Journal of Applied Sciences

ISSN 1812-5654

science alert

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Journal of Applied Sciences 14 (24): 3424-3435, 2014
ISSN 1812-5654 / DOI: 10.3923/jas.2014.3424.3435

Synthesis of Cellulose Acetate Membrane from the Egyptian Rice Straws

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Abstract: In Egypt, approximately 4.5 million tons from 35 million tons of the annual production of recoverable cereal are disposed by burning and it creates a big problem. Isolation of cellulose with high yield and purity is a long-standing goal in cellulose development because of the complexity of cell wall structure of rice straw. Chemical composition of Egyptian rice straw was determined (moisture, ash, LMWC, wax and protein) and total carbohydrates. Cellulose was extracted by different alkaline NaOH concentration till optimum conditions determined. A series of acetylated celluloses with various degrees of substitution were prepared by homogeneous acetylation of celluloses. The FT-IR, ^{1}H NMR and ^{13}C NMR were used to investigate the changes of chemical structures and physical characteristics. Three cellulosic membranes fabricated from cellulose acetate/polyethersulfone composite. The scanning electron microscope was measured and characterized by pore-free upper surface and a porous bottom surface. A water uptake ratio was measured at room temperature for three membranes of crude (M1), soluble acetone (M2) and soluble chloroform cellulose acetate (M3) as 708, 527 and 710% (w/w), respectively.

Key words: Cellulose derivatives, cellulose acetate, cellulosic membranes, poly ethersulfone, degree of substitution

INTRODUCTION

Rice straws represent an enormous underutilized energy resource which has a great potential as feed for ruminants and also as raw materials for paper, chemicals and other technical products (Theander, 1985). The isolation of highly pure cellulose from rice straw has been the subject of extensive studies for many years because of the complexity of cell wall structure (Brendel *et al*., 2000; Sun and Hughes, 1998). The Even combination of the chemical "alkaline treatment" and the mechanical treatments is necessary for the dissolution of lignin, hemicelluloses and other non cellulosic substances (Sun *et al*., 2004a). In general, ammonium hydroxide (NH_4OH) usually produces a positive response (Buchala *et al*., 1972; Hoije *et al*., 2005) but is generally less effective than NaOH (Sun *et al*., 1998; Xiao *et al*., 2001). In recent years, there has been strong emphasized to develop new cellulose-based materials because of the biodegradability and renewable aspects of these materials. Acetylation of cellulose with acetyl chloride or acetic anhydride has been known for a long time. Cellulose acetate is one of the most commercially important cellulose derivatives. It is widely used in textiles because of its low cost, toughness, gloss, high transparency, natural feel and other favorable aesthetic properties. The proposed study is strongly related to applying our novel biorefinery concept that allows for a nearly quantitative utilization of rice straw by separating and valorizing cellulose. The conversion and partial degradation of native cellulose extracted, purified and then acetylation by different analytical instruments. Cellulosic membranes fabricated from Cellulose Acetate (CA)/polyethersulfone (PES) composite and study physical and chemical properties for using in different fields.

MATERIALS AND METHODS

Materials: Rice straw was collected from Belbes, Sharkya, the Nile delta, Egypt. The collected RS wastes were dried

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and then milled into powder. Polyethersulfone (PES) provided by Basf chemical company. Other chemicals (AC_2O, NaOH, n-BuOH, MeCOMe, Acetone, dimethylsulfoxide (DMSO), N-methyl-2-pyrrolidone (NMP) used in the present study were analytical grade-products purchased from sigma-Aldrich, Merck and BDH.

Methods: The following chemical composition; moisture, ash, crude protein, crude lipids, wax and Low Molecular Weight Carbohydrates (LMWC) were determined according to AOAC (1970). Total carbohydrates were determined after complete acid hydrolysis (Dubois *et al*., 1956). The resulted acid hydrolyzates were examined by PC using n-BuOH/MeCOMe/H_2O (4:5:1) (Jayme and Knolle, 1956) and aniline phthalate as spraying reagents (Partridge, 1949). Quantitative determination of separated sugars was carried out according to Wilson (1959). Total nitrogen of the investigated samples (0.3 g) was determined to adopt the usual micro-Kjeldahl's method (Black, 1948). The crude protein was calculated by multiplying the total nitrogen by 6.25. IR spectra were collected directly from the cellulose powder on to a detector prism using a Bruker Vectra 22 FTIR Spectrometer equipped with a DuraSampleIR II™ detector. All spectra were taken at a spectral resolution of 4 cm^{-1} between wave number range 4000-400 cm^{-1}. Sample and background were scanned with 60 scans. The top and bottom snapshots of membrane were taken with a JEOL 5410 Scanning Electron Microscope (SEM) conducted at 10 KV. The nuclear magnetic resonance (^1H NMR and ^{13}C NMR) was done for extracted samples and modified using JEOL ECA 500 MHz. The DP was performed viscosimetrically after dissolving cellulose in solvents of which the most common are cupriethylenediamine (CED) and cadmiumethylenediamine (Cadoxen).

Pulping procedures of rice straw: In this study, rice straw was first dried in sunlight and then cut into small pieces (1-3 cm). The cut RS were grinded and the fractions passing through 60 meshes (less than 0.250 mm size screen) were selected for subsequent extraction of cellulose. The ground wastes were further dried in a hot air oven for 16 h at 60°C and washed with distilled water at ambient temperature to remove the dust and impurities on the surface then dried. The dried rice straw was soaked in 2:1, v/v Toluene/Ethanol mixture for 24 h to remove wax, pigments and oils followed by oven-drying at 55°C for 24 h. In 75 mL Sodium hydroxide (pH 12, 1, 4 and 18%) 5 g of dewaxed rice straw was treated at (90, 55, 90 and 22°C), respectively for 1 h (liquid to solid ratio, 15 mL g^{-1}) for three times. The reaction mixture was filtrated, the residue crude cellulose was subsequently washed with distilled water to be neutral and then air dried (AOAC, 1970).

Bleaching crude cellulose: One gram crude cellulose (rice straw, rice husk, wheat straw and/or bagasse) separately added to 2 g sodium hypochlorite in a suitable amount of distilled water at 80°C for 2 h and then filtration. The residue cellulose washed thoroughly with distilled water till neutralization and completely deride at 70°C.

Bleached cellulose purification: Three grams of extracting bleached cellulose in 250 mL-beaker in water bath at 20°C, maceration with 15 mL of 17.5% sodium hydroxide (w/w) for 1 min (by rod flattened to disk one end). The 10 mL NaOH more was added for 45 sec and then another 10 mL for 15 sec. The mixture was allowed to stand for 3 min and 10 mL more was added for 10 min. The 30 mL NaOH was added at different intervals (10 mL for 2.5 min, 10 mL for 5 min and 10 mL for 7 min). The beaker was covered with glasswatch and left in water bath for 30 min. The contents of the beaker filter with suction using sintered glass. The residue has been rinsed with 8.3% NaOH solution and then 25 mL at 20°C. Cellulose was washed with distilled water at 20°C (400 mL) and then neutralization of 2 N acetic acid for 5 min. The acetic acid was removed by suction and the residue was washed with water until free of acid, dried at 105°C (Sun *et al*., 1998).

Cellulose acetylation: Two gram purified cellulose was immersed in 30 mL (15 parts) methylene chloride, 5 mL (2.5 parts) glacial acetic acid, 0.04 g (0.02 part) 98% H_2SO_4 and 0.5 mL (0.25 part) acetic anhydride were added to 100 mL round bottom flask. The temperature was then raised gradually and kept at 80°C while stirring for 4 h. Cooling the reaction mixture to room temperature and then filtrale it. In order to extract the remaining cellulose acetate, the residue collected and then 60 mL chloroform was dissolved in it and stirring them for 30 min at 25°C and then filtrate this again. Collect all filtration then drying to yield cellulose acetate as a film coating inside the flask. Ethanol was used to remove the acetate film from the flask. Filtration through a coarse filter paper yielded acetate as residue and ethanol as filtrate. The cellulose acetate was dried at 80°C in a vacuum oven overnight. Synthetic crude cellulose acetate has mixture that can be separated by dissolving the mixture CA in acetone at 25°C and then filtrate this mixture. The residue and the filtrate were dried at 80°C in a vacuum oven overnight. The Degree of Substitution (DS) was determined by determination of total carbohydrate, FT-IR, ^1H NMR and ^{13}C NMR. The FT-IR spectroscopy was applied as rather a simple and easy technique to distinguish the chemical

alteration in cellulose due to the acetylation by using powdered acetylated samples. For this purpose, dried samples were milled and passed through a sieve with mesh 40.

Membrane preparation: Three CA/PES membranes (50% CA+50% PES) were prepared by the wet phase inversion process. The CA polymer solutions synthesized by dissolving individual 20% crude, acetone soluble and chloroform soluble CA in DMSO, acetone and chloroform, respectively. The PES polymers were prepared by dissolving 20% in NMP as shown in Table 1. The homogeneous solution was sprinkled and cast on glass plate substrate and moved toward coagulation bath for immersion precipitation at 20±2°C. As the final stage, the prepared membranes were dried at 80-90°C for 10 min.

Scanning Electron Microscopy (SEM): Scanning Electron Microscopy (SEM) was used to observe the morphology of CA/PES membranes. The membrane sample was coated with gold to provide electrical conductivity.

Fourier-Transformed Infrared Spectroscopy (FT-IR): The FT-IR spectroscopy has been extensively used in cellulose and acetylated cellulose research, since it presents a relatively easy method of obtaining direct information on chemical changes that occur during acetylation.

Membranes water uptake ratios: Water uptake was measured at room temperature for the prepared membranes. Experimental determination of transport parameters enables us to compare membranes without the skewing effects of extended features such as membrane thickness which contributes in a nonlinear fashion to performance in polymer electrolyte fuel cells. Three types of membranes were soaked in distilled water at room temperature for 24 h to determine the water uptake ratios as evidence for the ability of membranes for the desalination.

$$\text{Water uptake ratios (\%)} = \frac{m_1 - m_0}{m_0} \times 100$$

where, m_0 and m are the weights of dry and wet membranes (g), in order to minimize the experimental errors, the membrane uptake of each sample was measured several times and the results were reported as the average.

RESULTS AND DISCUSSION

Chemical composition and total carbohydrate: Different methods are used to study rice straw chemistry, such as wet chemistry. Since, they are actually tedious and time consuming, finding rapid and easy methods to be used and techniques is of great concern. Chemical composition of RS was determined (11% moisture, 18% ash, 2% lipids, 7% LMWC, 6% wax and 1% protein (% w/w)). Total carbohydrates were measured after hydrolysis by sulfuric acid 35%, 1 N and 6 N trifluoroacetic acid 38 and 63.8% (% w/w), respectively. Monosaccharide constituents after sulfuric acid hydrolysis of RS indicated the presence traces L-arabinose, D-xylose and 100% (% w/w) D-glucose. The 1 N TFA gave traces from D-glucuronic acid, 12.5% L-arabinose, 59.5% D-xylose (due to over hydrolysis) and 28% D-glucose. The 6 N TFA gave traces from D-glucuronic acid, 9.38% L-arabinose, 34.56% D-xylose and 56% D- glucose.

Pulping optimization and total carbohydrate determination: Cellulose was extracted by different alkaline concentration and temperature to obtain the optimum conditions. Firstly, extraction was performed by sodium hydroxide with pH = 12 at 90°C, approximately 53% cellulose was attained and then total carbohydrates were determined after strong hydrolysis 39% by mild hydrolysis 1 N TFA 58% and 6 N TFA 53% (Table 2). Secondly, 1% NaOH at 55°C was used, 52% cellulose obtained and total carbohydrates by sulfuric was 43%, 1 N TFA 70% and 6 N TFA 64%. Thirdly 44% crude cellulose acquired by 4% NaOH at 90°C and total carbohydrates measured using sulfuric acid at 32%, 1 N TFA 48% and 6 N TFA 42%. Fourthly18% NaOH at 25°C gave the best yield 58% but the total carbohydrates were decreased by sulfuric acid 29%, 1 N TFA 40% and 6 N TFA 32%. It is of interest as the yield increased by18% NaOH at 25°C, the total carbohydrates decreased. Results are summarized in Table 2, the extraction by 1% NaOH at 55°C is the optimum method for obtaining crude cellulose depending on the yield and total carbohydrate content. Monosaccharide constituents after acid hydrolysis of holocellulose indicated presence traces from D-glucuronic acid, D-glucose, L-arabinose and D-xylose in different ratios depends on acid hydrolysis (Table 3). D-glucuronic acid found as traces, whether hydrolysis by sulfuric or triflouroacetic acid. The concentrations of L-arabinose

Table 1: Compositions of CA/PES membranes

Membrane	CA (%)	PES (%)	Prepared film
M1	Crude CA 20% in DMSO	20% in NMP	50% crude CA+50% PES
M2	Acetone soluble CA 20% in Acetone	20% in NMP	50% acetone CA+50% PES
M3	Chloroform soluble CA 20% in DMSO	20% in NMP	50% chloroform CA+50% PES

Table 2: Yield of extracted cellulose from RS (% w/w) and total carbohydrates

Yield of extracted cellulose (% w/w)		Total carbohydrates of acid hydrolysis (% w/w)		
Extraction conditions	Cellulose	Sulfuric acid	1 N TFA	6 N TFA
NaOH pH 12, 90°C	52.9±0.63	39.0±0.25	58.0±0.38	53.0±0.51
1% NaOH, 55°C	51.6±0.35	43.0±0.26	69.0±0.54	64.0±0.38
4% NaOH, 90°C	44.0±0.53	31.0±0.68	47.5±0.52	41.0±0.67
18% NaOH, 25°C	57.5±0.76	28.0±0.81	39.0±0.89	31.0±0.68

Table 3: Monosaccharide constituents for extracted holocellulose (% w/w)

Extracted cellulose	D-glucuronic acid			D- glucose			L-arabinose			D-xylose		
methods	Sulfuric acid	1 N TFA	6 N TFA	Sulfuric acid	1 N TFA	6 N TFA	Sulfuric acid	1 N TFA	6 N TFA	Sulfuric acid	1 N TFA	6 N TFA
Ph 12	Nil	t	t	100	24.3	27.2	t	19.8	18.6	t	55.9	54.2
1%	Nil	t	t	100	26.0	28.5	t	21.0	20.4	t	53.0	51.1
4%	Nil	t	t	100	43.1	59.0	t	10.6	1.2	t	46.3	39.8
18%	Nil	t	t	100	53.1	100	t	9.0	t	t	37.9	t

t: Traces (<1%); Traces from glucornic acid in all samples

and D-xylose were decreased by increasing the concentration of sodium hydroxide, otherwise concentration of glucose increased. One percent of sodium hydroxide has well extracted crude cellulose than others, depending upon the monosaccharide constituents after acid hydrolysis. Ash content for the extracted holocellulose was determined 9.6% (w/w), support total carbohydrates and monosaccharide results that crude cellulose has hemicellulose and lignin impurities.

Bleaching crude cellulose: Cellulose bleaching is a chemical process carried out to purify the cellulose by decreasing the color (dissolving the other compounds), so that it becomes whiter to use it in different chemical composition. There are many methods for bleaching cellulose for examples, mechanical bleaching retains most of lignin and hemicelluloses present in cellulose. Alkaline sodium hypochlorite is the most commonly used bleaching agent that can selective oxidized non-aromatic conjugated groups (lignin) responsible for absorbing visible light. Chlorine replaces hydrogen on the aromatic rings of lignin via., aromatic substitution, oxidizes pendant groups to carboxylic acids and adds across carbon-carbon double bond in the lignin side chains. Chlorine also attacks cellulose but the reaction occurs predominantly at pH 7 where un-ionized hypoclorous acid HClO are the main chlorine species in solution. To avoid excessive cellulose degradation, chlorination is carried out at pH<1.5:

$$Cl_2+H_2O \rightleftharpoons H^++Cl^-+HClO$$

At pH 8, the dominate species are hypochlorite, ClO^-, which is also useful for lignin removal. The main objection to use of chlorine for bleaching cellulose is the large amounts of soluble organochlorine compounds produced and released into the environment. Crude cellulose rice straw was bleached and the yield was more than 85%.

α-cellulose extraction: It is well established that when subjected to strong alkali solutions, crystalline native cellulose, cellulose I becomes swollen and upon washing shrinks back to yield a new allomorph, cellulose II. For example, mercerization of the cellulose fiber in aqueous solution of NaOH breaks hydrogen bonds and weak Van der Waal's forces between the cellulose chain molecules and results in reorganization to cellulose II when the swelling agent removes. At present, it seems generally accepted that the cellulose I structure is made of parallel chains, whereas the crystal structure of cellulose II is described as antiparallel. In addition, small amounts of cellulose II have been observed to form during kraft pulping. The α-cellulose content in the extracted crude cellulose was investigated, rice straw 83%. The results were obtained from acid hydrolysis of α-cellulose indicates that total carbohydrates more than 97% in all cellulose agriculture residues, this means the purification process was succeeded to obtain mainly pure cellulose (as glucose).

Cellulose characterization: The DP of cellulose sample isolated from rice straw in the range of 532-608. The polydisperity of native straw cellulose is probably quite low which means that DP_n and DP_w do not deviate much from each other. The molecular weight of cellulose can be defined by its average DP. Measurements of its polymer properties indicate that cellulose in solution belongs to the groups of random coiling polymers. The high viscosity and the other polymer properties show that cellulose is a solvent-swollen polymer which in solution occupies a compact structure.

Homogenous acetylation of cellulose: The optimum condition for acetylation of RS cellulose was investigated in terms of reaction time and temperature using 8°C for 240 min. The rate of acetylation (%) increased progressively with increasing the reaction temperature

upto 80°C for 240 min and after that cellulose degradation and RS cellulose loses its original appearance. Long reaction time allows acetic anhydride to react with cellulose thus substitute with the free hydroxyl group of cellulose. However, at long reaction time degradation of cellulose and hydrolysis of cellulose acetate occurs (Hu *et al*., 2011; Li *et al*., 2009). Conventional acetylation of cellulose rice straw gave a yield of product 15.1 (% w/w), the mass yield value expected to be much less than 15.1 (% w/w) due to resistance to chemical reactions the percent of cellulose accessible to acetylation. Total carbohydrate of crude cellulose acetate was measured 33.5 (% w/w). Synthetic crude cellulose acetate has mixed from CA acetone soluble 65.7 (% w/w) and CA chloroform soluble 34.3 (% w/w) (Table 4). The melting points for different acetate products were measured; crude acetate was 231°C, acetone soluble CA was 150°C and chloroform soluble CA was 265°C decomposition. Evidently, the results indicate the important roles played by the reaction time and temperature. The yield (%) and DS increased as the reaction time and temperature increased. It was proposed that cellulose was acetylated heterogeneously at the beginning of the reaction. The solid cellulose is going through rapid surface acetylation and then as the acetylation progressed, the acetylated cellulose gradually dissolved in the reaction medium followed by subsequent acetylation of the remaining unreacted hydroxyl groups (Biswas *et al*., 2007). In addition, a significant increase in the swelling ability of cellulose and the diffusion rate of acetic anhydride was made by high temperature. The acetic anhydride reacts with hydroxyl groups involving a nucleophilic attack on the acyl carbon center of the acetic anhydride molecule by a lone pair of the alcoholic hydroxyl group followed by subsequent loss of acetic acid to generate the ester (Biswas *et al*., 2005; Hill *et al*., 1998).

For isolation and utilization of cellulose from rice straw in a pure and undergraded form, its polymer properties need to be studied; however, no reasonably simple methods for elucidation of polymer properties are available. There are many technologies to characterize the physicochemical properties of cellulose FT-IR and NMR.

Fourier-Transformed Infrared Spectroscopy (FT-IR): The FT-IR spectroscopy has been extensively used in cellulose and acetylated cellulose research, since it presents a relatively easy method of obtaining direct information on chemical changes that occur during acetylation (Table 5). The FT-IR spectrum of cellulose is always similar, except for the intensity of absorption bands. In the spectrum, the absorption from 3000-3750 cm^{-1} is a broad peak represents the OH stretch, intramolecular and intermolecular H bridge between the OH groups. The absorption at 2900 cm^{-1} relates to the CH and CH_2 stretching and the one at 1372 cm^{-1} to the O-H bending. The peak at 893 cm^{-1} represents the glycosidic C_1-H deformation with ring vibration contribution, which is characteristic of β-glycosidic linkages between glucose in cellulose. A peak at 1426 cm^{-1} relates to the CH_2 symmetric bending. The Total Crystallinity Indices (TCI) and Lateral Order Indices (LOI) can be obtained from the 1429/893 and 1372/2900 cm^{-1} absorbance ratios, respectively. The TCI and LOI represent the relative crystallinity degree and the changes of absorbance ratios can reflect the cellulose crystallinity changes. Based on this method, we have investigated the change of holocellulose and purified cellulose. The results showed that the crystallinity of holocellulose was increased by purification into cellulose. Furthermore, the absorption bands at 750 and 710 cm^{-1} in the FT-IR spectrum of cellulose are assigned to the Iα and Iβ phases, respectively. The FT-IR spectra of cellulose have

Table 4: Cellulose acetate yield (% w/w), melting points and Degree of Substitution (DS)

Samples	Yield (% w/w)	Melting points	DS
Crude acetate	15.1	231°C	2.83
Acetone soluble-acetate	65.7	150°C	2.59
Chloroform soluble-acetate	34.3	265°C	3.17

Table 5: Assignment of FT-IR spectra of cellulose and cellulose acetate

Wavenumber (cm^{-1})	Assignments
3000-3750	OH stretch, intramolecular and intermolecular H bridge between the OH groups
2850-2980	CH_2 antisymmetric stretch and CH_2 symmetric stretch
1725-1730	C-O stretch from acetyl or COOH groups
1640-1630	Adsorption of water
1455-1470	CH_2 symmetric ring stretch at pyran ring; OH in plane deformation
1416-1430	CH_2 scissors vibration
1374-1375	CH deformation
1335-1336	OH in plane deformation
1315-1317	CH_2 tip vibration
1277-1282	CH deformation
1200-1235	OH in plane deformation
1125-1170	C-O-C antisymmetric stretch (arabinosyl side chains)
1100-1110	C-O-H bending typical of xylans(ring antisymmetric stretch)
1040-1050	C-O stretching in C-O-C glycosidic bonds
890-900	C1 group frequency or ring frequency (typical for β anomers)

exhibited a broad band in the region 3448-3417 cm^{-1} that indicates the free O-H stretching. During acetylation, the chemical substitution of hydrophilic OH groups by hydrophobic acetyl groups occurs in cellulose and it changes the typical spectra in the rice straw cellulose acetate (Fig. 1). The four major changes observed in the spectrum of acetylated RS cellulose as compared to the RS cellulose on acetylation are (i) A decrease in the hydroxyl (OH) stretching band at 3322 cm^{-1}, (ii) An increase in the carbonyl (CO) stretching band at 1751 cm^{-1}, (iii) An increase in the carbon hydrogen (CH) bending vibration at 1369 cm^{-1}, (iv) An increase in carbon oxygen (CO) stretching vibration at1220 cm^{-1} (Sun *et al*., 2004b). According to spectra, this broadband indicates the free O-H stretching in case of cellulose has been decreased consequently from crude acetate, soluble acetone acetate and soluble chloroform acetate vies versa absorption band from 1725-1730 CO stretch from acetyl or COOH groups increased due to increasing the degree of substitution. To establish structure-property relationships of Cellulose Esters (CE) and to evaluate synthesis paths and products, a detailed structural analysis is an unambiguous prerequisite. The spectrum (3, 4 and 5) in Fig. 1 provides strong evidence of acetylation by showing the presence of three important ester bonds at 1751 (CO ester), 1369 (CH bond in $OCOCH_3$ group) and CO stretching band of acetyl group at 1220 cm^{-1} (Saikia *et al*., 1995). A strong band at 1051 cm^{-1} is due to the COC pyranose ring skeletal vibration. The disappearance of peaks in region 1840-1760 $cm^{-1}$and at 1700 cm^{-1} in spectrum (B) indicated that the product is free of the unreacted acetic anhydride and the by-product, acetic acid (Sun *et al*., 2004b).

^{1}H-NMR, ^{13}C-NMR and DS determination: The application of NMR spectroscopy was among the first attempts for the structure elucidation of CA. Attempts were made to exploit ^{1}H NMR spectroscopy for the structure determination. Cellulose extracted from rice straw was converted into cellulose acetate (crude, soluble acetone and soluble chloroform acetate). The acetylation of cellulose was confirmed by NMR of the products cellulose acetate. The Degree of Substitution (DS) was determined by proton NMR (Table 4). By NMR, we used the ratio of the seven anhydrocellulose proton absorbance in the range of 3.5-5.2 ppm to the absorbance of three methyl proton of acetyl group in the range of 1.9 and 2.2 ppm (Basta and Hosny, 1998; Heinze and Rahn, 1996; Mao and Ritcey, 1999). The degree of substitution was calculated by dividing 1/3 of the acetyl peak area by 1/7 of the anhydroglucose area. The DS Acetyl calculated by the ratio of spectral integrals of acetyl moiety and repeating unit. The DS of crude cellulose acetate was calculated 2.83, soluble acetone 2.59 and soluble chloroform 3.17. According to these results, we can confirm that the average degrees of substitution at the individual 2, 3 and 6 hydroxyl positions of the glycosyl ring (DS_2, DS_3 and DS_6) are approximately the same, the reactivity of the individual hydroxyl groups towards acetylation is roughly the same (Fig. 2-4).

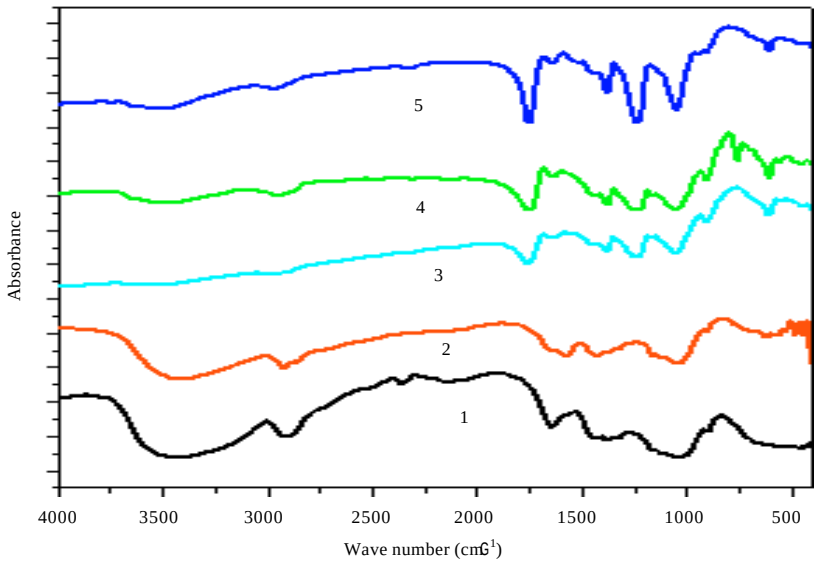

Fig. 1: Fourier transforms infrared (FTIR), (1) Spectra of the cellulose, (2) Purified-cellulose, (3) Crude acetate, (4) Acetone soluble -acetate and (5) Chloroform soluble -acetate cellulose RS

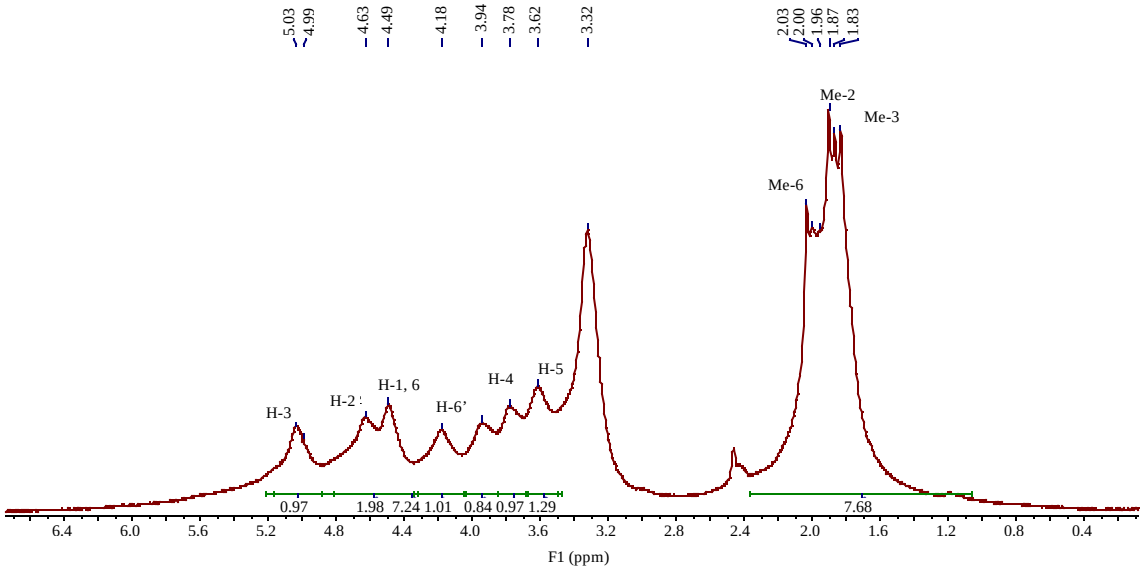

Fig. 2: [1]H NMR spectrum of crude cellulose acetate for cellulose rice straw, together with spectra assignments. 'Me': Methyl protons of the acetyl unit and 'H': Protons on the anhyroglucose unit. Subscript refers to the position of acetyl or proton on anhydroglucose

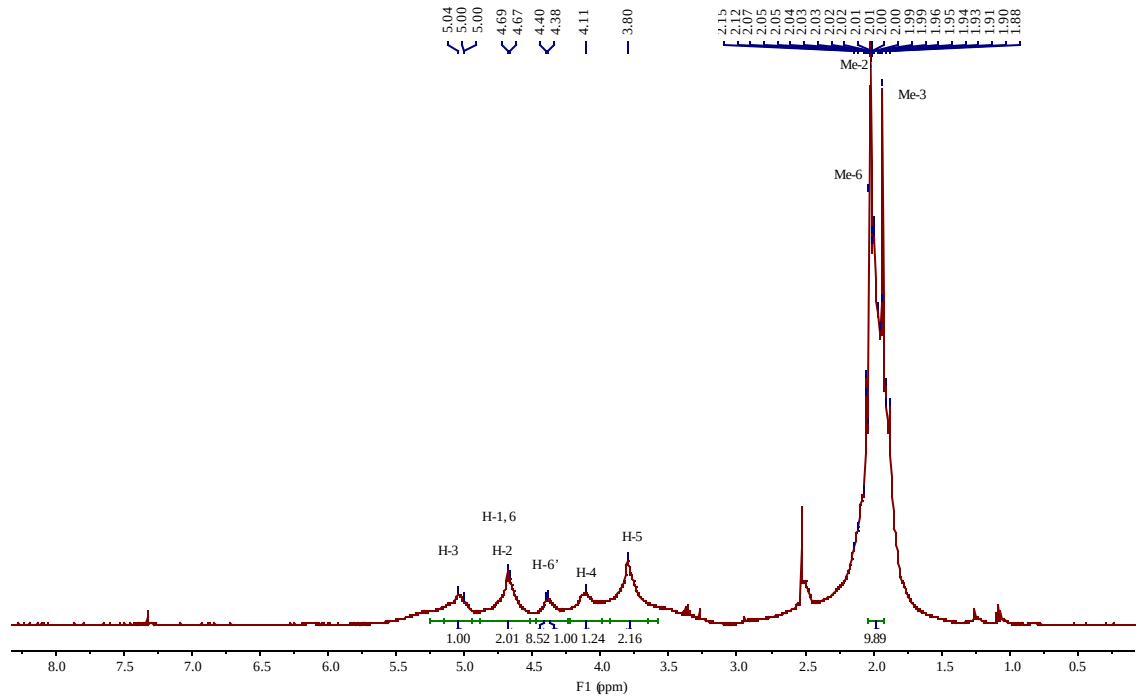

Fig. 3: [1]H NMR spectrum of soluble acetone acetate for cellulose rice straw, together with spectra assignments. 'Me': Methyl protons of the acetyl unit and 'H': Protons on the anhyroglucose unit. Subscript refers to the position of acetyl or proton on anhydroglucose

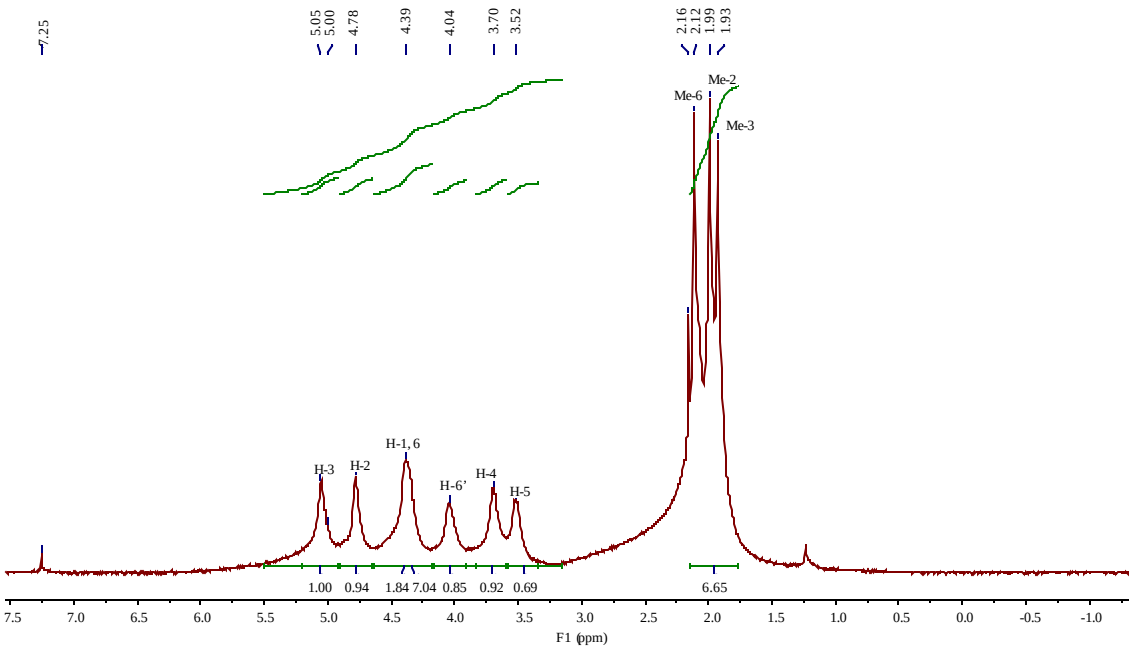

Fig. 4: [1]H NMR spectrum of soluble chloroform acetate for cellulose rice straw, together with spectra assignments. 'Me': Methyl protons of the acetyl unit and 'H': Protons on the anhyroglucose unit. Subscript refers to the position of acetyl or proton on anhydroglucose

^{13}C-NMR: The ^{13}C-NMR showed significant signals appeared at δ 170.4 revealed to carbonyl carbon and at δ 20.5 assigned for methyl carbons that signals did not present at the cellulose spectrum (C1 δ 100.3, C2 δ 71.7, C3 δ 72.5, C4 δ 76.3, C5 δ 62.3 and C6 δ 71.4) before acetylation that confirmed our supposed form of acetyl cellulose structure. Even the carbons in which attached to an acetyl group becomes slightly down field than the parent structure. Also, ^{13}C spectrum showed a number of substituted carbons than cellulose spectrum and chloroform soluble cellulose acetate indicated the highest number of carbons then crude acetate and acetone cellulose acetate, respectively (Fig. 5-7).

Membrane characterization: In this study, CA/PES membranes have been successfully prepared via., casting method with a suitable solvent and water as a non solvent. The cross section, top and bottom surfaces of M_1, M_2 and M_3 are shown in Fig. 8. The SEM views of the CA/PES membrane revealed that the skin surface was pore free while the bottom (glass side) surface was highly porous. The cross sections, surfaces showed that the CA/PES membrane was highly porous with a relatively very small dense layer. In addition, membrane M_1 exhibited a finger-like structure, M_2 exhibited (sponge-like structure+a big micro-voids) while M_3 exhibited (sponge-like structure+finger-like+big micro-voids). High precipitation rates (small gelation times) lead to form asymmetric membranes with a "finger" like structure and low precipitation rates (long gelation times) lead to form asymmetric membranes with a "spongy" like structure.

FT-IR: Spectroscopes of membranes have assignments of cellulose acetate and PES composite together and support the investigated result before. M3 membrane (chloroform soluble acetate) showed the absence of OH broad band at 3500 cm^{-1} (Fig. 9).

Membranes water uptake: Water uptake of the prepared membranes at room temperature are reported here. Specifically, we have determined the amount of water taken up by membranes immersed in liquid water. The ratio of water contents was determined for three different membranes, 708% is the water uptake of crude membrane (M1) (the membrane can absorb more than 7 times of his weight), 527% is the water uptake of acetone soluble acetate membrane (M2) (the membrane can absorb more than 5 times of his weight), 710% is the water uptake of chloroform soluble acetate membrane (M3) (the membrane can absorb more than7 times of his weight). The ability of the prepared CA/PES membranes for water uptake is uniquely uniform in performance and quality for different

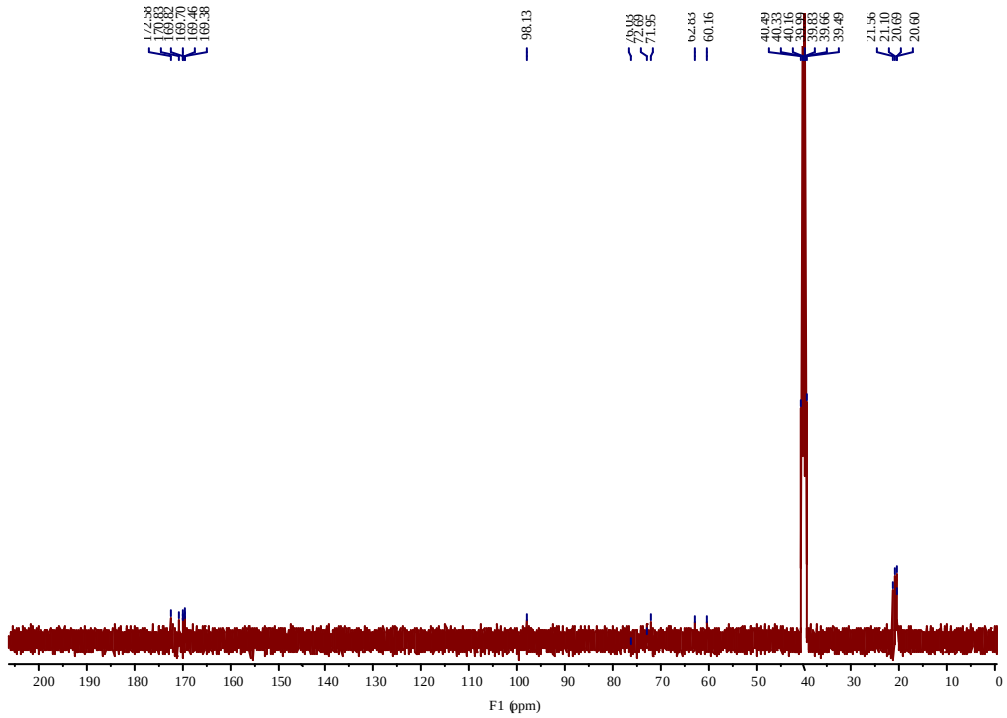

Fig. 5: ^{13}C NMR spectrum of crude cellulose acetate for cellulose rice straw

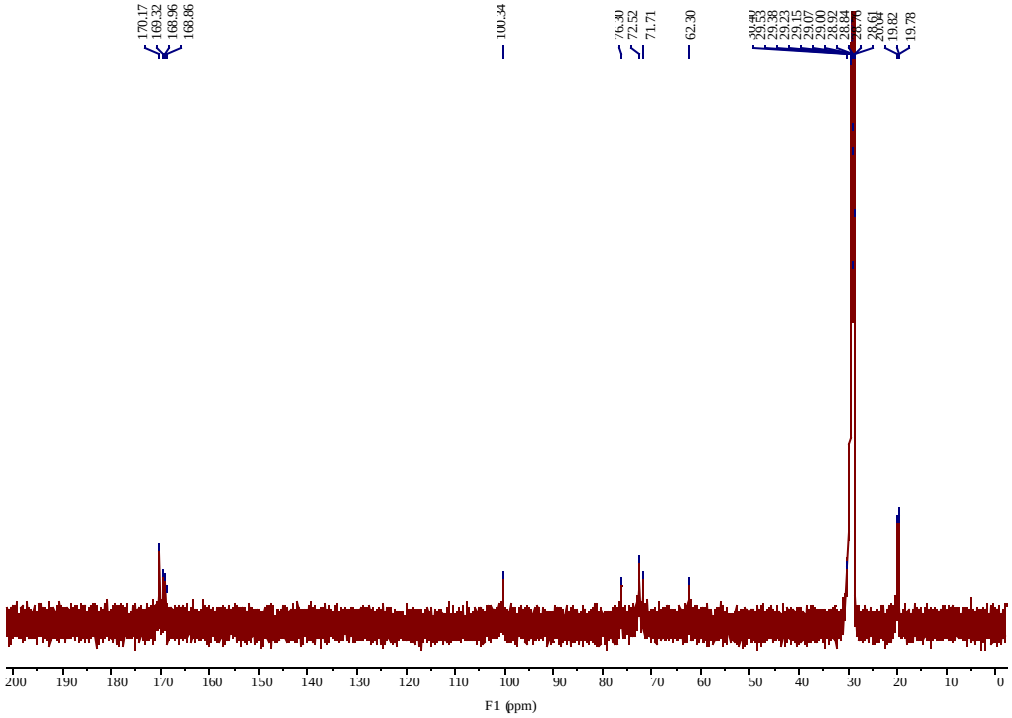

Fig. 6: ^{13}C NMR spectrum of acetone soluble cellulose acetate for cellulose rice straw

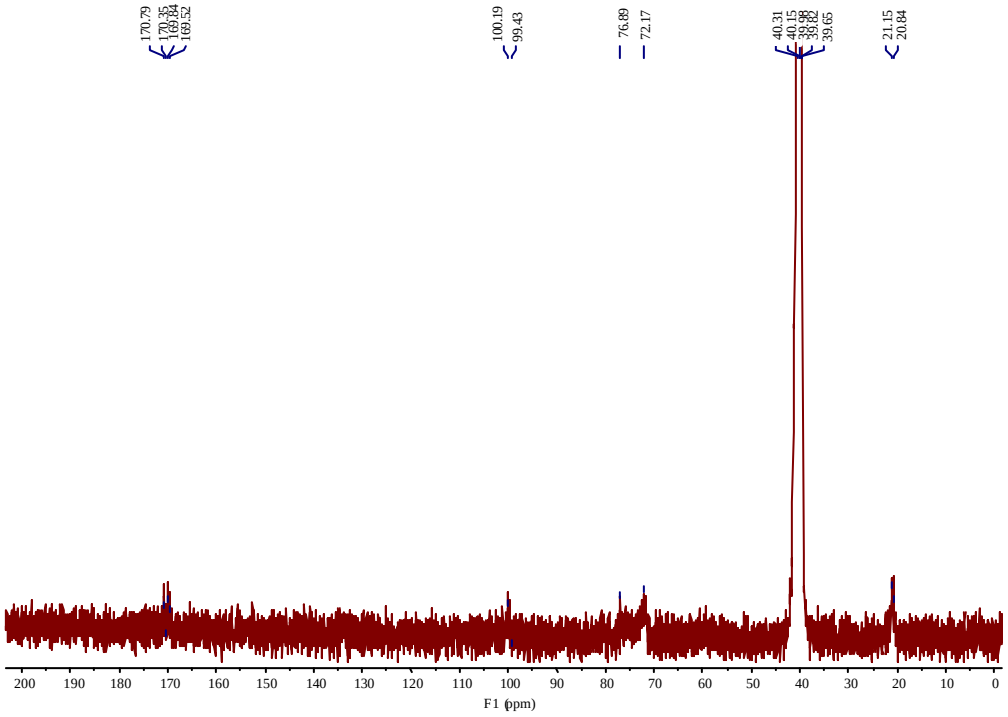

Fig. 7: ^{13}C NMR spectrum of chloroform soluble cellulose acetate for cellulose rice straw

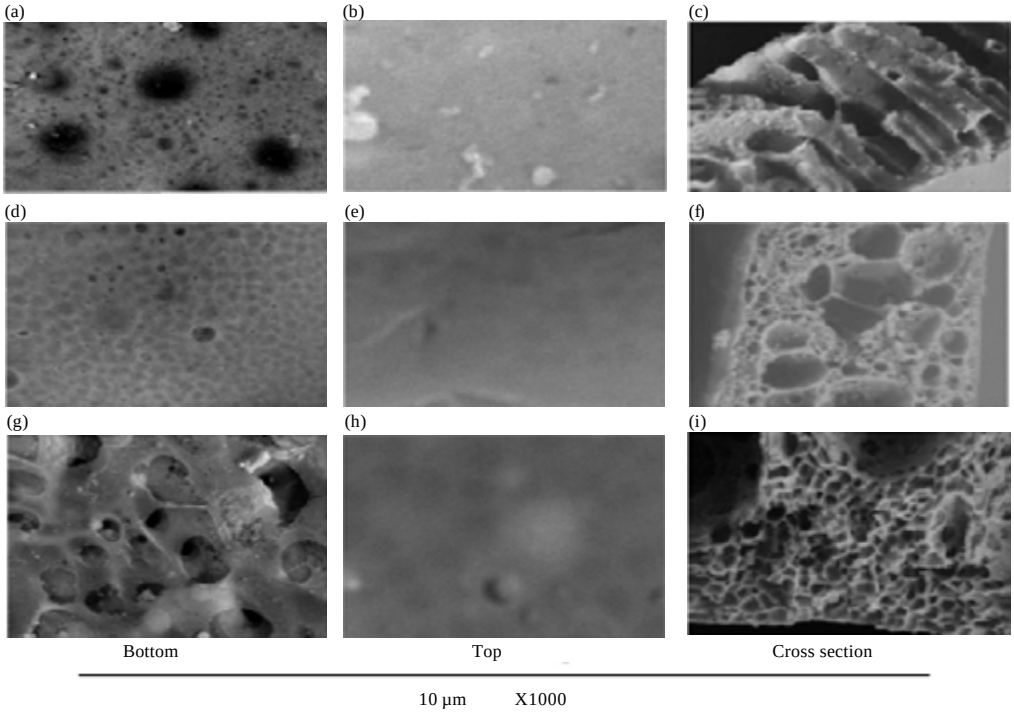

Fig. 8(a-i): SEM views of (a-c) Crude CA membrane M_1, (d-f) Acetone soluble CA M_2 and (g-i) Chloroform soluble CA M_3

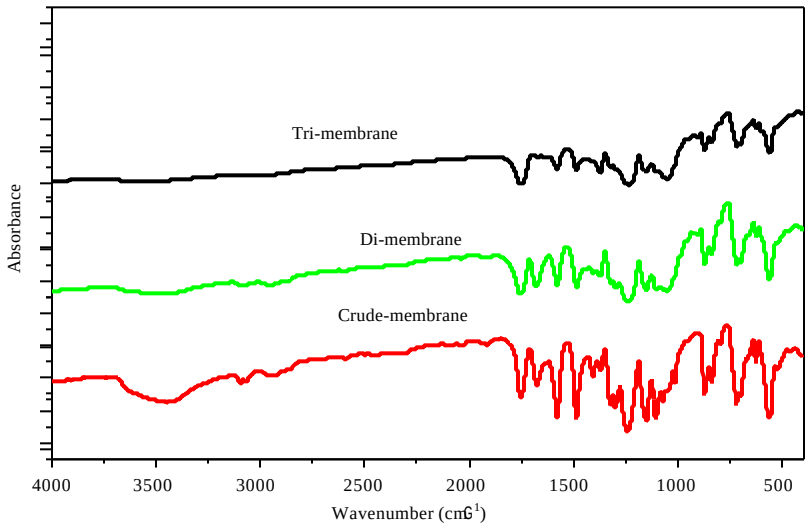

Fig. 9: Fourier transforms infrared (FT-IR) spectra of three cellulosic membranes and PES composite

uses that can minimize troublesome and costly problems in the future. Membranes can be used in water purification through reverse osmosis and electro dialysis (still unpublished).

CONCLUSION

This study provides us a thorough overview of rice straw chemistry. We concerned with the fundamentals of rice straw structure and chemical composition. And then covers different alkaline cellulose extraction methods and determining the optimum conditions. After that, we successfully fabricated bio-membrane from cellulose acetate/polyethersulfone (SPE) composite and we studied the physical properties and the nature of the surface in order to direct it to the appropriate application such as in the area of water desalination and other uses. In the last, we have focused on the identification and characterization of the cellulosic membranes by FT-IR spectroscopy, NMR and other tests that prove the percentage of mutation. The results showed that the acetylation modification was successful and that the products of the chemical modification were high and promising quantitatively and qualitatively.

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