

Extraction of cellulose from waste palm kernel and its hydrolysis to glucose

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ABSTRACT

A new method has been demonstrated for the extraction of cellulose from waste Palm kernel cake using acid base treatment. The method was giving 19.19% of cellulose. The FT-IR of the extracted cellulose was shows the present of the main functional groups at the expected range. Cellulose extracted from waste Palm kernel cake was hydrolysed to glucose in 4 h, with 100 % of selectivity at 100 °C. The catalyst is stable during the hydrolysis.

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KEYWORDS

Cellulose;
Ammonium sulphate;
Hydrolysis;
Glucose;
Palm kernel cake.

INTRODUCTION

Palm kernel (PK) is one of the abundant by-products. It is produced annually in large quantities, about 1.9 million tons of PK is left over by oil extraction process from oil palm industry^[1]. These amounts are significant enough to consider palm kernel cake as bio resource of raw materials for many industries. The utilizing of the PK could lead to produced cellulose, hemicellulose and lignin^[2]. Hence, PK as alternative sources for cellulose production not only enhances the usage of PKC. It is also able to solve the environment problem. Sodium chlorite is a moderately strong oxidizing agent which used for extracting cellulose and does not introduce the possibility of heavy metal contamination^[3]. Besides, acetic acid actively takes part in the hydrolysis of hemicelluloses. The strong oxidizing property of sodium chlorite yields pure cellulose with no lignin remaining inside.

Until recently, most ionic catalysts were synthesised and used for different purposes in liquid solutions. These ionic liquids were showing very good catalytic activity

compared with the commercial strong acids such as H_2SO_4 , HCl, and H_3PO_4 , which have limitations due to a tedious work-up procedure and the necessity of post neutralization of the strongly acidic media leading to production of undesired wastes. Therefore many challenges are facing the researcher regarding the characterization and the recycling of these ionic liquid catalysts. We have recently reported the synthesis of a new type of ionic catalyst in solid form with less environmental concerns. It is recyclable and can be used for the same purposes as where the ionic liquids catalysts are used^[4].

Recently, a new technique has been developed towards the production of second generation (2G) biofuels without the use of expensive enzymes^[5]. Producing 2G bioethanol from dead plant tissue is environmentally friendly, but it is also currently expensive because the process that is used today needs expensive enzymes. The goal is to produce bioethanol from cellulose containing waste plant parts. Cellulose is the major polymeric component of plant material and is the most abundant polysaccharide on Earth. In nature, a variety of

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microorganisms are known for producing a set of enzymes capable of degrading this normally insoluble polymer to soluble sugars, primarily cellobiose and glucose^[6]. As cellulose is very difficult to break down, it cannot directly be used as a food source. Cellulose is found everywhere in nature in rich quantities, for example in the stems of the corn plant, rice husk, and palm fronds. If we can produce bioethanol from the waste of PK, we have probably come a long way to make biofuel production more acceptable. In fact we can now report about an entirely new molecular compound, which can also replace enzymes in the work of breaking down cellulose to sugar for the production of 2G biofuels, following up on the procedures leading to the earlier reported sulfonic acid compound^[5,7].

MATERIALS AND METHODS

Raw materials

The chemicals used in this study were Sodium hydroxide (System, 99%), Nitric acid (Scharlau, 65%), Cyclohexanol (Riedle-De Haen, 99%), Cyclohexanone (Riedle-De Haen, 99%), Dimethylformamide (DMF) (System, 99.5%), Dinitrosalicylic acid (DNS) (BDH, 99%), Glucose (BDH, 99%), Lithium chloride (Sigma, 99%), Sulphuric acid (Poch, 95%). All chemicals used were AR grade or of high purity and were used directly without further purification.

Extraction of cellulose from palm kernel

Palm kernel used in this study was collocate from AL-Muthanna palms in south of Iraq. The PK was washed with distilled water, and then dried in an oven at constant temperature. The oil from PK was removed by using soxhlet extractor with n-hexane for 6 h. The extractive-free sample of PK was dried in an oven at 60 °C for 18 h and stored in refrigerator before use^[8]. The cellulose was extracted from free oil PK by using acidified sodium chlorite solution. 3.3 g of oil free PK was mixed with 100 mL of 7.5 % aqueous NaOH solution. The mixture was stirred for 1 h at room temperature. The pre-treated PK was then filtered and washed with 95 % ethanol and distilled water repeatedly twice to remove the base. The hemicellulose-free PK was then dried in oven at 60 °C for 24 h. 2.0 g of

hemicelluloses free palm kernel was mixed with 100 mL distilled water, 15 mL glacial acetic acid and 2 g of sodium chlorite. The mixture is stirred for 2 h at 75 °C. The residue was filtered and washed with 95 % ethanol and distilled water^[9]. This step was repeated twice. Similarly, the washed palm kernel is dried in oven at 60 °C for 24 h. This method gave about 0.95 g (19.19 %) of cellulose.

Catalytic hydrolysis of cellulose procedure

The cellulose hydrolysis was carried out in the liquid-phase in a 50 mL round bottom flask equipped with magnetic stirrer and water condenser. 20 mL of DMF, 0.2 g of LiCl, 1.0 mL of water and 0.18 g cellulose (which extracted from PK) were separately transferred to the round bottom flask containing 0.2 g of the ammonium sulphate. The hydrolysis temperature was fixed at 100 °C. The hydrolysis mixture was refluxed for 4 h. A 0.5 mL portion of the clear hydrolyte solution from the reaction mixture was transferred into a vial and 2.0 mL of deionized water was added. To this solution, 2.0 mL of DNS reagent and 2.0 mL of 2.0 N NaOH were added and the mixture was incubated in a water bath maintained at 90 °C for 5 min^[10-11]. The DNS reagent was prepared according to a IUPAC method^[12]. The reagent blank sample was prepared with 2.0 mL of deionized water, 2.0 mL of DNS reagent, and 2.0 mL of 2.0 N NaOH, and heated similarly to the other samples. Then the absorbance was measured at 540 nm, against the reagent blank, and glucose concentrations in the solutions were estimated by employing a standard curve prepared using glucose. The catalytic activity with different mass of catalyst (50, 100, 150, and 200 mg), different temperatures (80, 90, and 100 °C), and different solvents, (i.e. 1-butanol, cyclohexanol, and cyclopentanone), were studied by using the same procedure as described above.

RESULTS AND DISCUSSION

FT-IR spectral analysis

FT-IR spectra of the extracted cellulose from waste PK compared with that of standard cellulose were shown in Figure 1(a, b). They are showed strong absorption at 3460-3421 cm^{-1} which is attributed to O-H stretching vibration. This absorption band is com-

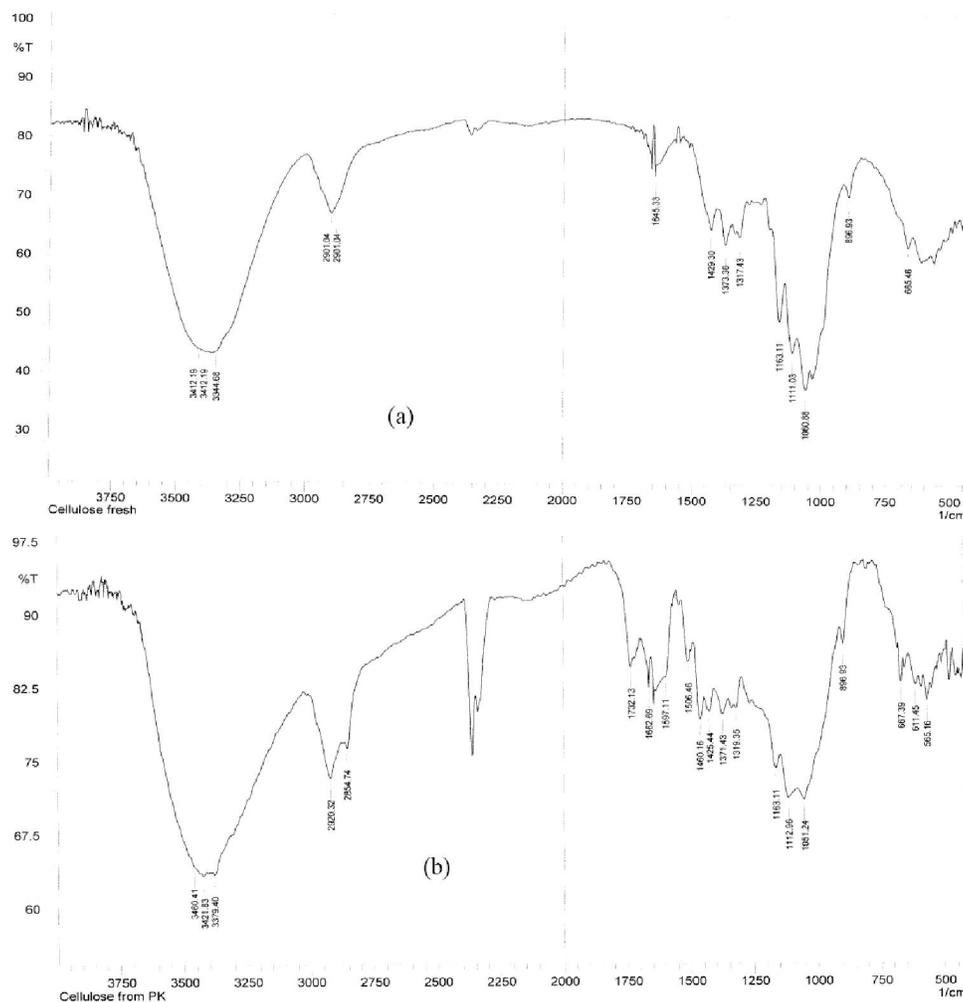


Figure 1 : The FT-IR of the cellulose. (a) Pure cellulose and (b) cellulose extracted from PK

posed of two vibrations located at 3285 cm^{-1} (attributed to intermolecular hydrogen bonds) and 3335 cm^{-1} (attributed to intra-molecular hydrogen bonds)^[13]. The O–H vibration of the pure cellulose shows absorption band located at 3344 cm^{-1} . The absorption bands at 2918 cm^{-1} and 2891 cm^{-1} are attributed to C–H symmetric and asymmetric vibrations. The vibration band at 1649 cm^{-1} in both samples is due to the O–H of water. The presence of this band indicates that the remaining water molecules were strongly bonded to cellulose macromolecules via hydrogen bonding. The vibration at 1429 cm^{-1} in the fresh cellulose is due to the $-\text{CH}_2-$ group. This absorption band was observed at 1460 and 1425 cm^{-1} . The vibration at 1163 cm^{-1} is assigned for the C–O–C stretching which appears almost simultaneously with the vibration located at 991 cm^{-1} (attributed to β -linkage that present in the structure of cellulose). The vibration located at 1161 cm^{-1} on the

pure cellulose spectrum is assigned to the anti-symmetric bridge C–O–C stretching vibration^[14]. The vibration band shifted to be 1112 cm^{-1} in the PK spectrum. From the FT-IR spectra, most of the bands of the extracted cellulose are match well with that of the standard cellulose. This indicates that the cellulose was successfully extracted from the waste PK and that sufficient removal of lignin and hemicelluloses was done from the used raw biomass.

Hydrolysis of cellulose over ammonium sulphate catalyst

The ammonium sulphate was used to hydrolyze cellulose in a liquid-phase reaction. Various parameters were evaluated to optimize the hydrolysis conditions on the fully completed cellulose hydrolysis, such as the effect of hydrolysis time, mass of catalyst, temperature, and solvent effects.

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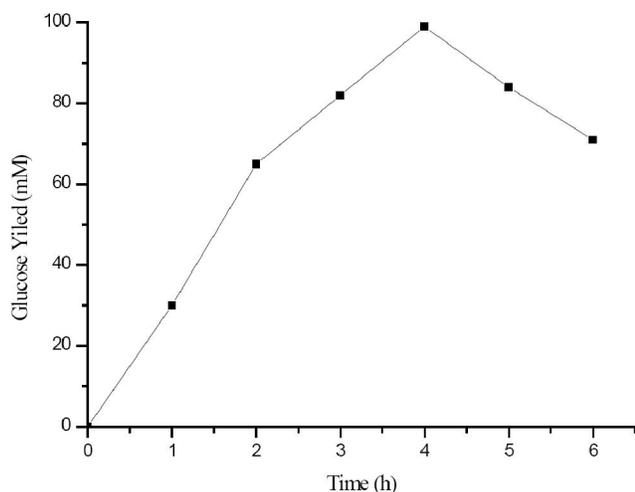


Figure 2 : The hydrolysis of cellulose over ammonium sulphate as a function of the hydrolysis time

TABLE 1 : The effect of different parameters on the hydrolysis of cellulose to glucose over ammonium sulphate. The reaction was run over 4 hours at 100 °C of hydrolysis temperature and 200 mg of catalyst mass

Parameters	Variants	Glucose Yield (mM %)
Variation of ammonium sulphate Mass (mg)	50	43
	100	65
	150	91
	200	99
Variation of hydrolysis temperatures (°C)	100	99
	90	85
	80	60
Variation of solvent effects in LiCl	DMF	99
	Cyclohexanol	78
	Cyclopentanone	70

(a) Influence of hydrolysis time

The effect of hydrolysis time on the hydrolysis of cellulose to glucose over homogenous ammonium sulphate ($(\text{NH}_4)_2\text{SO}_4$) is shown in Figure 2. The hydrolysis was carried out with 200 mg catalyst using a DMF / LiCl as a solvent at 100 °C. The homogeneous ammonium sulphate showed 99 % of glucose at 4 h and then the hydrolysis was decreased due to the hydrolysis of glucose itself. The hydrolysis of cellulose over ammonium sulphate was reaching the optimum after 4 h of hydrolysis time after which it decreases due to the hydrolysis of the glucose to other products. The selectivity of the hydrolysis of cellulose to glucose was 100 % at the first 4 h of the hydrolysis.

The hydrolysis conditions were 200 mg catalyst mass, 100 °C hydrolysis temperature.

(b) Effect of catalyst mass

Different amount of ammonium sulphate was stud-

ied to optimize the mass of the catalyst and the results are shown in TABLE 1. It was observed that the maximum hydrolysis was reached to 99% over the 200 mg was used. The other mass was give less than this result. Therefore 200 mg of catalyst was chosen as the optimum mass of catalyst.

(c) Influence of hydrolysis temperature

The effect of temperature on the hydrolysis of cellulose to glucose over ammonium sulphate is shown in TABLE 1. The hydrolysis increased when the reaction temperature was increased from 80 to 100 °C. The hydrolysis was ca. 99 % at 100 °C. This clearly indicates that the using of ammonium sulphate is more effective to promote the hydrolysis of cellulose.

(d) Influence of the solvents system effects

In this study it is found that the cellulose was highly soluble in DMF and cyclohexanol containing LiCl. This is similar to previous findings studying other catalyst^[5]. The effect of the solvent on the hydrolysis of cellulose over ammonium sulphate was shown in TABLE 1. The hydrolysis was studied over different solvents i. e., cyclohexanol, cyclohexanone, and DMF. All these solvents contain LiCl.

The chloride ion is playing a vital role in the solubility of cellulose. The metal ions are tightly linked with the carbonyl group of DMF while the chloride ions are left unencumbered. Thereby Cl^- is highly active as a nucleophilic base and plays a major role by breaking up the inter- and intra-hydrogen bonds^[15]. This could make the hydrolysis of cellulose much easier.

CONCLUSION

Cellulose was hydrolysis successfully from PK by using acid base treatments. The extraction of cellulose from PK was found to be 19.19%. The FT-IR clearly showed the presence of OH, C-H, C=O absorption bands at the expected range. The ammonium sulphate was used to hydrolyze of cellulose to other glucose at 100 °C for 4 h. The catalytic activity of the catalyst reaches 99 % of the glucose from cellulose and the selectivity was 100 %. The catalyst is simple and stable during the hydrolysis.

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