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Modification of silica with 2,4-dinitrophenylhydrazanomethylphenol for monosaccharide productions

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ABSTRACT

2,4-dinitrophenylhydrazanomethylphenol (DNPHMP) was immobilized onto silicate rice husk ash to form a heterogeneous catalyst denoted as RHDNPH. The elemental and EDX analysis of RHDNPH showed the nitrogen is incorporated into silica. The RHDNPH had 154.6 m^2g^{-1} as a specific surface area. The FT-IR clearly showed the appearance of –NH and C=N absorption band at the expected range. The TGA curve shows that the RHDNPH was stable at the temperature of less than 200 ˚C. Hydrolysis experiments of cellulose were conducted in liquid phase reaction at 140 ˚C, and 150 mg of catalyst mass in 11 h. The maximum hydrolysis of cellulose was 84 % with 100 % selectivity of glucose over the catalyst. The catalyst was simple in its preparation, stable during the cellulose hydrolysis in addition to repeatedly without a significant loss of its catalytic activity.

Keywords*: Surface modification, Hydrolyses of cellulose, Rice husk ash, Salicylaldehydephenylhydrazone, Glucose.*

1. Introduction

Cellulose is the major polymeric component of plant material. It is the most abundant organic compound in nature and does exist in the cell wall of plants as complex fibrous carbohydrates [1]. Chemically cellulose is a linear polymer of β-1,4-glycosidic bonds monomer units. The structural portion of cellulosic biomass is a composite of cellulose chains joined to each other by van der Waals forces and hydrogen bonds into crystalline structures [2]. The application and interest in cellulose has particularly increased in recent years with the utilization of different catalysis in the production of bioethanol from lignocelluloses [3], converted to energy, chemicals, foods, and feedstocks [4]. Such utilization provides a clean, renewable material source that could dramatically improve the environment, economy and energy security [5]. Many researchers have focused on the hydrolysis of cellulose with dilute acids and concentrated acids [6], enzymes [7] and other types of catalysts. Hydrolysis of cellulose is a key technology for effective use of lignocelluloses because glucose can be efficiently converted into various chemicals, biofuels, foods and medicines [8].

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Rice husk (RH) is one of the by-products obtained during milling of rice, is primarily composed of silica and organic compounds [9]. Rice husk ash is obtained by burning the RH in a furnace at moderate temperature. The silica (SiO_2) content [10] of the ash is more than 94%. The nature of silica is able to grafting with organic compound to formation hybrid organic-inorganic catalysis. In this respect different catalysts were prepared in our libratory like Melamine [11], saccharine [12], Phenylalanine [13], imidazole [14], and sulfanilic acid [15] and used for different purposes.

Hydrazones have attracted considerable attention due to their interesting chemical and structural properties. Hydrazones are a class of organic compounds with the structure $R1R2C=NNH_2$. They are related to ketones and aldehydes by the replacement of the oxygen with the $–NNH_2$ functional group [16]. Hydrazone compounds obtained by the reaction of aromatic and heterocyclic hydrazides with mono and di-aldehydes or ketones have revealed very versatile behavior in metal coordination. Many researchers have synthesized a number of new hydrazones because of their ease of synthesis [17,18]. Hydrazones have been studied as a group of the most useful spectrophotometric reagents. The combining of carbonyl compounds and hydrazine, the sensitivity as an analytical reagent and/or solubility of the

hydrazones could be improved and the donating environment could be changed [19]. The shortcoming of hydrazones was their lack of selectivity for metal ions. Much effort has been devoted to developing masking agents for use with hydrazones [20,21]. However, the using of salicylaldehyde phenyl-hydrazone as a heterogenous catalyst for the cellulose hydrolysis was not been reported as the best of the knowledge. Here we report the immobilization of salicylaldehyde phenylhydrazone onto silica rice husk ash and its application for the hydrolysis of cellulose.

2. Experimental

2.1. Raw materials

All chemicals were used directly without further purification. These include sodium hydroxide (Systerm, 99%), nitric acid (Systerm, 65%), 3-(chloropropyl)triethoxysilane CPTES (Sigma, 99%). 2,4-dinitrophenylhydrazine (BDH, 99%), salicyl-aldehyde (hi-media, 98%), toluene (GCC, 98%), dimethylsulfoxide (GCC, 98%), methanol (GCC, 98%), ethanol (GCC, 100%), acetone (Sigma, 98%), cellulose (BDH, 98%), lithiumchloride (BDH, 98%), dimethylformamide DMF (Riedel-dehaen, 99%), Dinitrosalycilic acid (DNS) (BDH, 99%), triethylamine (Merck, 98%), cyclopentanon (Riedel-dehaen, 99%), cyclohexanol (Riedel-dehaen, 99%), butanol (Fluka, 98%). The rice husk (RH) was collected from a rice mill in Samawa, Iraq.

2.2. Samples characterization

The samples were characterized by FT-IR using Shimadzu system in KBr disk. The ^{1}H NMR and ^{13}C NMR spectra of DNPHMP were obtained by using bruker (400 MHz) system in d_6-DMSO as solvent. X-Ray diffraction pattern (XRD) obtained by using Stoe, Stidy-mp Diffractro meter system. Thermal analyses TGA obtained by using STA1500 Rheometric Scientific System. A nitrogen adsorption analysis was obtained by using Nova 2000 Quantachrome analyzer. Scanning electron microscopy–energy dispersive X-ray (SEM-EDX), was obtained by Philips XL30 system. Elemental analyses results was obtained by Optima [7300 DV] system.

2.3. Synthesis of 2-((2-(2,4-dinitrophenyl)hydrazono) methyl)phenol (DNPHMP)

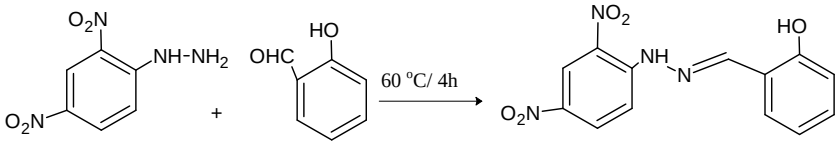
The DNPHMP was synthesized according to the reported method [22]. In general, 0.01 mol (1.98 g) of 2,4-dinitrophenylhydrazine was dissolved in 15 mL of ethyl alcohol and then it was added gradually to ethanolic solution of salicylaldehyde 0.01 mol (1.06 mL). The mixture was refluxed at 60 °C for 2 h. The reaction was monitoring by TLC using a mixture of chloroform:benzene (2:1) as an eluent. A red precipitate was separated out and washed with acetone. The product was dried in an oven 50 °C for 5 h (Scheme 1). The yield was 80.0%, m.p.= 259.3 °C. FT-IR: $\bar{\nu}$ = 3410 (-OH), 3271 (N-H), 3105 (Ar-H), 1616 (C=N) cm^{-1}. ^{1}HNMR (400 MHz, d_6-DMSO): δ= 2.5 (6H, s, 2 × CH_3), 3.3 (1H, s, NH), 6.6-8.2 (7H, m, 2 × ArH), 10.1 (1H, s, OH), 11.7 (1H, s, CH) ppm. ^{13}CNMR (100 MHz, d_6-DMSO): δ= 117.9 (ArC, C9 & C2), 118.2, 121.09, 121.6 , 128.9 (Ar C12, C4, & C13), 124.6 (ArC, C5 & C10), 128.03 (ArC, C3 & C6), 131.29, 133.5, 145.9, 148.1 (ArC, C11, C7, C8 & C1) ppm.

2.4. Extraction and modification of silica from RHA and synthesis of RHDNPH catalyst

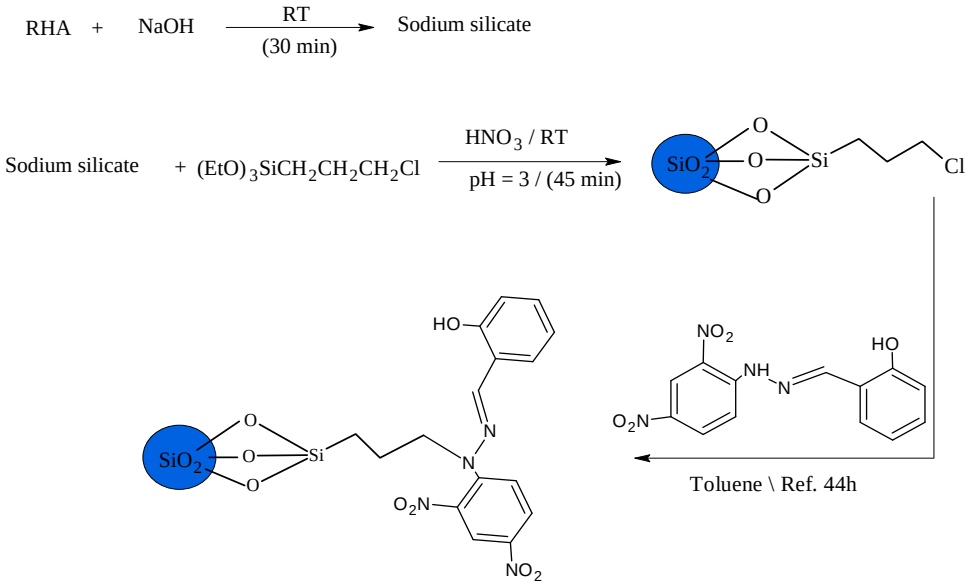
The RHA was chosen as the source of amorphous silica [23]. The silica was extracted from RH according to a reported method [24,25]. RHA silica was functionalized with CPTES according to the reported method [26]. The resulting solid was labeled as RHACCl. RHDNPH was prepared by adding 0.01 mol (2.0 g) of DNPHMP to the 1.0 g of RHACCl and 0.01 mol (1.30 mL) Et_3N in dry toluene (30 mL). The reaction mixture was refluxed at 110 °C in an oil bath for 44 h. The solid was filtered, washed with 50 mL methanol, 50 mL DMSO and then dried at 100 °C for 24 h. Finally, it was grind to produce a fine powder which was labeled as RHDNPH (Scheme 2). About 0.75 g from RHDNPH was obtained by using this method.

2.5. Catalytic 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) 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 140 °C. The hydrolysis mixture was refluxed for 14 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 [27,28] and the mixture was incubated in a water bath maintained at 90 °C for 5 min.



Scheme 1. The synthesis of DNPHMP.



Scheme 2. The sequence for the synthesis of RHDNPH.

The DNS reagent was prepared according to an IUPAC method [29]. 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, 120, 130, and 120 °C), different solvents like DMF, 1-butanol, cyclohexanol, and cyclohexanone were studied by using the same procedure as in above.

2.6. 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.

2.7. Hydrolysis procedure for homogenous catalyst

The hydrolysis using homogenous catalyst was studied with DNPHMP control catalysts. 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 0.31 g (0.001 mol) from DNPHMP. After the reaction temperature reached 140 °C, 0.18 g (20 mmol) of cellulose was added. The hydrolysis mixture was refluxed. Samples for analysis (~ 0.50 mL) were withdrawn at regular intervals from the hydrolysis mixture by means of a syringe equipped with filter (cotton wool) and glucose concentrations in solutions were calculated by employing a standard curve prepared using glucose.

3. Results and Discussion

3.1. Characterization of RHDNPH catalyst

Silica which extracted from rice husk ash has been modified with DNPHMP to produced solid catalyst. The RHA and RHACCl have been characterizing elsewhere [26].

3.2. Elemental analysis

Table 1 shows the elemental analysis of RHDNPH, which determined by a combination of elemental and EDX analysis. Due to the heterogeneous nature of the silica samples, these values can be only treated qualitatively. The elemental analysis showed that the nitrogen is present in RHDNPH, while this element is not present in RHA and RHACCl [26]. The C content for RHDNPH was slightly higher than RHACCl, which was as expected. The EDX analysis also showed the presence of nitrogen in RHDNPH from which it can further conclude that the DNPHMP was incorporated into silica.

3.3. X-Ray diffraction pattern (XRD) and N_2 adsorption analysis

The XRD pattern (Fig. 1) showed a broad diffraction band at 2θ angle ca. 22.8, which was typical for amorphous silica. This was similar to the observation of RHACCl [26].

Fig. 2 shows the nitrogen adsorption isotherm obtained for RHDNPH. Inset is the pore size distribution graph.

Table 1. The physical parameters obtained for RHDNPH. The C, H and N content determined by a combination of elemental and EDX analysis (shown in bract). The results of BET analysis are also shown.

Sample	Elemental %			Specific Surface area (m^2 g^{-1})	Average pore volume (cc g^{-1})	Average pore diameter (nm)
	C	H	N			
RHDNPH	16.49 (11.2)	2.86 (-)	3.14 (1.6)	155	0.17	1.47

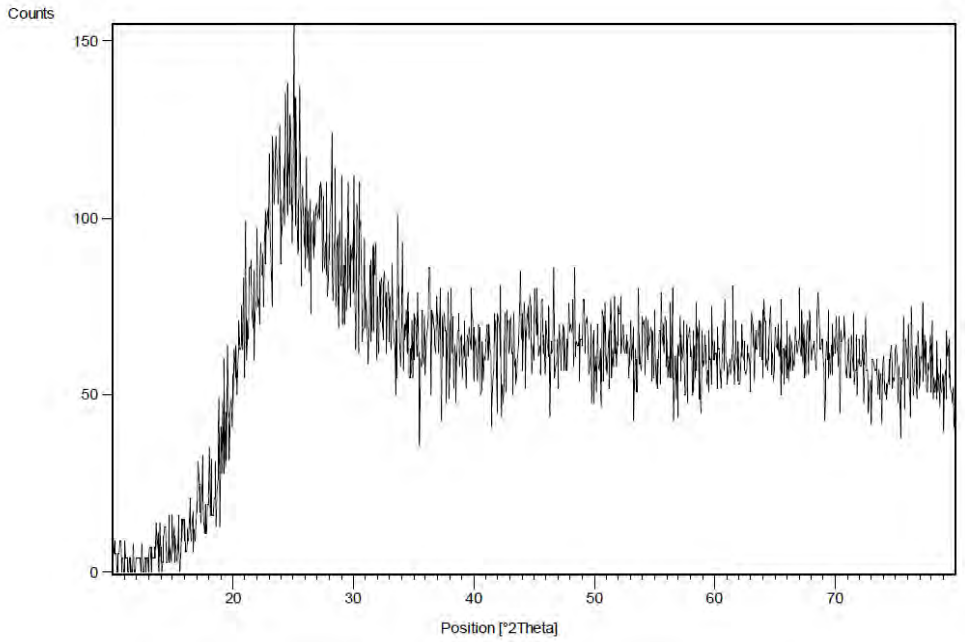


Fig. 1. The X-ray diffraction pattern of RHDNPH.

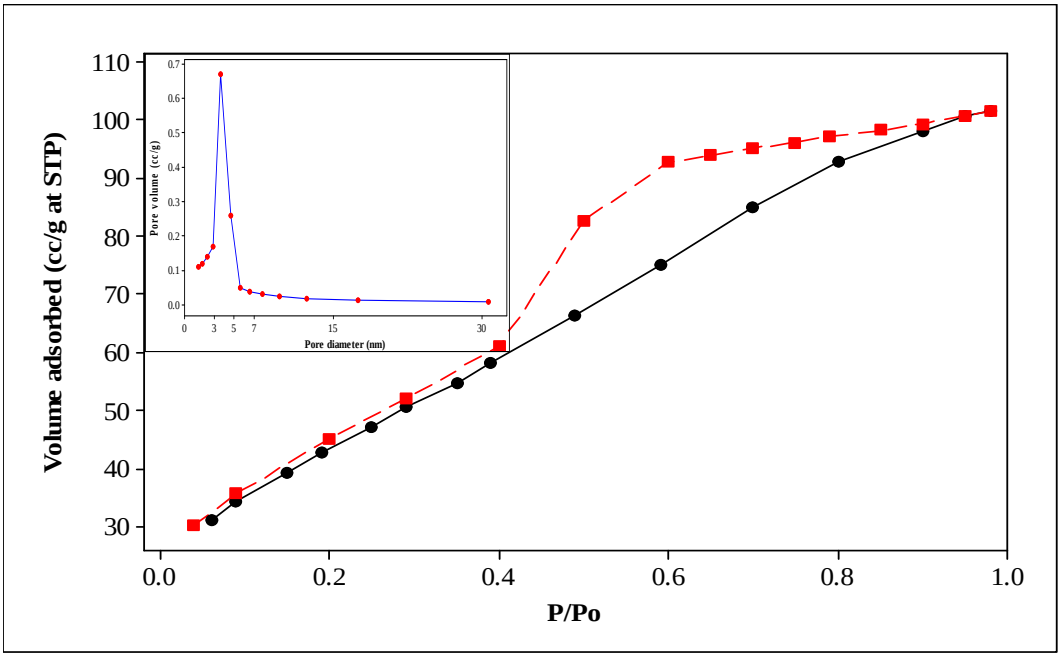


Fig. 2. The N_2 adsorption/desorption isotherms of RHDNPH with the corresponding pore size distribution inset.

The hysteresis loop was observed in the range of 0.4 < P/Po < 1.0, which is associated with capillary condensation according to the IUPAC classification. The isotherm shown is of type IV and exhibits an H2 hysteresis loop [30]. Close observation of the program revealed that the hysteresis loop did not close but it was rather open ended. This indicates the presence of some degree of microspores retaining the nitrogen and hence failing to close the hysteresis loop. This is clearly seen in the pore size distribution curve, where the maxima in the microspore region (< 2 nm) and a major maximum at ca. 4 nm can be observed. It can therefore be concluded that RHDNPH consists of microspores with the narrow pore range of 3–4 nm. The BET analysis revealed the specific surface area of RHACCl to be 633 m^2 g^{-1} [26]. However, the specific surface area of RHDNPH was found to be 154 m^2 g^{-1} (Table 1). The decrease in the surface area was indicated that the DNPHMP was incorporate with the RHACCl and led to decrease in the service area.

3.4. Thermal analysis

Fig. 3 shows the TGA-DTA curve of RHDNPH. The graph shows four characteristic decomposition stages. The first started at 40 to 185 °C, due to the loss of absorbed water (ca. 0.90 %), and the second mass loss (ca. 4.15 %) occurred between 185–273 °C due to the decomposition of the DNPHMP and propyl groups anchored onto the silica [31]. The continuous weight loss (ca. 23.48 %) between 300 – 440 °C was due to decomposition of the remaining organic DNPHMP and propyl anchored on the silica surface. The forth decomposition stage between 440–680 °C was due to the condensation of silanol groups at higher temperatures [32]. In the DTA curve, it was observed four exothermic transformations the first is a peak which occurs between 40 °C and 185 °C, with a maximum at 90 °C and the second occurs between 185 °C and 273 °C, with a maximum at 250 °C, while the third occurs between 300 °C and 440 °C with a maximum at 350 °C. The last exothermic transformations is occurs between 440 °C and 680 °C, with a maximum at 500 °C. The first exothermic change due to the loss of adsorbed water, while the second, third and fourth attribute to the arrangement of the structure of the polymer [33]. The TGA-DTA provided further evidence for the successful immobilization of DNPHMP onto silica.

3.5. Scanning electron microscope SEM

The SEM of RHDNPH was shown in Fig. 4. It seems that the catalyst has shown large particles distributed randomly onto smooth surface of silica.

3.6. Hydrolysis of cellulose over RHDNPH catalyst

The RHDNPH was used to hydrolyze cellulose in liquid-phase reaction. Further various parameters such as effect of hydrolysis time, mass of catalyst, temperature, solvents effects on glucose formation were evaluated to optimize the hydrolysis conditions.

3.7. Influence of hydrolysis time

The effect of the time on the hydrolysis of cellulous to glucose over RHDNPH, RHA, RHACCl, homogenous DNPHMP and the solvent system without catalyst (DMF/LiCl) are shown in Fig. 5. The hydrolysis was carried out with 150 mg of catalyst, at 140 °C. The initial hydrolysis of cellulous to glucose during the fifth hour was less than 10 % and it was increased to a maximum of 84 % in 11 h.

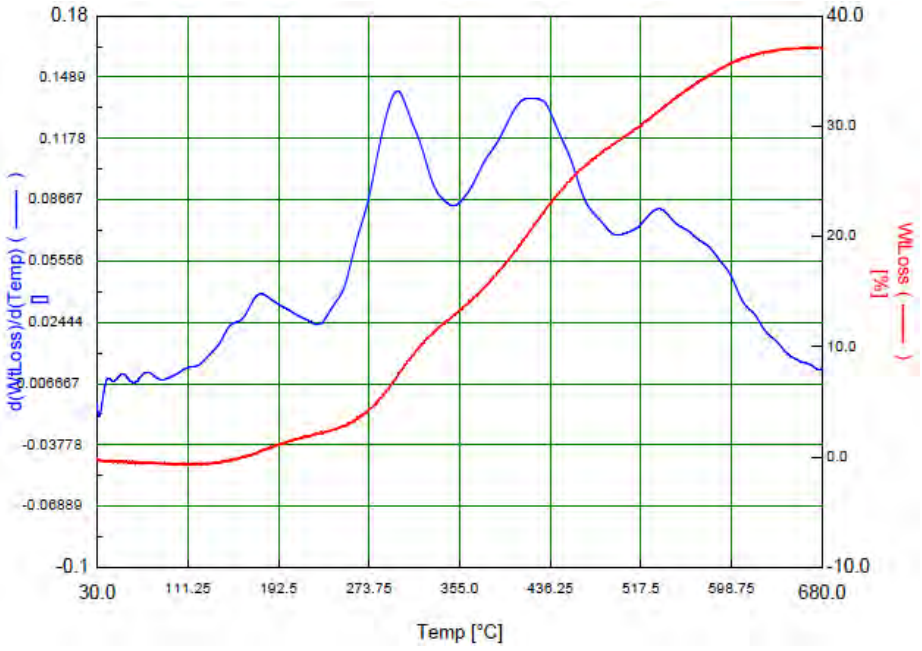


Fig. 3. The TGA/DTA curve of RHDNPH.

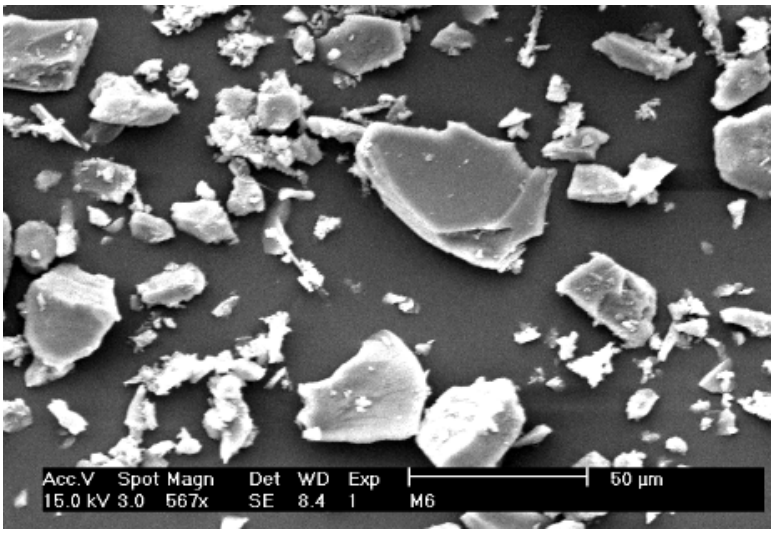


Fig. 4. The SEM image of RHDNPH.

However, it was observed that when the hydrolysis time was increased, more than 11h, there was no change on the hydrolysis of cellulose. Therefore the optimum time of the hydrolysis of cellulous to glucose over RHDNPH is 11 h. The homogeneous DNPHMP also showed 81 % of glucose at 11 h. We believe that this is the first report of DNPHMP being used as a catalyst in hydrolysis of cellulose or in other reactions. The heterogenation of DNPHMP is now much more meaningful and should be taken advantage of since it gives reasonably high hydrolysis. To show the effect of the active center of the RHDNPH the hydrolysis of cellulose to glucose was investigated by using the RHA and RHACCl as shown in Fig. 5. The maximum conversion of cellulose over RHA and RHACCl was less than 17 % and 31 % respectively. The maximum hydrolysis of cellulose over DMF without catalyst was 20 % in 11 h. The low hydrolysis of cellulose over RHA and RHACCl comparing with high hydrolysis of cellulose over RHDNPH indicates that the activity of RHDNPH is a proportional with the active centers.

3.8. Effect of catalyst mass

The hydrolysis of cellulose was carried out by varying the amount of RHDNPH (ranged 50 and 200 mg) while keeping the other parameter fixed as 11 h as a hydrolysis time at 140 ˚C. The results are presented in Table 2.

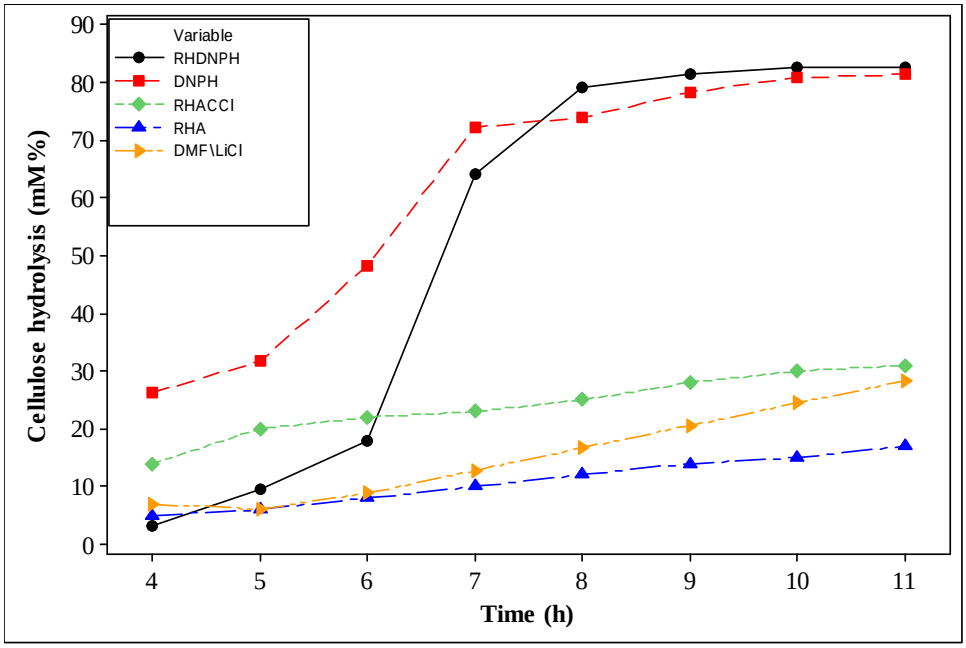


Fig. 5. The hydrolysis of cellulose to glucose over RHDNPH, RHA, RHACCl, DNPH and DMF\LiCl without catalyst as a function of hydrolysis time.

Table 2. The effect of different parameters on the hydrolysis of cellulose to glucose with RHDNPH. The reaction was run over 11 hours.

Parameters	Variants	Glucose Yield (mM %)
Variation of catalyst mass (mg)	50	49
	100	63
	150	84
	200	80
Variation of hydrolysis temperature (°C)	RT	19
	120	63
	130	64
	140	84
Variation of solvent effects in LiCl	DMF	84
	Cyclohexanol	61
	Cyclopentanone	52
	1-Butanol	10
Reusability with 150 mg of catalyst	Fresh catalyst	84
	1st reuse	81
	2nd reuse	80
	3rd reuse	80

It is clearly shown when the catalyst's mass were increasing from 50 to 150 mg, the percentage of cellulose hydrolyzed to glucose increased too from 49 to 84 %. Further increase in the catalyst mass had decreased the catalytic activity. The increased hydrolysis of cellulose with the catalyst mass could be attributed to the availability of a greater number of catalytically active sites. Therefore 150 mg was chosen as the optimum mass of the catalyst.

3.9. Influence of hydrolysis temperature

The effect of the temperature on the hydrolysis of cellulose to glucose over RHDNPH is shown in Table 2. The yield of glucose was increased when the hydrolysis temperature increased from room temperature (RT) to 140 °C.

3.10. Influence of solvents effect

The hydrolysis of cellulose is varying according to its solubility into different solvents. The effect of the solvent that was used as a media on the hydrolysis of cellulose to glucose over RHDNPH is shown in Table 2. The hydrolysis was studied over different solvents like cyclopentanone, cyclohexanol, DMF, and 1-butanol. It was observed that the hydrolysis of cellulose over different solvents was followed the following order:

DMF > Cyclohexanol > Cyclopentanone > 1-Butanol

The hydrolysis of cellulose was depending on the solubility of cellulose in the solvent. The DMF contain more than one center able to form a hydrogen bonding with the cellulose and this could lead to increasing the solubility of cellulose and make the hydrolysis much more easily comparing with the insoluble one.

3.11. Catalyst recycling

After the first hydrolysis was run using the RHDNPH catalyst with the mixture, it was then washed with hot DMF and LiCl (this step was repeated three times) and the catalyst was activated at 110 °C for 24h. Next, fresh cellulose and DMF with LiCl were added to the catalyst and a second run was conducted, as was a third, using the same procedure. As shown Table 2, the product yields in the second and third runs were similar to that in the fresh run. These results indicated that catalytic performance was not lost during the course of the catalytic runs.

3.12. Hydrolysis kinetic

The data obtained in this study was used to determine the reaction kinetic parameters of the RHDNPH catalyst. These data was found to be in agreement with pseudo zero order rate low. The apparent rate constant for the cellulose hydrolysis over RHDNPH increased from 0.005 to 0.0066 mol L h, when the temperature was increased from 110 to 140 °C and also the cellulose hydrolysis was increased. This could be due to the proportional relation between the temperature and rate of the reaction. The data obtained from this equation at different temperatures are shown in Fig. 6.

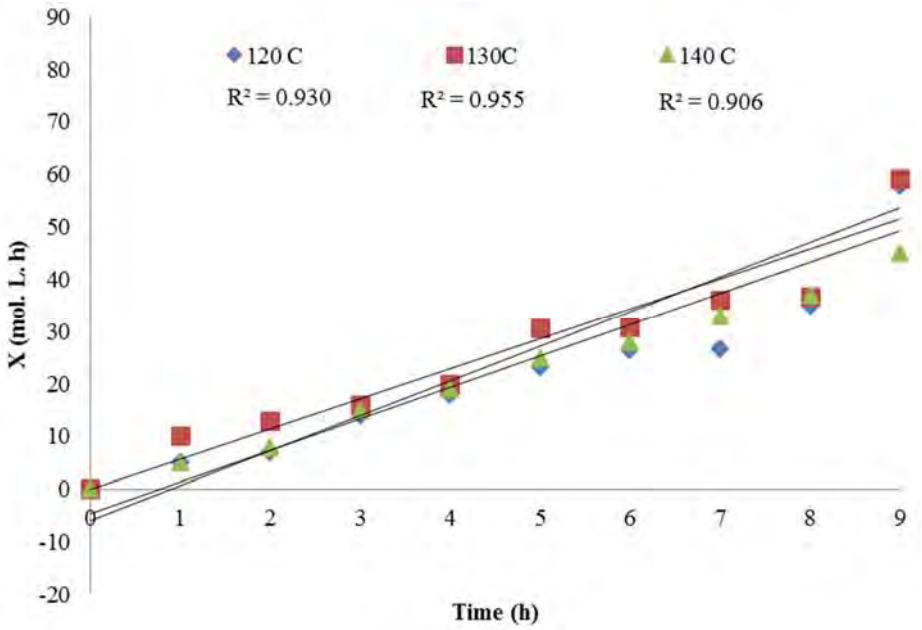


Fig. 6. The pseudo zero rate plots for the hydrolysis of cellulose over the surface of RHDNPH. The correlation coefficients were also shown.

Using plot of ln k_a as a function of T^{-1} (Fig. 7) using the equation 1, both the frequency factor (A) and the activation energy (E_a) were determined. The activation energy (E_a) for RHDNPH was 9.6 Kcal mol^{-1}. The low activation energy is shown that the RHDNPH is an efficient catalyst for the cellulose hydrolysis.

The results are listed in Table 3.

$$\text{Ln } k = \text{Ln } A - Ea/RT \quad \textbf{(1)}$$

Where A (L mol^{-1} min^{-1}) is the frequency factor, Ea (kcal mol^{-1}) is the activation energy, R (J mol^{-1} K^{-1}) gas constant; T (K) is the reaction temperature.

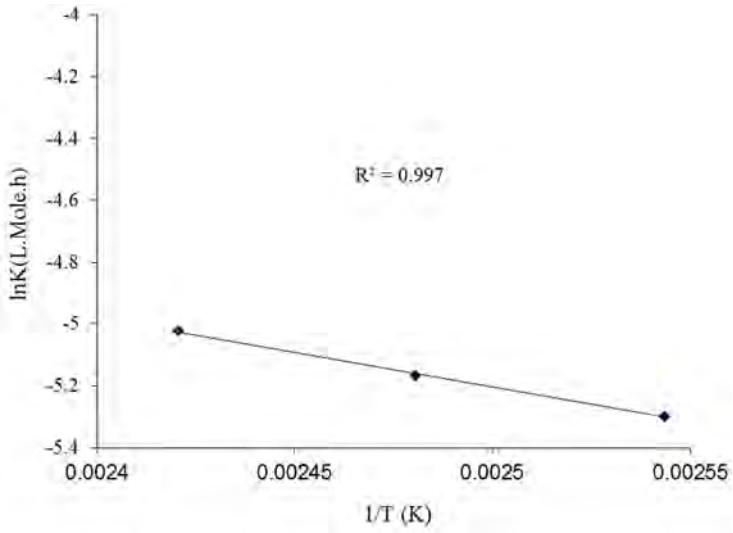


Fig. 7. The Arrhenius plot for the cellulose hydrolysis over the surface of RHDNPH at different temperatures.

Table 3. The kinetic parameters for the cellulose hydrolysis over the surface of RHDNPH. ka is the apparent rate constant, Ea activation energy and A frequency factor.

Temperature (K)	393	403	413
k_a (mol L h)	0.005	0.0057	0.0066
A (L $mol^{-1}h^{-1}$)	1.0×10^5		
E_a (kcal mol^{-1})	9.6		

4. Conclusions

DNPHMP was reacted with silica extracted from rice husk ash to form RHDNPH catalyst. The nitrogen adsorption-desorption study show that the specific surface area of the catalyst was 154.6 m^2 g^{-1}. The TGA/DTA shows the catalyst could be stable and it may decompose in between 215–380 °C. The evidence from the all spectroscopy showed the successful formation of RHDNPH. The RHDNPH was used to hydrolyze cellulose to glucose. Approximately 84 % of cellulose was hydrolyzed at 140 °C for 11 h over the catalyst. The catalyst was simple in the preparation, stable during the hydrolysis and could be used several times without losing its activity.

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