



# Cellulose hydrolysis over silica modified with chlorosulphonic acid in one pot synthesis



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## ABSTRACT

Titration of chlorosulphonic acid against sodium silicate was carried out via a simple one pot synthesis at room temperature to form an acid catalyst denoted as  $\text{RHSO}_3\text{H}$ . The BET measurements of the catalyst showed the surface area to be  $80\text{ m}^2\text{ g}^{-1}$ . The FT-IR clearly showed the presence of  $-\text{SO}_2-$  absorption band at the expected range. The XPS showed the presence of O, Si, and S. The presence of S 2p on the XPS spectra indicated that the sulphonic acid groups ( $-\text{SO}_3\text{H}$ ) are included into the catalyst structure. The  $\text{RHSO}_3\text{H}$  was efficient for the hydrolysis of cellulose, with maximum glucose yields over 99% at  $120^\circ\text{C}$  with 100% selectivity. As the solubility of cellulose is very important factor to make the hydrolysis much more easily. It was observed that the mixture of DMF/LiCl or cyclohexanol/LiCl has high ability to dissolve cellulose. The catalyst was simple in its preparation, stable during the cellulose hydrolysis in addition to repeatedly without a significant loss of its catalytic activity.

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## 1. Introduction

Over the last two decades, a special attention has been paid to the rice husk (RH). Due to it being available free, with a high silica content and suitable for recycling makes it economically viable to be used as a raw material [1]. The controlled burning of RH in air leads to the formation of rice husk ash (RHA), which contains ca. 95% silica [2]. RHA is a great environment threat causing damage to land and surrounding area where it is dumped. Therefore, commercial use of RH and its ash is the alternative solution to disposal problem.

Nowadays the environmental benefits of wood or other forms of biomass/agricultural wastes associated with the producing of solid, liquid and gaseous fuels which is attracting wide attention. Agricultural waste has an important contributor into the world economy. Today, various forms of agricultural wastes energy are consumed all over the world [3]. Cellulose is a bioorganic molecule with a long linear chain polymer of several monomeric D-glucose units linked by  $\beta$ -1,4-glycosidic bonds. It is the most abundant organic compound in nature and does exist in the cell wall of plants as complex fibrous carbohydrates [4]. Natural fibers mainly consist of

cellulose, lignin, and hemicellulose in addition to low quantities of pectin, pigments and extracts.

Cellulose hydrolysis can be achieved by using enzymes [5], or by diluting and concentrating acids [6]. In a preliminary experiment, cellulose was hydrolyzed using 70% w/w sulphuric acid in a sealed reactor. After 9 h of hydrolysis, there was approximately 31% of the glucose has been obtained [7]. A new route to high yield sugars from cellulose based upon the use of phosphoric acid 60% and sulphuric acid 70% at  $85^\circ\text{C}$  for hydrolysis, this route produced glucose with a yield of approximately 90% after about 4 h of hydrolysis [8]. While Changzhi et al. [9] hydrolyzed cellulose at  $175^\circ\text{C}$  for 7 h using 85%  $\text{H}_3\text{PO}_4$  as a catalyst, there is only 16% of the glucose was obtained under these conditions.

In the present study, the modification of silica extracted from RH with chlorosulphonic acid was described in more direct and simple method. As the product is a solid acid, it can be applied in the hydrolysis of cellulose to glucose.

## 2. Materials and method

### 2.1. Raw materials

The chemicals used in this study were Sodium hydroxide (System, 99%), Aceton (GCC, 99%), Nitric acid (Scharlau, 65%), 1-Butanol (Fluka, 99%), Cellulose (Riedle-De Haen 99%), Chlorosulphonic acid

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(J.T. Baker, 99.8%), Cyclohexanol (Riedle-De Haen, 99%), Dimethylformamide (DMF) (System, 99.5%), Dinitrosalicylic acid (DNS) (BDH, 99%), Dioxane (Riedel-De Haen, 99.5%), Glucose (BDH, 99%), Lithium chloride (Sigma, 99%), Sulphuric acid (Poch, 95%), Toluene (GCC, 95%). The RH was collected from a rice mill in Samawah, Iraq. All other chemicals used were AR grade or of high purity and were used directly without further purification.

## 2.2. Extraction and modification of silica from RHA

### 2.2.1. Sources of silica

The RH was chosen as the source of amorphous silica [10] as it was available in abundance. The silica was extracted from RH according to a reported method [11,12].

### 2.2.2. The one-step preparation of solid silica-sulphonic acid

About 3.0 g of RHA was added to 100 mL of 1.0 M NaOH in a plastic container and stirred for 30 min at room temperature to converted silica to sodium silicate. The sodium silicate formed was filtered to remove undissolved particles. The solution was then titrated slowly with 3.0 M nitric acid and 3.0 mL (51.0 mmol) of chlorosulphonic acid with constant stirring. The change in pH was monitored by using a pH meter. A white gel started to form when the pH reached 10.0. The titration was continued until the pH of the solution reached 3.0. The gel was aged for 24 h at room temperature. It was later separated by centrifuge. The separation process was repeated 6 times with copious amount of distilled water, and the final washing was done with acetone. The sample was then dried at 110 °C for 24 h and finally, it was ground to a fine powder, which weighed 6.4 g. It was labelled as RHSO<sub>3</sub>H.

## 2.3. Sample characterization

The RHSO<sub>3</sub>H was characterized by Powder X-ray diffraction (System). XPS was performed in a SPECS system, including a Phoibos 100 analyzer. The samples were in the form of a white small size grained powder. This powder was deposited on the top surface of a double sided sticky carbon tape attached to a stainless steel sample holder. The deposited powder was uniformly covering the carbon tape and inserted in the vacuum system and pumped down to  $3 \times 10^{-10}$  Torr overnight. XPS spectra were recorded with Mg K<sub>alpha</sub> and Al K<sub>alpha</sub> radiation, and the spectra were compared to discriminate between Auger and photoemission peaks. Two spectra are shown: A wide scan spectrum covering a wide range of binding (and kinetic-) energies, recorded with Al K<sub>alpha</sub> radiation, and a resolution of around 2.5 eV, for monitoring the concentration of the elements in the sample, and a detailed scan with a resolution of 1.4 eV, which serves to detect chemical shifts and to separate overlapping peaks. The latter spectrum was recorded with Mg K<sub>alpha</sub> radiation, which gives a slightly better resolution than for Al K<sub>alpha</sub>. The resolution for the survey scans was 2.5 eV. Element peaks were identified with the CasaXPS software. The FT-IR spectra were recorded on a 8400 S Shimadzu using KBr disk. UV-visible was recorded on a 1650 pc Shimadzu. The scanning electron microscopy (SEM) was recorded on a (Leica Cambridge S360) and energy dispersive spectrometry (EDX) (Edax Falcon System). The Atomic Force Microscopy (AFM) were obtained using CSPM-AA3000, SEM/EDX (Leo 35VP from Zeiss) AEM (PHI Model 560).

### 2.3.1. Cation exchange capacity (CEC)

1.0 g of sodium chloride was dissolved in 25 mL of distilled water in a conical flask with a magnetic stirrer. 1.0 g ( $\pm 10$  mg) sample of RHSO<sub>3</sub>H was added to the solution and left to stir for 30 min. 2–3 drops of phenolphthalein was added and the sample was titrated

with standard NaOH solution. An average of three separate titrations was performed to obtain an average value for the CEC of RHSO<sub>3</sub>H.

### 2.3.2. Pyridine acidity test

The sample, together with a beaker containing pyridine was placed in a dessicator equipped with a valve connected to a membrane vacuum pump (AMB Greiffenberger Antriebstechnik, MZ2C, CE 2002/06). The system was evacuated for 1 h at a rate of  $1.7 \text{ m}^3 \text{ h}^{-1}$ . The system was kept under closed vacuum for 48 h. The atmosphere in the desiccator was evacuated again for 1 h at the same pump rate. The sample was then removed and analyzed by FT-IR in KBr disc.

## 2.4. Catalytic hydrolysis procedure

### 2.4.1. Hydrolysis of cellulose

The cellulose hydrolysis was carried out in 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 and cellulose (0.18 g, 20 mmol) were separately transferred to the round bottom flask containing 0.2 g of the catalyst (pre-dried at 110 °C for 24 h and cooled in desiccators to minimize moisture content). The hydrolysis temperature fixed at 120 °C. The hydrolysis mixture was refluxed for 8 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 [13,14]. The DNS reagent was prepared according to an IUPAC method [15]. 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 similar to the samples. Then the absorbance was measured at 540 nm, against the reagent blank, and glucose concentrations in solutions were calculated by employing a standard curve prepared using glucose. The catalytic activity with different mass of catalyst (50, 100, 150, and 200 mg), different temperatures (RT, 100, 110, and 120 °C), different solvents i.e. (toluene, dioxane, 1-butanol, cyclohexanol, and ethanol), and RHA-blank catalyst were studied by using the same procedure as in above.

### 2.4.2. The reusability of the catalyst

Reusability experiment was conducted by running the hydrolysis successively with the same catalyst under the same hydrolysis condition. The hydrolysis was first run with the fresh catalyst to complete conversion and then the catalyst was filtered and washed with hot dioxane then with hot mixture of DMF and LiCl and dried at 110 °C. After regeneration, the catalysts were reused under the optimised reaction conditions.

### 2.4.3. Hydrolysis procedure for homogenous catalyst

The hydrolysis using homogenous catalyst was studied with sulphuric acid. Typically, a 50 mL capacity two necked round-bottom flask, equipped with a magnetic stirrer (700 rpm) and water condenser was used. 20 mL of DMF was transferred by pipette into the round bottom flask containing 8.8 mg (6.9 mmol) of sulphuric acid. After the reaction temperature reached 120 °C, 0.18 g (20.0 mmol) of cellulose was added. The hydrolysis mixture was refluxed. Samples for analysis ( $\sim 0.50$  mL) were withdrawn at regular intervals from the hydrolysis mixture by means of a syringe equipped with filter (cotton wool). 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. The glucose concentrations in solutions were calculated by employing a standard curve prepared using glucose.

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