A new approach has been demonstrated for the synthesis of solid ammonium sulphate attached to silica rice husk ash. The 3-(aminopropyl)triethoxysilane was immobilized onto silica at room temperature to functionalize the silica with ammine end groups (–NH₂). The amine group was sulphated with sulphuric acid to produce a novel micro-rod-like shaped acidic catalyst (as seen with TEM) designated RHNH₃SO₄H (RH = rice husk). The TGA analysis shows that the catalyst is stable at temperatures below 200°C. The acidity measurement of the catalyst indicates that it has Bronsted acid sites. Cellulose extracted from waste of rice husk and cellulose extracted from office paper were hydrolysed to glucose in 6 h, and the glucose was hydrolysed afterwards to other products within 13 h. The catalyst is reusable many times without a significant loss of catalytic activity.

1. Introduction

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 H₂SO₄, HCl, and H₃PO₄, which have limitations due to a tedious work-up procedure and the necessity of postneutralization 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 catalysts in solid state form with less environmental concerns. Those catalysts are recyclable and can be used for the same purposes as where the ionic liquids catalysts are used [1].

Rice husk (RH) is a major by-product of the rice-milling industries and it is causing disposal problems. Moreover, after its burning approximately 20% ash content comprises over 95% of amorphous silica which has very fine particle size, very high purity, high surface area, and high porosity. These properties would give rice husk utilization a very economically attractive perspective [2, 3]. One important application of silica is due to its ability to be modified with different silylating agents, which can introduce basic groups through an anchored pendant chain. The traditional procedure for immobilization of 3-(aminopropyl)triethoxysilane (APTES) onto different types of silica involves long reaction times, nonenvironmentally friendly organic solvents, harsh refluxing condition, and multiple steps [4–6]. Moreover, the vast majorities of these protocols call for expensive chemicals and techniques and cause environmental pollution. A more direct and simple method was introduced by us to immobilize APTES onto silica to give a -CH₂–NH₂ functionality on the silica surface [7, 8].

Recently, a new technique has been developed towards the production of second generation (2G) biofuels without the use of expensive enzymes [9]. 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 microorganisms are known for producing a set of enzymes capable of degrading this normally insoluble polymer to soluble sugars, primarily cellobiose and glucose [10]. 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 corn stems and keep the corn cobs for food, 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 [9].

2. Materials and Methods

2.1. Raw Materials. The chemicals used in this study were sodium hydroxide (Systerm, 99%), acetone (GCC, 99%), 3-(aminopropyl)triethoxysilane (Merck, 98%), nitric acid (Scharflau, 65%), 1-butanol (Fluka, 99%), cellulose (Riedle-De Haen, 99%), cyclohexanol (Riedle-De Haen, 99%), cyclohexanone (Riedle-De Haen, 99%), dimethylformamide (DMF) (Systerm, 99%), dinitrosaliclylic acid (DNS) (BDH, 99%), glucose (BDH, 99%), lithium chloride (Sigma, 99%), sodium chloride (Sigma, 99%), potassium chloride (Sigma, 99%), sulphuric acid (Poch, 95%), potassium chloride (Sigma, 99%), and sulphuric acid (Poch, 95%). The rice husks (RH) were 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. Sources of Silica. The rice husk ash (RHA) was chosen as the source of amorphous silica as it was available in abundance. The silica was extracted from rice husk using a previously reported method [11, 12].

2.3. Sources of Cellulose

2.3.1. Extraction of Cellulose from RH. RH was used as a source of cellulose as well as of silica. The cellulose was extracted from RH according to the method reported in [13]. In general the RH was washed twice with water and dried at room temperature for 24 h. A weight of 35g of waste paper was cut into small pieces and mixed with sodium hydroxide solution 7.5% in a plastic container equipped with stirrer. The mixture was stirred for 6 h and then filtered. The filtrate was titrated against 5.0 M sulphuric acid solution until the pH reached 5.0. After separating the mixture, the solid was washed with distilled water and dried at room temperature. This method gave about 1.0 g, 20% of cellulose.

2.3.2. Extraction of Cellulose from Waste Paper. Waste paper was also used as raw material for extraction of cellulose by a simple and economic method. Waste paper was collected from waste boxes of the offices in Al-Muthanna University. The cellulose was extracted from RH according to the method reported in [13]. In general, 5.0 g of waste paper was cut into small pieces and mixed with sodium hydroxide solution 7.5% in a plastic container equipped with stirrer. The mixture was stirred for 6 h and then filtered. The filtrate was titrated against 5.0 M sulphuric acid solution until the pH reached 5.0. After separating the mixture, the solid was washed with distilled water and dried at room temperature. This method gave 6.0 g, 17.14% of cellulose.

2.4. Synthesis of RHNH₄SO₄ H Catalyst. The APTES was functionalization onto RHA to produce RHAPrNH₂ according to the method reported elsewhere [7]. The primary amine in RHAPrNH₂ was sulphated to the solid ammonium sulphate at room temperature. In general, 25 mL of 0.05 M sulphuric acid was added to the 2.0 g of dry RHAPrNH₂ in a 50 mL round bottom flask and it was stirred for 24 h. The solid ammonium sulphate formed was filtered and washed with copious amount of water and then dried in an oven at 100°C for 24 h. The resulting compound was labelled as RHNH₄SO₄ H. About 1.9 g was collected using this method.

2.5. The Surface Acidity of RHNH₄SO₄ H. The surface acidity measurement of RHNH₄SO₄ H was done as in the method reported in [2]. In general RHNH₄SO₄ H together with a beaker containing pyridine was placed in a desiccators equipped with a valve connected to a membrane vacuum pump (AMB Greifeningber Antriebstechnik, MZ2C, CE 2002/06). The system was evacuated for 1 h at a rate of 1.7 m³ h⁻¹. The system was kept under sealed vacuum for 48 h. The atmosphere in the desiccators was then evacuated again for 1 h at the same pump rate. Then, the solid compound was removed and analyzed by FT-IR on a KBr disc.

2.6. Catalytic Hydrolysis Procedure

2.6.1. Hydrolysis of Cellulose. The cellulose hydrolysis was carried out in the liquid phase in a 50 mL round bottom flask equipped with magnetic stirrer and water condenser connected to the chiller to control the water temperature in between 10 and 15°C. 20 mL of DMF, 0.2 g of LiCl, and 0.18 g cellulose were separately transferred to the round bottom flask containing 150 mg of the catalyst (predried at 110°C for 24 h and cooled in desiccators to minimize moisture content). The hydrolysis temperature was fixed at 120°C. The hydrolysis
mixture was refluxed for 13 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 were added 2.0 mL of DNS reagent and 2.0 mL of 2.0 N NaOH and the mixture was incubated in a water bath maintained at 90 °C for 5 min [14, 15]. The DNS reagent was prepared according to IUPAC method [16]. 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, 200, and 500 mg), different temperatures (100, 110, and 120 °C), different solvents, (i.e., 1-butanol, cyclohexanol, and cyclopentanone), and different solvent salt mixtures (LiCl, NaCl, and KCl) was studied by using the same procedure as described above.

2.6.2. The Reusability of the Catalyst. Reusability experiments were conducted by running the hydrolysis successively with the same catalyst under the same hydrolysis conditions. The hydrolysis was first run with the fresh catalyst to complete conversion and then the catalyst was filtered and washed with hot dioxane and then with a hot mixture of DMF and LiCl and dried at 130 °C. After regeneration, the catalysts were reused under the optimised reaction conditions.

2.6.3. Hydrolysis Procedure for Homogenous Catalyst. The hydrolysis using the homogenous catalyst was studied with ammonium sulphate. 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 4.6 mmol of ammonium sulphate. After the reaction temperature reached 120 °C, 0.18 g 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). 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.

2.7. Sample Characterization. The prepared RHNH₃SO₄H was characterized by elemental analysis (Perkin Elmer Series II, 2400), thermogravimetric analyses (TGA SDTA851°), from 30 to 900 °C at a heating rate of 20 °C min⁻¹ under nitrogen flow. Powder X-ray diffraction (Siemens Diffractometer D5000, Kristalloflex), nitrogen adsorption porosimetry (Automatic Physisorption Autosorb-1 CLP, Quantachrome, USA), FT-IR spectroscopy (Perkin-Elmer System 2000), scanning electron microscopy (SEM) (Leica Cambridge S360), and energy dispersive spectrometry, EDX (Edax Falcon System), were all used as well. The TEM micrographs were obtained using Philips CM12 equipment.

The XRD pattern (not shown) did not show sharp diffraction patterns. This is an indication that the sample is amorphous.

3. Results and Discussion

3.1. CHN Analysis. Table 1 shows the chemical analysis of RHA, RHAPrNH₂, and RHNH₃SO₄H using a combination of elemental and EDX analysis.

| Sample            | C      | H      | N      | S      | Si      |
|-------------------|--------|--------|--------|--------|---------|
| RHA               | 0.42   | 1.76   | —      | —      | (29.09) |
| RHAPrNH₂ [7]      | 9.67   | (19.52)| 2.31   | 6.08   | (23.48) |
| RHNH₃SO₄H         | 10.07  | (20.79)| 2.99   | 2.20   | (3.43)  |

3.2. Infrared Spectroscopy Analysis. Figure 1 shows the FT-IR spectra of RHAPrNH₂, RHNH₃SO₄H, and its difference spectrum. The strong and broad band in the range 3500–3400 cm⁻¹ region corresponds to the hydrogen bonded Si–OH groups. The RHAPrNH₂ and the difference spectra show bands at 3153 cm⁻¹ corresponding to the free NH₂ [17] and a weak band at 2939 cm⁻¹ corresponding to the aliphatic C–H stretching. The strong band at 1384 cm⁻¹ is related to the NO₃⁻ ions. The RHAPrNH₂ treated with H₂SO₄ showed some changes on the FT-IR spectrum. The band at 3153 cm⁻¹ (corresponding to the free NH₂) disappeared. This indicates the successful transformation of –NH₂ group to –NH₃ group. However, we also observe the disappearance of the strong band at 1384 cm⁻¹ (for nitrate ion), which may be due to a replacement by –SO₄⁻ ions. This fact was confirmed by appearance of two bands at 1308 and 1162 cm⁻¹, assigned to the presence of the SO₂ group which is the main component of –SO₄ group [9].

The RHA spectrum (not shown) does not show these bands. In RHA the Si–O–Si vibration appears at 1082 cm⁻¹. This band was observed to shift to 1067, 1054 cm⁻¹ in RHAPrNH₂ and RHNH₃SO₄H, respectively.

3.3. Powder X-Ray Diffraction (XRD) and Nitrogen Adsorption Analysis. The XRD pattern (not shown) did not show sharp diffraction patterns. This is an indication that the sample is amorphous.
amorphous. A broad diffraction band at 2θ angle of ca. 22° was observed which is typical for amorphous silica.

Figure 2 shows the nitrogen adsorption isotherm obtained for RHNH₃SO₄H and inset is shown in the pore size distribution graph. The hysteresis loop observed in the range of 0.4 < P/Pₒ < 1.0 is associated with capillary condensation according to the IUPAC classification. The isotherm shown is type IV and exhibited an H3 hysteresis loop [19].

The BET analysis showed a specific surface area of RHNH₃SO₄H was 113 m² g⁻¹, while the specific surface area of RHAPrNH₂ was reported to be 1.32 m² g⁻¹ [7]. The increase in the surface area of RHNH₃SO₄H could be due to the use of H₂SO₄, which may remove the entire nitrate ion (as it is shown in FT-IR) and reduce the crowding on the surface and thus lead to opening the pores. The RHNH₃SO₄H (Figure 2) showed a broad pore size range from 5 to 90 nm with an average pore volume of 0.22 cc g⁻¹ which is in the mesoporous range.
3.4. Thermogravimetric Analysis (TGA)/Differential Thermal Analysis (DTA). Figure 3 shows the TGA-DTA of RHNH$_3$SO$_4$H. The graph shows four characteristic decomposition stages. The first weight loss (ca. 6.2%) is due to the loss of adsorbed water, and the second mass loss (ca. 14.4%) is due to the decomposition of the aminopropyl sulphate groups anchored to the silica. According to this mass loss we found that 0.046 mmol/g of aminopropyl sulphate had been loaded onto RHNH$_3$SO$_4$H. This value was in agreement with our previous study with other ligands [20]. The slow, continuous weight loss (ca. 10.8%) was due to the condensation of silanol groups at higher temperatures.

In the DTA curve in Figure 3 three exothermic transformations were observed. The first peak occurs between 29 and 187°C, with a maximum at 75°C, the second occurs between 187 and 436°C, with a maximum at 330°C, and the third occurs between 436 and 902°C with a maximum at 520°C. The first exothermic change is due to the loss of adsorbed water, while the second and third are attributed to the arrangement of the structure of the polymer [21].

3.5. The SEM and TEM Analysis. The SEM micrographs at different magnifications are shown in Figure 4. These show the presence of a porous surface. The porosity is directly linked to the high specific surface area determined by the nitrogen adsorption studies. However, the SEM shows small particles with a bright, smooth surface. The smoothness of these particles is emphasized at the higher magnifications. These SEM micrographs are probably in good agreement with the BET analysis with regard to the specific surface area and specific pore volumes.

The TEM micrographs at different magnifications are shown in Figure 5. The RHNH$_3$SO$_4$H has rod-like morphology, and the diameters of the microrods are in the range of 0.1 μm to 0.26 μm and the length is about several millimetres.

3.6. Pyridine Adsorption Studies. The pyridine adsorption study of RHNH$_3$SO$_4$H obtained before and after pyridine adsorption in the region of 1700–1400 cm$^{-1}$ (as shown in Sup. 1 in the Supplementary Material available online at http://dx.doi.org/10.1155/2014/128547). By comparing the two FT-IR spectra, after and before the pyridine test, two new bands in the regions 1544 cm$^{-1}$ and 1489 cm$^{-1}$ have been observed. These two bands indicate the presence of Brønsted acid sites [22].

3.7. Hydrolysis of Cellulose over RHNH$_3$SO$_4$H Catalyst. The RHNH$_3$SO$_4$H 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, solvent effects, and salt effects.

3.7.1. Influence of Hydrolysis Time. The effect of the hydrolysis time on the hydrolysis of cellulose to glucose over RHNH$_3$SO$_4$H and homogenous ammonium sulphate (NH$_4$)$_2$SO$_4$ [18] is shown in Figure 6. The hydrolysis was carried out with 150 mg catalyst using a DMF/LiCl as a solvent at 120°C. The initial hydrolysis of cellulose to glucose during the first hour was 65% and it reached the maximum hydrolysis of 98% in 6 h. The homogeneous ammonium
sulphate (4.6 mmol/g) showed 99% of glucose at 4 h and then the hydrolysis was decreased due to the hydrolysis of glucose itself. It was well known that the homogenous catalyst is more effective than the heterogeneous one. 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 hydrolysis of cellulose over RHNH$_3$SO$_4$H was reaching the optimum after 6 h of hydrolysis time. At this point the behaviour of both catalysts is the same. The only difference is processing time. After the optimum time of the cellulose hydrolysis over RHNH$_3$SO$_4$H, the glucose would start to hydrolyze to other products too. It was observed that the cellulose was fully hydrolysed to glucose after 6 h and the glucose itself was hydrolyzed to other products during the next 6 h. The selectivity of the hydrolysis of cellulose to glucose was 100% at the first 6 h of the hydrolysis. The advantages of using RHNH$_3$SO$_4$H as a catalyst in the hydrolysis of cellulose are the easy of recover and the repeatedly.

3.7.2. Effect of the Catalyst Mass. The hydrolysis of cellulose was carried out by varying the amount of RHNH$_3$SO$_4$H between 50 and 500 mg at 120 °C. The effect of the amount of the catalyst on the hydrolysis of cellulose to glucose is shown in Figure 7. When the catalyst mass was increased from 50 to 150 mg, the cellulose hydrolysis increased from 68 to 98%. Further increase of the catalyst mass had no significant effect. The increase in the conversion with catalyst mass could probably attribute to the availability of a greater number of catalytically active sites. Therefore 150 mg was chosen as the optimum mass of the catalyst.

3.7.3. Influence of Hydrolysis Temperature. The effect of temperature on the hydrolysis of cellulose over RHNH$_3$SO$_4$H is shown in Figure 8. The hydrolysis increased when the reaction temperature was increased from 100 to 120 °C. The hydrolysis was ca. 99% at 120 °C. Most researchers set the hydrolysis temperature at 100 °C. To confirm the effect of hydrolysis temperature on the yield of glucose, we are comparing with our previous study on SO$_3$H-functionalized silica catalyst for cellulose hydrolysis to glucose [9]. The maximum glucose yields at 100 °C were 80% after 8 h when our previous catalyst used SO$_3$H-functionalized silica. By using RHNH$_3$SO$_4$H the glucose yield was reaching ≈92% at 100 °C and 98% at 120 °C in 6 h. This clearly indicates that the use of RHNH$_3$SO$_4$H is more effective to promote the hydrolysis of cellulose.

3.7.4. 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 catalysts [9]. The effect of the solvent on the hydrolysis of cellulose over RHNH$_3$SO$_4$H was shown in Table 2. The hydrolysis was studied over different solvents, that is, cyclohexanol, cyclohexanone, and 1-butanol as well as DMF. All these solvents contain LiCl. It was observed that the hydrolysis of cellulose over these solvents was increased according the following order:

\[
cyclohexanol \approx DMF > cyclopentanone > 1\text{-butanol.} \quad (1)
\]

The solvent-metal chloride interaction was also studied by using different metal chlorides, that is, LiCl, NaCl, and KCl in DMF. It was observed that the hydrolysis of cellulose...
Figure 5: The TEM images of RHNH$_3$SO$_4$H, at different magnification.

Table 2: The effect of different parameters on the hydrolysis of cellulose with RHNH$_3$SO$_4$H.

| Parameters                           | Variants                        | Glucose yield (mM %) at 6 h | Glucose yield (mM %) at 13 h |
|--------------------------------------|---------------------------------|-----------------------------|------------------------------|
| Variation of cellulose hydrolysis from different sources | Pure cellulose                  | 98                          | 10                           |
|                                      | Cellulose from paper            | 94                          | 11                           |
|                                      | Cellulose from rice husk        | 93                          | 18                           |
| Variation of metal chloride          | LiCl                            | 98                          | 10                           |
|                                      | NaCl                            | 91                          | 9                            |
|                                      | KCl                             | 90                          | 13                           |
| Variation of solvent effects in LiCl| DMF                             | 98                          | 11                           |
|                                      | Cyclohexanol                    | 98                          | 10                           |
|                                      | Cyclopentanone                  | 91                          | 15                           |
|                                      | 1-Butanol                       | 89                          | 18                           |
| Reusability of catalyst with 150 mg  | Fresh catalyst                  | 98                          | 10                           |
|                                      | 1st reuse                       | 93                          | 11                           |
|                                      | 2nd reuse                       | 93                          | 13                           |

The reaction was run over 13 hours at 120°C of hydrolysis temperature and 150 mg of catalyst mass.
over these metal chlorides was increased according to the following order:

\[ \text{LiCl} > \text{NaCl} > \text{KCl} \]  \hspace{1cm} (2)

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 \( \text{Cl}^- \) is highly active as a nucleophilic base and plays a major role by breaking up the inter- and intrahydrogen bonds \[23\]. This could make the hydrolysis of cellulose much easier.

3.7.5. Catalyst Experiments on Cellulose from Different Sources. The effect of \( \text{RHNH}_3\text{SO}_4\text{H} \) on the cellulose extracted from different sources (waste of rice husk and waste office paper) is shown in Table 2. The run was done under the optimum conditions of the catalyst which were 150 mg catalyst mass, reaction temperature of 120°C, and 6 h reaction time. It was observed that the hydrolysis of the extracted cellulose from waste of RH was 93%, while the hydrolysis of cellulose extracted from waste paper was 94%. This clearly indicates that the catalyst was very active for the hydrolysis of cellulose from any sources.

3.7.6. Catalyst Recycle Experiments. Table 2 shows the \( \text{RHNH}_3\text{SO}_4\text{H} \) recycle experiments. After the first reaction was run using the catalyst at 120°C for 13 h, the mixture, including the solid catalyst and the cellulose residue, was then filtered and washed with hot cyclohexanol and then with hot mixture of DMF and \( \text{LiCl} \) (repeated three times), and finally the catalyst was heated at 130°C for 24 h. Next, fresh cellulose and DMF with \( \text{LiCl} \) were added to the catalyst obtained and a second run was conducted using the same procedure. As shown in Table 2, the product yield in the second run was similar to that in the first run, without any loss in the catalytic activity during the first 6 h of the hydrolysis. After the 6 h of the hydrolysis time a decrease in the cellulose hydrolysis was observed due to the hydrolysis of glucose to other products. These results indicated that catalytic performance was not lost in the course of the catalytic runs.

4. Conclusion

APTES was reacted with sodium silicate by following a purely homogenous route to form RHAPrNH\(_2\) which converted to the solid ammonium sulphate-like structure. According to
the BET result the RHNH$_3$SO$_4$H had a 113 m$^2$ g$^{-1}$ specific surface area. The FT-IR clearly showed the presence of $-$SO$_2$ absorption bands at the expected range. The TEM shows that the RHNH$_3$SO$_4$H forms with a rod-like morphology. The diameters of the microrods are in the range of 0.1 $\mu$m to 0.26 $\mu$m. The RHNH$_3$SO$_4$H was used to fully hydrolyze cellulose to other products at 120°C for 13 h. The catalytic activity of the catalyst reaches the 98% of the glucose from cellulose and the selectivity was 100% at 6 h, after the hydrolysis continues to form other products for up to 13 h. The catalyst is simple to prepare and stable during the hydrolysis, and it can be used several times without significant loss of its catalytic activity.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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