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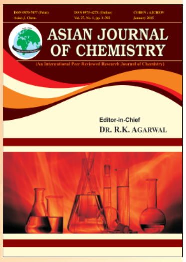

Hydrothermal Conversion of Rice Husk on Solid Acid Catalysts

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Liquefaction of rice husk using hydrothermal treatment with solid catalyst was investigated. Study shows that all solid catalysts tested exhibited high catalytic activities. The solid acid catalysts have higher activity than other catalysts. The catalysts were characterized by FT-IR and NH_3-TPD. The result of FT-IR shows that the Cl^- of catalyst is in the form of ClO_4^-; therefore, ClO_4^--Fe_2O_3-La_2O_3/ZrO_2-SiO_2 can be made into solid super acid catalysts. The result of NH_3-TPD indicates that ClO_4^--Fe_2O_3-La_2O_3/ZrO_2-SiO_2 catalyst has two kinds of surface acidity sites. GC-MS analysis shows that the major conversion products were phenol, 3-methyl-1, 2-cyclopentanedione, 6-methoxy-8-nitro-4-trifluoromethylquinoline and 2-methoxy-phenol. The liquefaction characteristics were found to be influenced by the reaction conditions including temperature, holding time, catalyst dosage and water to rich husk (W/R) ratio.

Keywords: Hydrothermal, Conversion, Rice husk, Solid acid, Catalyst.

INTRODUCTION

The global economy largely depends on the transportation of goods and services and 96 % of the transportation sector which takes 62 % of annual worldwide fuel consumption is basic on fossil fuel[1]. Due to the increasing demand of thermal and electric energy in industry and municipal management, the demand of fossil fuel is drastic diminishing. Excessive exploitation of natural resource also causes degradation of the environment and the decrease of plant-life on the earth[2]. Moreover, the fossil carbon reserve is finite and has limited the growth of industry[3]. Progressive exhaustion of fossil fuels reserves and pressure of reduction greenhouse gas emissions cause high motivation in the search of alternative renewable sources for energy generation and/or as raw materials for chemicals production[4].

Because of the depletion of the world's petroleum reserves and environmental degradation, there is a great demand for alternative sources of petroleum-based fuel, including diesel and gasoline fuels[5]. Biomass can serve as a source for both energy and carbon[6]. Biomass and biological materials from living organisms are considered as carbon-neutral sustainable resources for the bio energy and biomaterial production[7]. Biomass energy, the use of which does not increase the content of atmospheric carbon dioxide, is one of the attractive points for researchers and policy-makers as well as industries in the world[8]. Biomass resources include wood and wood wastes, agriculture crops and their waste byproducts, municipal solid waste, animal waste, waste from food processing and aquatic plants and algae[9]. Moreover, comparing to the combustion of fossil fuels, production and use of energy from biomass has the potential to generate lower greenhouse gas emissions, because of the carbon sequestration by biomass. In this respect, the "Roadmap for Biomass Technologies" has predicted that 20 % of transportation fuel and 25 % of chemicals will be produced[8] from biomass in 2030.

Due to the high moisture content and low heating value, biomass is not suitable to be used in energy production directly and need to be converted into transportable liquid fuel[10]. These conversion processes include fast pyrolysis and high pressure liquefaction, catalytic gas liquefaction, hydrolysis and fermentation and others such as agrochemical fuel extraction and biophotolysis. In these processes thermo-chemical conversion is a commonly method to upgrade biomass. The direct thermo-chemical conversion technologies are classified into two groups: high pressure liquefaction (hydrothermal treatment) and fast pyrolysis[11]. Hydrothermal liquefaction is one of the most effective technologies that biomass can be converted into fuels and chemical products[12].

In hydrothermal liquefaction, catalyst (alkali and/or metal) is often used to increase the yield of desired products and the reaction rate[13]. The research results show that homogenous catalysts are very effective in the liquefaction of biomass[14]. Heterogeneous catalysts for hydrothermal liquefaction also get attention from researchers. Shi *et al*.[15] have studied the effects of metallic oxide catalysts. The bio-crude yield of 23.8 % and 32.5 wt % were obtained without catalyst and with La_2O_3 catalyst, respectively.

Solid acids catalysts combine the advantages of heterogeneous base catalysts and mineral acids. Other advantages peculiar to this class of catalysts include: (1) the catalyst are tunable, selective, easily regenerated and recycled. (2) Corrosion problem is minimized even in the presence of acid species. (3) Applicability in continuous flow process. The rational development of recyclable solid acids catalysts is the major focus of recent advances[1]. In this paper, researchers focus on new catalytic systems of solid catalysts for conversion of biomass. The rice husk conversion under SiO_2-ZrO_2-supported catalysts using hydrothermal treatment was investigated. The catalysts before or after reaction were characterized by FT-IR and NH_3-TPD. The productions of conversion were characterized by GC-MS.

EXPERIMENTAL

Rice husk used for this study was obtained from a local supermarket in Jiangxi province of China. Rice husk was milled and screened and only the fraction less than 60 meshes were used in this research. The samples were dried at 105°C for 24 h before use.

Preparation of SiO_2-ZrO_2 support: SiO_2-ZrO_2 support was prepared as follows: ethanol solution of $ZrO(NO_3)_2$ and ethanol solutions of ethyl silicate were mixed first. Drop water slowly into the mixed solution under stirring. Then, the slurry was stirred continuously for 4 h at room temperature, then aging at 60 °C for 1 day. The sample was then dried using supercritical drying with ethanol in a stainless steel autoclave.

Preparation of catalyst

La_2O_3 /ZrO_2-SiO_2 catalyst: La_2O_3/ZrO_2-SiO_2 catalyst was prepared by impregnation. La_2O_3 was deposited on the ZrO_2-SiO_2 support with aqueous solution of $La(NO_3)_3$. Then the sample was dried at 383 K for 4 h and finally calcined at 773 K for 4 h. This catalyst was called C1.

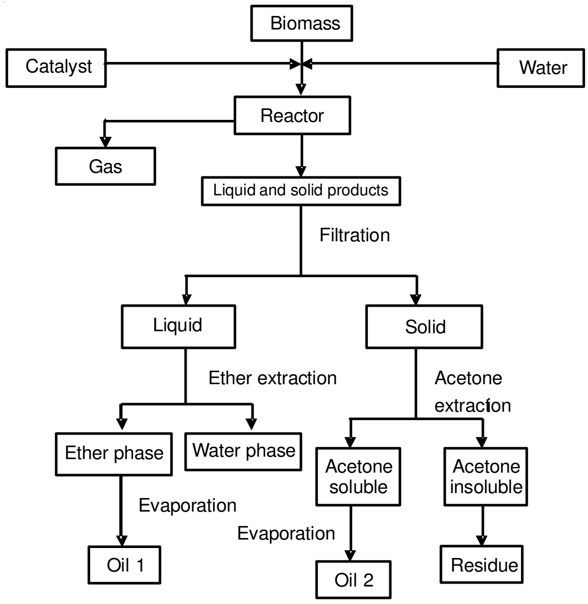
ClO_4^--Fe_2O_3/SiO_2-ZrO_2 catalyst: Aqueous solution of $FeCl_3$ was deposited on the ZrO_2-SiO_2 support by impregnation. The detail of the preparation of catalysts is described as same as the preparation of La_2O_3/ZrO_2-SiO_2 catalyst. This catalyst was called C2.

ClO_4^--Fe_2O_3-La_2O_3/ZrO_2-SiO_2 catalyst: Using same method as above the aqueous solution of $FeCl_3$ was deposited on the La_2O_3/ZrO_2-SiO_2 by impregnation. After drying and calcination we got the ClO_4^--Fe_2O_3-La_2O_3/ZrO_2-SiO_2 catalyst. This catalyst was called C3.

SO_4^{2-}-Fe_2O_3-La_2O_3/SiO_2-ZrO_2 catalyst: Fe_2O_3-La_2O_3/SiO_2-ZrO_2 was impregnated with $(NH_4)_2SO_4$ solution for 5 h. After dry the sample was calcined at 550 °C for 4 h. This catalyst was called C4.

Procedure: The hydrothermal treatments were performed in a stainless steel autoclave with stirring. The reaction temperature was in the range of 200-300 °C. The autoclave contents were heated to desired temperature at a heating rate of 10 °C/min and the final temperature was kept at definite time. Then the autoclave was cooled to room temperature with an electric fan.

The procedures for separation and extraction of reaction products are presented in **Scheme-I**. Solid and liquid products were separated by filtration. During filtration, ion-exchanged water was used for washing solid products. This solution was extracted with diethyl ether. The etheral solution was treated according to the literature[16] and this fraction was called oil 1. Solid products were extracted with acetone in a Soxhlet extraction apparatus. After removal of the acetone under reduced pressure in a rotary evaporator, the remaining fraction was called oil 2.



Scheme-I: Separation procedure

The liquefaction yield was calculated by the following equation[17]:

$$\text{Liquefaction yield} = \left[1 - \frac{\text{Weight of dried residue}}{\text{Weight of starting biomass}}\right] \times 100$$

Characterization of catalysts: The FT-IR spectra of catalysts were recorded at room in a Nicolet 5700 spectrometer in the range 4000-375 cm^{-1}, with a resolution of 4 cm^{-1} (32 scans). The NH_3-TPD characterization of catalysts was carried out in a flow apparatus with helium as carrier gas. At first the sample was flushed with helium at room temperature for 1 h and then heated at 10 °C/min rate in helium up to 100 °C. After a period of 1 h at this temperature, it was further heated at 10 °C/min rate to 750 °C. During this temperature increase, the ammonia desorption of the catalyst was recorded.

Characterization of liquefaction product: The products of liquefaction were analyzed by GC-MS [Agilent-6890N/59731; column: HP-5MS 30 m × 0.25 mm, 0.25 μm]. The peaks were identified by means of NIST02 library.

RESULTS AND DISCUSSION

Effect of catalysts: At first, the effects of catalysts on rice husk conversion were investigated. Rice husk sample was converted in the stainless steel autoclave with different catalysts. The reaction conditions are as follow: the ratio of water to rice husk (W/R) was 30:1, the dosage of catalyst was 4 %, the reaction temperature was 250 ºC and the holding time was 2 h. The results of reactions are displayed in Fig. 1. The results of Fig. 1 revealed that all the solid catalysts used in this test had catalytic activities for rice husk conversation under given reaction conditions. It is obvious that the activities of catalyst are enhanced by added Cl^- or SO_4^{2-}.

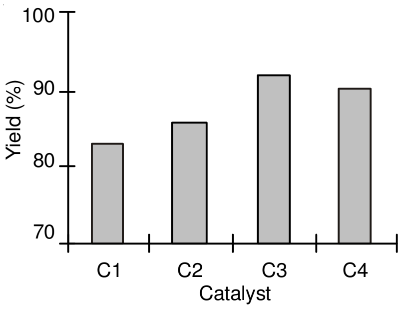


Fig. 1. Effect of catalysts on rice husk conversion

We characterized the fresh and used $ClO_4^--Fe_2O_3-La_2O_3/ZrO_2-SiO_2$ catalysts with FT-IR (Fig. 2), respectively. In Fig. 2 the bands observed as a shoulder at about 1115 and 620 cm^{-1} were assigned to the stretching vibration of ClO_4^-[18,19]. Thus, for the solid catalyst it has been proposed that the Cl^- was in the form of ClO_4^- before and after rice husk conversion reaction. The reasons that latter three catalysts in Fig. 1 had higher catalytic activities than the other one may be the formation of solid super acid after addition of Cl^- or SO_4^{2-}.

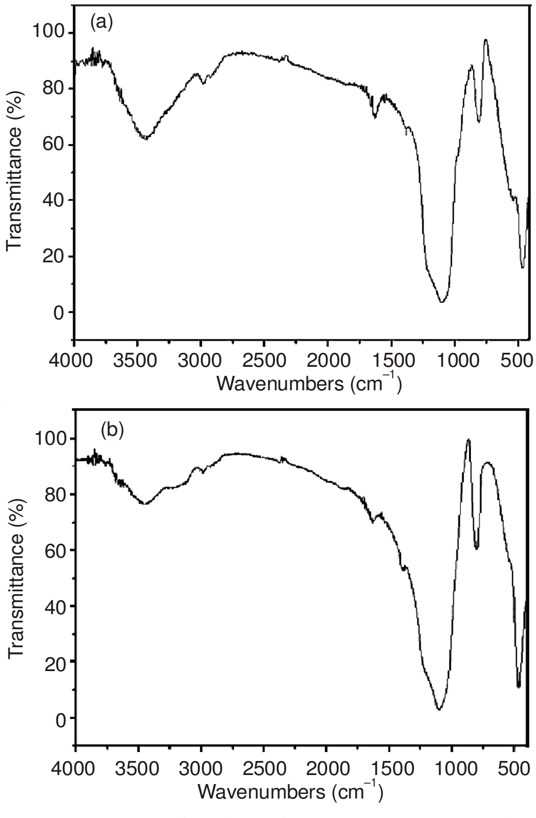


Fig. 2. FT-IR spectrum of catalyst $ClO_4^--Fe_2O_3-La_2O_3/ZrO_2-SiO_2$ before (a) and after (b) reaction

In contrast of $ClO_4^--Fe_2O_3-La_2O_3/ZrO_2-SiO_2$ and $SO_4^{2-}-Fe_2O_3-La_2O_3/SiO_2-ZrO_2$ catalyst, it was obvious that the catalytic activity with addition of ClO_4^- was higher than the addition of SO_4^{2-}.

As shown in Fig. 1, the $ClO_4^--Fe_2O_3-La_2O_3/ZrO_2-SiO_2$ catalyst yielded higher amount of liquefaction products than the $ClO_4^--Fe_2O_3/ZrO_2-SiO_2$ catalyst. This indicated that La_2O_3 was good promoter in this catalyst. The liquefaction yield of rice husk using $ClO_4^--Fe_2O_3-La_2O_3/ZrO_2-SiO_2$ catalyst was the highest in our tests and therefore this catalyst was used in all other tests.

Effect of reaction holding time: The liquefaction of rice husk is shown as a function of reaction holding time in Fig. 3, which demonstrates that the liquefaction increased with increasing holding time up to 2 h. After the maximum value is reached at 2 h, the activity decreased slowly. This is similar to the results reported in the literature[20,21]. As showed in Tables 1and 2, the products of rice husk conversation under our test conditions had multi functional group compounds, such as acid, aldehyde, phenol, ketone and so on. These compounds would be reacted with each other resulting in polymerization with increasing holding time, therefore, the liquefaction yield decreased.

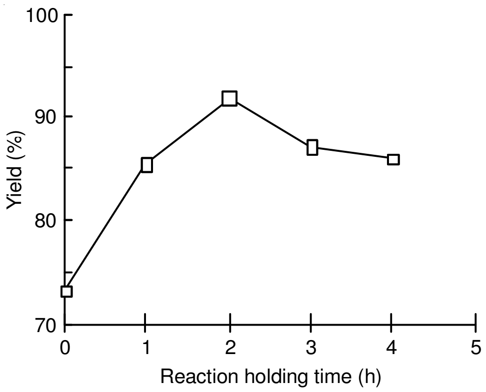


Fig. 3. Effect of reaction holding time on rice husk conversion

Effect of reaction temperature: Temperature is an important parameter for chemical reaction. The effect of reaction temperature on rice husk conversion is showed in Fig. 4. In the temperature range from 200-300 ºC the liquefaction yield increases from 62-100 % with the increasing of temperature. This clearly shows that the effect of reaction temperature on rice husk is large.

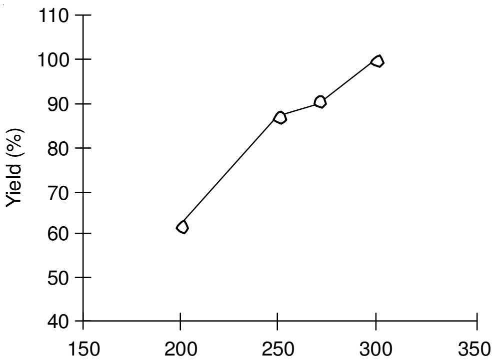


Fig. 4. Effect of reaction temperature on rice husk conversion

Effect of catalyst dosage: Fig. 5 indicates that the catalyst exhibited highest activity at 2 %. The acid catalyst provides active site for biomass conversion as well as may promote polymerization of the conversion products under acid catalysts at high dosage.

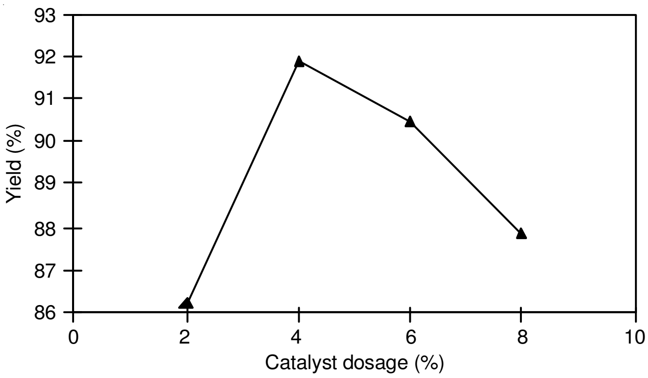


Fig. 5. Effect of catalyst dosage on rice husk conversion

Effect of water to rice husk (W/R) ratio: In this test, W/R was changed from 20-40 while keeping all the other conditions constant. The results are presented in Fig. 6.

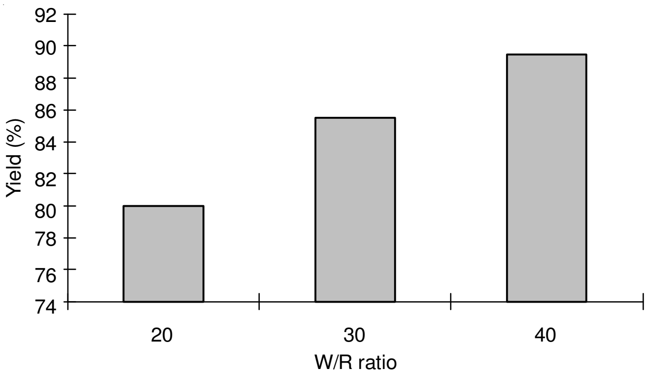


Fig. 6. Effect of W/R ratio on rice husk conversion

It can be seen from Fig. 6 that the liquefaction yield increases with increasing W/R ratio. Catalytic reaction is a surface reaction. The more contact number of catalyst with reactants the higher catalytic activity it is. It is benefit to facilitate contact numbers of catalyst with reactants by increase W/R ratio and therefore increase the liquefaction yield.

TPD: The ammonia thermo-desorption is usually carried out in order to determine the surface acidity of catalysts[22]. The result of NH_3-TPD for ClO_4^--Fe_2O_3-La_2O_3/ZrO_2-SiO_2 catalyst were given in Fig. 7. The NH_3-TPD profile in Fig. 7 shows two peaks at 590 and 720 °C. It indicates that ClO_4^--Fe_2O_3-La_2O_3/ZrO_2-SiO_2 had two kinds of surface acidity sites. According to the literature[23], one of the surface acidity sites has high activity and is deactivated easily; the other one has a little lower activity, but it is more stable. The latter is beneficial to the catalyst life.

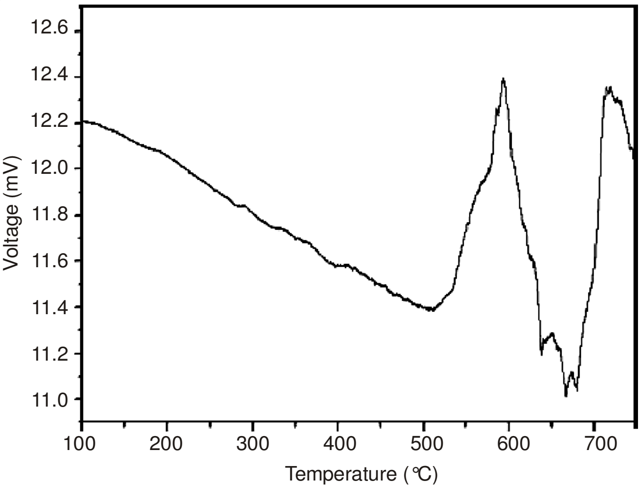


Fig. 7. NH_3-TPD profile of ClO_4^--Fe_2O_3-La_2O_3/ZrO_2-SiO_2

GC-MS: The route of biomass to bio fuel involves cleavage of C-C and/or C-O and/or OH bond, molecular rearrangement reaction, dehydration reaction and so on. Different catalysts have different intrinsic properties, activate different chemical bands and result in different products in biomass conversion[24-28]. As shown in Tables 1 and 2, the major products of rice husk under ClO_4^--Fe_2O_3-La_2O_3/ZrO_2-SiO_2 catalyst in hydrothermal reaction are phenol, 3-methyl-1,2-cyclopentanedione, 6-methoxy-8-nitro-4-trifluoromethyl quinoline and 2-methoxyphenol.

TABLE-1
IDENTIFICATION OF COMPOUNDS IN OIL-1 BY GC-MS ANALYSIS

No.	R.T. (min)	Area (%)	Name of compound
1	3.23	0.74	1,4-Pentadiene, 2,3,3-trimethyl-
2	3.44	2.23	2-Butenoic acid, 4-oxo
3	3.48	0.60	1,1-Dodecanediol, diacetate
4	3.59	2.39	2-Furancarboxaldehyde, 5-methyl-
5	3.93	10.77	Phenol
6	4.35	28.09	1,2-Cyclopentanedione, 3-methyl-
7	5.16	22.36	Phenol, 2-methoxy-
8	5.81	2.78	Cyclopent-2-ene-1-one, 2,3,4-trimethyl-
9	6.04	1.07	12-Oxabicyclo[9.1.0]dodeca-3,7-diene, 1,5,5,8-tetramethyl-, [1R-(1R*,3E,7E,11R*)]-
10	6.11	2.14	Cyclohexane, 1R-acetamido-4cis-acetoxy-2,3cis-epoxy-
11	8.65	1.69	Phenol, 4-ethyl-2-methoxy-
12	9.03	1.61	Pyrazine, 2-methoxy-3-(1-methylethyl)-
13	9.27	1.18	2-Furancarboxaldehyde, 5-(hydroxymethyl)-
14	10.59	4.31	2,6-Dimethoxy-phenol
15	12.02	7.03	Vanillin
16	18.19	1.58	2-Hydroxyfluorene
17	21.25	2.85	1,2-Benzenedicarboxylic acid, butyl cyclohexyl ester

TABLE-2
IDENTIFICATION OF COMPOUNDS IN OIL-2 BY GC-MS ANALYSIS

No.	R.T. (min)	Area (%)	Name of compound
1	4.06	61.52	Phenol
2	6.85	0.73	3-Hexanol
3	21.21	1.13	9-[3-Hydroxypropyl]hypoxanthine
4	26.13	0.64	9*H*-Xanthen-9-one, 1-hydroxy-3,5,6-trimethoxy-
5	32.99	5.35	1,2-Benzenedicarboxylic acid, bis(2-ethylbutyl)ester
6	35.62	27.74	6-Methoxy-8-nitro-4-trifluoromethylquinoline
7	39.76	1.00	Benzoic acid, 2-[(trimethylsilyl)amino]-3-[(trimethylsilyl)oxy]-, methyl ester

Conclusion

Under the reaction condition used in this study, rice husk can be liquified using hydrothermal treatments with the help of the solid catalysts. The solid super acid catalyst that contains ClO_4^- has higher activity than others. The reaction conditions, such as temperature, holding time, catalyst dosage and water to rich husk (W/R) ratio, have impact on the liquefaction of rice husk. The ClO_4^--Fe_2O_3-La_2O_3/ZrO_2-SiO_2 catalyst has two kinds of surface acidity sites. With this catalyst, the major products of liquefaction are phenol, 3-methyl-1,2-cyclopentanedione, 6-methoxy-8-nitro-4-trifluoromethyl quinoline and 2-methoxy-phenol.

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