi kimia hampas kelapa sawit tanpa pengolahan didapati mengandungi 39.9% selulosa, 28.9% hemiselulosa, 20.3% lignin dan 3.6% abu. Kepekatan bahan-bahan kimia yang digunakan dalam pengolahan serabut ialah 1.5% untuk NaOH, $Ca(OH)_2$, KOH, Na_2CO_3, 5.0% $CO(NH_2)_2$ dan larutan amonia akuas. Di antara bahan kimia yang dikaji, didapati NaOH merupakan bahan yang terbaik dalam memisahkan 60% kandungan lignin daripada serabut selepas pengolahan selama 24 jam secara kaedah semburan. Ini diikuti oleh bahan kimia lain seperti Na_2CO_3(49%), NH_4OH (40%), $Ca(OH)_2$ (38%), KOH (27%) dan $CO(NH_2)_2$ (21%). Kandungan selulosa dan hemiselulosa adalah hampir tidak berubah biarpun setelah masa pengolahan dengan bahan-bahan kimia ini dipanjangkan. Kandungan abu ternyata tinggi pada serabut yang diolah dengan NaOH dan urea. Kaedah rendaman didapati melarutkan lebih banyak kandungan lignin dibandingkan dengan kaedah semburan.

ABSTRACT

The chemical composition of the untreated palm-press fibres was estimated to be 39.9% cellulose, 28.9% hemicellulose, 20.3% lignin and 3.6% ash content. The concentrations of the chemicals used in the treatment of the fibres were 1.5% each of NaOH, $Ca(OH)_2$, KOH, Na_2CO_3, 5.0% $CO(NH_2)_2$ and aqueous ammonia solution. Of the chemicals tested. NaOH was the most efficient, having removed 60% of the lignin from the fibres after treatment for 24 hours using the spraying method. Comparative percentages for other chemicals tested were Na_2CO_3(49%), NH_4OH (40%), $Ca(OH)_2$ (38%), KOH (27%) and $CO(NH_2)_2$ (21%). The cellulose and hemicellulose content remained almost unchanged even after a prolonged period of treatment by these chemicals. The ash content was higher in fibres treated with NaOH and urea. The soaking method dissolved higher lignin content compared to the spraying method.

INTRODUCTION

Fibrous agricultural residues represent a major but not well used source of energy both as fuel and animal feed. In Malaysia, the annual production of palm-press fibres and empty bunches as waste materials amounts to approximately 8 million metric tons.

Most of these residues are characterised by extensive lignification of the cellulose fibres, thus making it difficult to be degraded. Cellulases which can convert cellulose into glucose are highly specific in their actions and have no direct hydrolytic effect on lignin. Being macromolecular, cellulase enzymes cannot penetrate through the lignin seal surrounding the cellulose fibres. To overcome the lignin barrier hindrance, many methods of treatment have been suggested and thoroughly investigated (Fan *et al.* 1982: Lee *et al.* 1983; Moo-Young *et al.* 1985) during the last decade with the aim of improving the biodegradability of the crop residues. These treatments can be categorised under three headings :-

a) physical or mechanical treatment,
b) chemical treatment, and
c) biological treatment.

In this study, the effectiveness of the various chemicals in removing the lignin content of the palm-press fibres have been examined. The tests on the biodegradability of these treated fibres by cellulase enzymes will be reported elsewhere.

MATERIALS AND METHODS

Chemicals

The following chemicals were used in the treatment of the fibres :- 1.5% each of NaOH, $Ca(OH)_2$, KOH, Na_2CO_3, 5.0% $CO(NH_2)_2$ and aqueous ammonia solution.

Methods of Treatment

Two methods were used in this experiment.

a) Spray method. 700 g of the fibres were uniformly sprayed with approximately 300 ml of the chemical solution before been tied in a plastic bag and left at room temperature for 24 hours.
b) Soaking method. The principles of this procedure were similar to the Beckman treatment, i.e., soaking of the fibres in chemical solution at 10 L/Kg of dried material. Reaction time was 24 hours.

In both cases, the treated fibres were washed free of the chemicals until the pH of the washing reached the pH of the water, i.e., pH 7.0-7.2. The treated samples were further washed with several changes of fresh distilled water before being oven dried at 37°C.

Determination of Chemical Composition

The fibre components were estimated individually after a series of extraction procedures. The various components analysed included the cellulose, hemicellulose, lignin and the ash content. The method by Goering and Van Soest (1970) was adopted.

a) Neutral Detergent Fibre (NDF) method
   Extraction with a detergent such as sodium lauryl sulphate left a residue containing lignin, cellulose, hemicellulose plus some protein and minerals. This residue was called 'Neutral Detergent Fibre'.
b) Acid Detergent Fibre (ADF) method
   Detergent such as trimethylammonium bromide was used under an acid condition. The pectin and most of the protein and hemicellulose were removed leaving lignin and cellulose, referred to as the 'Acid Detergent Fibre'.
c) Lignin content
   The acid detergent fibre was treated with 72% (w/w) sulphuric acid; the cellulose was hydrolysed and the lignin remained.

RESULTS

As shown in Table 1, the chemical composition of the untreated palm-press fibres was estimated to be 39.9% cellullose, 28.9% hemicellulose, 20.3% lignin and 3.6% ash content.

Pretreatment of the fibres with the various chemicals (Table 2) showed that NaOH was the most effective in removing lignin from the fibres. As much as 60% of the lignin was lost after a 24-hour treatment by using the spraying method. This was followed by Na_2CO_3 (49%), NH_4OH (40%), $Ca(OH)_2$ (38%), KOH (27%) and $CO(NH_2)_2$ (21%).

In general, the cellulose and hemicellulose content of the fibres were unaffected by these treatments and remained fairly constant even after a prolonged period of treatment up to 5 days as shown in Table 3 for the NaOH treatment; other results are not shown. However, the lignin content of the fibres continued

TABLE 1
Chemical Composition of Untreated Palm-Press Fibres. Figures Represent Average of Duplicates.

	% Of Dry Matter			
	Cellulose	Hemicellulose	Lignin	Ash
Untreated	39.9	28.9	20.3	3.6

TABLE 2
Effect of Chemical Pretreatment on The Composition of Palm-Press Fibres. Figures Represent Average of Duplicates.

Chemicals	% Of Dry Matter			
	Cellulose	Hemicellulose	Lignin	Ash
NaOH	40.7	29.1	8.0	9.2
KOH	44.5	27.7	14.6	3.3
$Ca(OH)_2$	36.9	30.1	12.4	4.4
Na_2CO_3	38.1	27.5	10.2	4.9
NH_3 Soln.	36.5	31.9	11.9	3.4
$CO(NH_2)_2$	36.4	35.5	15.9	9.8

TABLE 3
Effect of NaOH Pretreatment Period on The Chemical Composition of Palm-Press Fibres. Figures Represent Average of Duplicates.

Pretreatment Period (Days)	% Of Dry Matter			
	Cellulose	Hemicellulose	Lignin	Ash
1	40.7	29.1	8.0	9.2
2	36.7	26.4	6.7	7.0
3	37.6	29.6	3.5	5.1

TABLE 4
Comparison of The Spraying and Soaking Method of Pretreatment (NaOH) for A One Day Period on The Chemical Composition of Palm-Press Fibres. Figures Represent Average of Duplicates.

Method of Pretreatment	% Of Dry Matter			
	Cellulose	Hemicellulose	Lignin	Ash
Spraying	40.7	29.1	8.0	9.2
Soaking	35.4	26.1	3.6	10.0

to decrease further leaving approximately 17% after treatment for 5 days.

The ash content (Table 2) was noticibly higher in fibres treated with NaOH and urea compared with the untreated fibres.

Comparison of the spraying and soaking method of treatment using NaOH was carried out. The results (Table 4) revealed that the soaking method was more efficient in dissolving the lignin than the spraying method for a one-day treatment period. Soaking the fibres for 24 hours removed as much as 82% of the lignin whereas the same amount was removed only after treatment for 5 days by the spraying method.

DISCUSSION

The potential of using lignocellulosic biomass materials in bioconversion processes is well recognised. Malaysia produces an abundant supply of the palm-press fibres and empty bunches which are regarded as wastes and have not been utilised satisfactorily. Every opportunity for the reuse of such waste materials either for the purpose of bioconversion into useful products or as animal feed and fertiliser, must be examined.

A major problem in the commercialisation of this potential is the inherent recalcitrance of these materials to biological transformation. Fibrous residues consist mainly of the

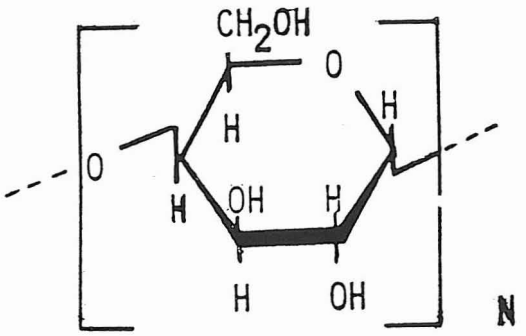

Fig 1a. The cellulose unit, β 1-4 glucopyranose

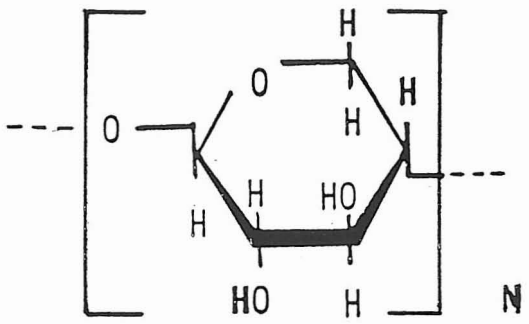

Fig 1b. The hemicellulose unit, β 1-4 xylopyranose

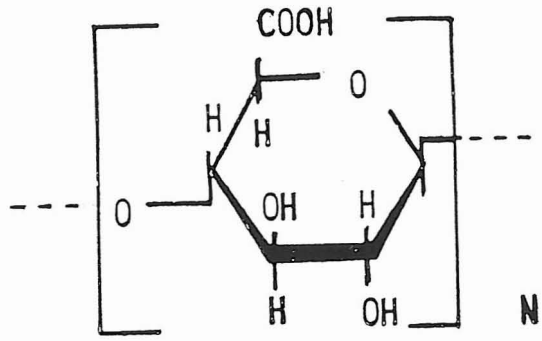

Fig 1c. The pectin unit, 1-4 α galactopyranuronic acid

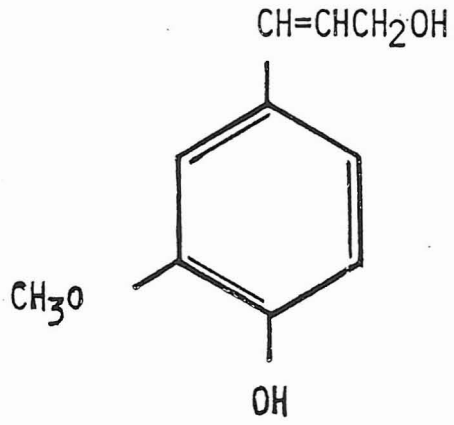

Fig 1d. The basic lignin unit corniferol derived from phenyl propane

structural components of plants. They are lignocellulosic in nature, possesing the components cellulose, hemicellulose, pectin and lignin. The cellulose molecule (*Fig. 1a*) is a polymer made up of as many as 10,000 glucose molecules in the pyranose form joined together in β 1-4 linkages. Hemicelluloses are made up of relatively short chains of xylose (*Fig. 1b*) or of a mixture of glucose and mannose, linked as with cellulose, in β 1–4 structures. The hemicelluloses have many side chains. The third type of carbohydrate in cell wall is pectin, based on galactose in the form of galacturonic acid residues joined in α 1-4 linkages (*Fig. 1c*). Accompanying these carbohydrates is lignin, a complex polymer that is based on derivatives of phenyl propane (*Fig. 1d*). In order to be effective, pretreatment techniques for enhancing the chemical and enzymatic reactivity of cellulose materials must alleviate two major constraints : the lignin seal, which restricts enzymatic and microbiological access to the cellulose: and cellulose crystallinity, which limits the rate of all forms of attack on the cellulose (Lamptey *et al.* 1986). Thus, in developing more effective pretreatment techniques for natural cellulosic materials, particular emphasis should be given on the physical and chemical methods by which crystallinity and the lignin barrier can be overcomed.

Chemical pretreatment with strong acids or bases, such as sulfuric acid or sodium hydroxide, effectively increase the hydrolysis of cellulose (Fan *et al.* 1982; Robards *et al.* 1983; Mulholland 1983). Of the chemicals tested, NaOH undoubtedly proved to be the most effective agent for delignification pretreatment. This is in agreement with the common practice in Europe, India and Australia where sodium hydroxide is used as a suitable agent to treat straw for animal feed.

Jackson (1978) described a simple method for spraying a weak solution of NaOH on to straw as well as a modified soaking, washing and draining method. These methods were tested using NaOH on the local palm-press fibres which showed that the soaking method was more effective in dissolving the lignin. The treatment of fibres with caustic soda could probably be further enhanced by increasing the surface area prior to treatment by either rupturing the cell wall or reducing the particle length as much as possible. The ash content which is a measure of the inorganic minerals was noticeably higher in fibres treated with NaOH and urea compared with the untreated fibres. This is probably due to the incomplete removal of the chemicals during washing with water or neutralising the treated fibres with acid or base after washing.

Although effective, sodium hydroxide is costly, corrosive, difficult to handle and a pollutant of land and water. Thus, to be economically feasible, it must be recovered for reuse. In addition, some of the chemicals used for treatment of lignocellulosic materials are often toxic or inhibitory to microorganisms (or their enzymes) so that their removal from the pretreated cellulosic materials must be almost complete. These factors combine to increase the expense and difficulty of such chemical treatment methods. Modification of the alkaline pretreatment included the aqueous ethanol-NaOH mixtures as reported by Nghiem *et al.* (1984) and combination of NaOH-gamma irradiation technique as a pretreatment scheme for the enhancement of soluble sugar production from corn stover by enzymic hydrolysis (Gonzales-Valdes *et al.* 1981).

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