Synthesis of advanced materials for bio-oil production from rice straw by pyrolysis

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Abstract
Bio-oil from rice straw is produced by pyrolysis with and without solid acid catalysts. Solid acid catalysts used in rice straw pyrolysis synthesis were the diatomite acidified by an ‘atomic implantation method’ and nano-sized porous Al-SBA1⁴.¹⁵. Catalysts were characterized by a field emission-scanning electron microscope (FE-SEM), transmission electron microscopy (TEM), x-ray diffraction (XRD), infrared spectroscopy (IR), N₂ adsorption/desorption, differential thermal analysis/thermogravimetric analysis (DTA/TGA) and NH₃ temperature programmed desorption (NH₃-TPD). The obtained results revealed that a similar bio-oil yield (liquid product) of 44–48% can be reached by pyrolysis in the presence of solid acid catalysts at 450 °C compared to that of pyrolysis without catalyst at 550 °C. Moreover, a low yield of gas product was observed. These results show significant potential applications of solid acid catalysts for the improvement of bio-oil yield in the pyrolysis of rice straw.

Keywords: rice straw, bio-oil, catalytic pyrolysis, nanostructured catalyst, fixed bed reactor

Classification number: 5.18

1. Introduction

Biomass is an organic material that stores sunlight and transforms it into chemical energy. It is one of the most promising renewable energy sources and widely used in third world countries [1, 2]. Biomass contributes to about 14% of the world’s primary energy supply today. In contrast to other renewable sources of energy (e.g. wind and solar) that give heat and power, biomass represents the only source of liquid, solid and gaseous fuels. The advantages of biomass over conventional fossil fuel are (i) their low sulfur and nitrogen contents and (ii) no net emissions of CO₂ into the atmosphere when biomass production balances consumption. Using biomass as a renewable energy source is an effective way to produce energy while reducing the greenhouse effect [3].

Rice straw is a biomass that is abundant in lignocellulose products, but only a minor portion of the agricultural residue is reserved as animal feed, household fuel or raw materials for the paper industry. Huge quantities of the remaining rice straw are not used as industrial raw materials and are burnt in the fields, causing significant environmental problems. For an agricultural country such as Vietnam, rice straw makes up about 66% of the total agricultural waste. Annually, Vietnam produces about 36–38 million tons of rice and therefore about 65–69 million tons of rice straw [4–6]. Therefore, rice straw can be recognized as a potential source of renewable energy based on benefits of both energy recovery and environmental protection. Lignocellulose is the main component of rice straw, which is a compact structure of cellulose (28–36%) and hemicellulose (23–28%) in close association with lignin (12–16%) [7].

Generally, biomass conversion processes can be divided into two main categories: biological (fermentation...
and anaerobic digestion) and thermochemical processes (combustion, gasification and pyrolysis). Among the various thermochemical conversion processes, pyrolysis is considered to be an emerging technology for converting biomass into fuel gases, liquids and solids, all of which can be used as an alternative fuel oil or chemical feedstock [2, 8–11]. In addition, pyrolysis is attractive because solid biomass and waste, which are difficult and costly to manage, can be readily converted to liquid products, bio-oils, that have many advantages in transport, storage, handling, retrofitting, combustion and flexibility in production and marketing [8, 10]. Biomass is combusted in the absence of oxygen, or is partially combusted in a limited oxygen supply, to produce three products: oil-like liquid (named bio-oil or bio-liquid), a gas mixture containing mainly carbon oxides, some methane and higher gaseous hydrocarbon in minor quantities, and carbon-rich solid residue [1]. Among them, bio-oil is the most interesting product, which is a very complex mixture of organic compounds, and its elemental composition approximates that of feedstock-biomass. This bio-oil can be utilized as a source for valuable chemicals such as phenols, after applying separation methods. It is also considered as a potential biofuel since it can be easily transported, burned directly in thermal power stations or in gas turbines, utilized as feedstock in a conventional petroleum refinery and upgraded to obtain valuable light hydrocarbon fuels [12, 13]. However, the high amount of water and oxygenate in the liquid products reduces the calorific value of the bio-oil and significantly changes its combustion characteristics. The presence of organic compounds with undesirable properties (organic acid, carbon) and of polycyclic aromatic hydrocarbons limits its potential for direct use in engines or turbines. In order to improve the quality of the bio-oil produced, as well as the efficiency of the processes converting biomass to fuels and chemicals, various catalysts have been introduced in pyrolysis. Zeolitic catalysts such as zeolite Y and zeolite sieve of molecular porosity (ZSM-5) are used in biomass conversion and upgrading processes [14, 15]. However, owing to the small pore size, applications of microporous zeolite materials are restricted to relatively large molecules.

The research and design of a tailored catalyst for the pyrolysis process and upgrading of the oil have gained the attention of many researchers. Mesoporous materials containing aluminum, such as Al-MCM-41, have potential in moderate acid-catalyzed reactions for large molecules [16–20]. Recently, studies on the activity of Al-MCM-41, which is modified by transition metals in the in-situ upgrading of biomass pyrolysis vapors, showed that MCM-41 has a pronounced effect on selectivity towards specific organic products [18–20]. However, it is inadequate with respect to thermal and hydrothermal stabilities. More recently, MSU [5] mesoporous aluminosilicates synthesized from zeolite seeds has been used as a catalyst for the in-situ upgrading of biomass pyrolysis vapors. It showed that MSU catalysts exhibit higher hydrothermal stability than that of Al-MCM-41 [21]. However, MSU materials possess strong acid sites, which are very selective towards polycyclic aromatic hydrocarbons and heavy fractions. A novel mesoporous silica SBA-15 material has been prepared using tri-block copolymer as a template [22]. Due to its larger pores and thicker walls, SBA-15 has much higher hydrothermal stability than that of MCM-41, but moderate acidity.

A combination of the large pore dimensions of mesoporous Al-SBA-15 materials with their mild acidity and high hydrothermal stability would be highly advantageous in producing good catalytic materials [23]. In the present paper the influence of the chemical composition of rice straw, pyrolysis temperature, particle size of rice straw, effect of catalyst, etc. on bio-oil yield have been taken in consideration and investigated.

2. Experimental

2.1. Rice straw composition

Rice straw samples used in this study were taken from a farm in Northern Vietnam. These samples were dried in the sun to remove most of the moisture, washed in water to separate physical impurities such as sand and combusted fractions, then dried further at 100 °C for 24 h. Finally, the samples were cut into small fractions with particle diameters of 0.3–0.5 mm.

A complete compositional analysis was performed on the rice straw samples that were used as feedstock for bio-oil production. This analysis included chemical composition as well as elemental and proximate analysis. Chemical composition was determined using the TAPPI® standard method. Elemental (ultimate) analysis was performed on a Flash EA 1112 element analyzer. Proximate analysis was carried out for moisture, combustible content and ash. The moisture was obtained from the difference between the original mass and the mass after drying for 2 h at 100 ± 5 °C. The combustible content was measured from the difference between the mass dried for 2 h at 100 ± 5 °C and the final mass burned for 3 h at 800 ± 5 °C. The final mass was the ash. IR spectra of rice straw were recorded from disk-membraned samples (1%) in KBr pellets by an Impact–410 IR spectra photometer. Thermal analysis of the rice straw was carried out using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) on a simultaneous thermal analyzer (Labsys SETARAM). Each sample was heated from room temperature to 600 °C at a heating rate of 15 °C min⁻¹.

The composition of rice straw is listed in table 1. The combustible matter of rice straw was 80.16 wt%, supporting the use of rice straw as an energy source. The content of C and O was 53.94 and 39.2%, respectively. It was obvious that sulfur and nitrogen were rare. The obtained results showed that rice straw is a potential resources fuel by pyrolysis.

2.2. Preparation and characterization of catalysts

Mesoporous Al-SBA-15 materials with Si/Al molar ratios of 20 were prepared using tetraethyl orthosilicate (TEOS) as the silicic source, aluminum isopropanoxide ([CH₃₂CHO])₃Al as the aluminum source and triblock co-polymer HO(CH₂(CH₃)O)₂₀(CH₂CH₂(CH₃)O)₇₀(CH₂CH₂O)₂₀H (Pluronic P123)

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4 MCM: Mobil Composition of Matter.
5 MSU: Michigan State University.
6 TAPPI: Technical Association of the Pulp and Paper Industry.
Table 1. Characteristics of the rice straw.

| Proximate analysis (wt%) | Component analysis (wt%) | Elemental analysis (wt%) \(^a\) |
|--------------------------|--------------------------|-------------------------------|
| Moisture | 7.08 | Cellulose | 60.62 | Carbon | 53.94 |
| Combustible | 80.16 | Hemicellulose | 25.64 | Hydrogen | 5.84 |
| Ash | 12.76 | Lignin | 15.74 | Nitrogen | 1.02 |
| | | | | Oxygen \(^b\) | 39.20 |
| | | | | Sulfur | 0.02 |

\(^a\)Dry-ash-free basic.

\(^b\)By difference.

as the structure directing agent. The Al-SBA-15 mesoporous materials were synthesized as follows [20]: 9 ml of TEOS and a calculated amount of aluminum isopropoxide taken to obtain a given Si/Al ratio (20) were added to 10 ml of aqueous solution of HCl at pH = 1.5. This solution was stirred for 3 h then added to a second solution containing 4 g of P123 in 150 ml of aqueous solution of HCl at pH = 1.5. The obtained mixture was stirred vigorously for 24 h and subsequently transferred to a teflon-lined autoclave for additional hydrothermal treatment at 73 K for 48 h under static conditions. The solid product was filtered, washed, dried at 373 K and then calcined at 823 K for 6 h to remove the template.

Low-angle x-ray diffraction (XRD) patterns were obtained on a Bruker D8 Advance instrument using CuKα radiation with generator operated at 40 kV and 40 mA. The patterns were recorded at room temperature (298 K). The scanning angle \(2\theta\) was 0.5–15°, the scanning step was 0.03°, and the step time was 0.3 s. Nitrogen adsorption/desorption isotherms at 77 K were established using an Omnisorp-100 apparatus. The specific surface area, \(S_{BET}\), was determined from the Brunauer–Emmitt–Teller (BET) equation. The mesopore size distribution was determined from the desorption branch of the \(N_2\) adsorption/desorption isotherms using the Barrett–Joyner–Halenda (BJH) formula. Transmission electron microscopy (TEM) images were obtained on a Jeol-JEM 1010. Scanning electron microscopy (SEM) images were obtained on a JSM-5300 LV. Ammonia temperature programmed desorption (\(NH_3\)-TPD) measurements were carried out on an Autochem II 2920 apparatus in a flow reactor. Samples were activated at 700°C for 1 h in a helium flow. Subsequently, ammonia was introduced by a helium stream containing 10% (vol) ammonia at 100°C. The physically adsorbed \(NH_3\) was removed by purging with the \(He\) flow at 100°C until the baseline was flat. The reactor temperature was then ramped at a rate of 10°C min\(^{-1}\).

2.3. Pyrolysis experiments

Pyrolysis experiments were performed in a 316 stainless steel fixed-bed tubular reactor (3.67 cm internal diameter and 60 cm length). It is externally heated by an electrical furnace and the temperature measured by a thermocouple inside the bed. For all experiments, the sample (~5 g mass, in each experiment) was placed on top of the fixed bed and 2 g of Al-SBA-15 catalyst was placed inside the reactor. The sweep gas from a nitrogen cylinder was dried and purified by a molecular sieve tube. The experimental conditions in the pyrolysis system were as follows: pyrolysis temperature of 400–600°C, heating rate of 20°C min\(^{-1}\), sweep gas flow rate of 160 ml min\(^{-1}\).

Figure 1. XRD pattern of the Al-SBA-15 sample.

The solid product (char) was removed and weighed after the experiment. The liquid phase was collected in a cold trap maintained at about 0°C using salty ice as the cooling agent. The liquid phase consisted of an aqueous and oil phase, separated by dichloromethane and weighed. The yield of the resulting products was thus calculated based on the mass of the sample feed. The gas yield was determined by the difference of this yield and that of the liquid phase.

3. Results and discussion

3.1. Characterization of Al-SBA-15 catalytic materials

Figure 1 shows the XRD patterns of Al-SBA-15 samples with Si/Ti molar ratios of 20. The patterns exhibited three diffraction peaks corresponding to the \((100)\), \((110)\) and \((200)\) reflections associated with \(P6mm\) hexagonal symmetry. The peak intensities of \(Al\) containing SBA-15 samples were similar to those of silicious SBA-15 [22]. This indicated the highly ordered mesostructure of these samples. These results proved that the introduction of Al into the SBA-15 framework by direct synthesis still maintained mesostructured ordering.

\(N_2\) adsorption–desorption isotherms of the calcined Al-SBA-15 sample are presented in figure 2(a). They exhibit isotherms of type IV of the IUPAC classification featuring a pronounced step due to capillary condensation of \(N_2\) in the primary mesopores. A steep increase and a H1-type hysteresis loop occur in the isotherms due to the capillary condensation and desorption of \(N_2\), which strongly suggest the presence of large mesopores in these samples. The pore size distribution of the Al-SBA-15 sample (figure 2(b)) exhibits a narrow distribution of nanopores, with average pore diameter of 102 Å.
The total specific surface area calculated by the BET method is 765 m$^2$ g$^{-1}$. The textural characteristics of the Al-SBA-15 sample are given in table 2.

Table 2. Textural characteristics of the functionalized Al-SBA-15 sample.

| Sample    | $S_{BET}$ (m$^2$ g$^{-1}$) | $V_{pore}$ (cm$^3$ g$^{-1}$) | $D_{pore}$ (Å) |
|-----------|-----------------------------|------------------------------|----------------|
| Al-SBA-15 | 765                         | 0.84                         | 102            |

TEM images of Al-SBA-15 (figure 3) show well ordered hexagonal arrays of 1D mesoporous channels and confirm that the Al-SBA-15 samples have a 2D $P6mm$ hexagonal structure. This result is in agreement with the XRD patterns and the $N_2$ adsorption measurements. The ordered mesostructure of the parent SBA-15 remains unaffected by the incorporation of Al. SEM images of Al-SBA-15 are given in figure 4, showing particles with a relatively uniform size of $\sim$200 nm.

The NH$_3$-TPD profiles of Al-SBA-15 (not shown here) give two typical peaks at about 175–185°C and about 350–360°C, which correspond to weak and strong acidic sites, respectively. However, the peak area at about 175–185°C is larger than that at about 350–360°C. This indicated that Al-SBA-15 is a catalyst with mild acidity.

3.1.1. Infrared spectroscopy. Figure 5 shows IR-spectra of the rice straw sample. An intensive band at 1646 cm$^{-1}$ is assigned to H–O–H bonding of absorbed water. A strong band at 3443 cm$^{-1}$ originates from OH stretching. A sharp and strong band at 1049 cm$^{-1}$ is attributed to C–O stretching in cellulose, hemicellulose and lignin, or C–O–C stretching in cellulose and hemicellulose [14]. The small absorbances at 1520, 1447 and 1335 cm$^{-1}$ correspond to the aromatic skeletal vibrations and ring breathing with C–O stretching in lignin [15]. A small sharp band at 903 cm$^{-1}$ arises from $\beta$-glucosilic linkages between the sugar units in cellulose and hemicellulose [15]. These results are in agreement with the characteristics of the rice straw as mentioned above.

3.1.2. Thermal analysis (TGA and DSC). Figure 6 illustrates the thermograms of rice straw. The TGA curves give an initial decrease at temperatures below 100°C due to the loss of moisture (7.7%).

After that, the rice straw starts to decompose at about 210°C. At 76% weight loss, decomposition temperature occurs at 315°C. DSC thermograms of rice straw give a big exothermic peak at 315°C, which is attributed to the decompositions of hemicellulose and cellulose. Figure 6 also
shows that decomposition residue remains, even at 700 °C. The residue seems to be composed mainly of the lignin portion of the rice straw. The DSC curves show that the maximum decomposition rate occurs in a temperature range of 200–400 °C. Therefore, we chose 400 °C as the minimum reaction temperature and 600 °C as the maximum reaction temperature in considering the energy consumption.

3.1.3. Ammonia temperature programmed desorption (NH$_3$–TPD). Figure 7 shows the NH$_3$-TPD profiles of Al-SBA-15, acidified diatomite, zeolite HY and zeolite HZSM-5. In the NH$_3$-TPD profiles of the samples there are two main peaks: a low temperature peak at 150–170 °C and a high peak at 350–450 °C, corresponding to the low and high acid strength sites of the solid acid catalysts.

Among the investigated samples, Al-SBA-15 showed the lowest acidity. The order of acid strength is as follows: Al-SBA-15 < acidified diatomite < zeolite HY < zeolite HZSM-5.

3.2. Pyrolysis of rice straw

It is well documented that pyrolysis of bio-mass can be performed in two ways: thermal pyrolysis (without catalysts) and pyrolysis with catalysts (catalytic cracking). Thermal pyrolysis is often carried out at high temperatures (500–700 °C) whereas pyrolysis with catalysts is performed at lower temperature (400–550 °C). We have chosen an intermediate temperature of 550 °C to investigate pyrolysis of rice straw. Figure 8 plots the product yield distribution of pyrolysis without catalyst and with different solid acid
catalysts. In comparison to pyrolysis without catalysts, pyrolysis with solid acid catalysts exhibited a higher gas product yield and lower liquid product yield. This can be explained by the fact that at a high enough temperature of 550 °C, a solid acid catalyst showed the high cracking activity of rice straw, favouring the formation of gas product yield and consequently reducing the liquid product yield (bio-oil, the desirable product). Thus, with increasing acidity which correlated to catalytic cracking activity, the liquid product yield decreased and gas product yield increased in the same order as indicated by acidity characterization (NH$_3$-TPD). Among solid acid catalysts, the Al-SBA-15 catalyst with lowest acidity exhibited the highest liquid product yield and lowest gas product yield. To improve the performance of the Al-SBA-15 catalyst, we performed pyrolysis of rice straw at a lower temperature of 450 °C. The distribution of the solid, gas and liquid yield is given in Table 3. As expected, a higher liquid product yield and lower gas product yield were observed. This result revealed the high efficiency of the nanoporous Al-SBA-15 catalyst as indicated by the fact that the same liquid product yield could be obtained but at a much lower pyrolysis temperature (100 °C), saving energy consumption.

4. Conclusions

Bio-oil from rice straw is produced by pyrolysis with and without solid acid catalysts. The solid acid catalysts used in the rice straw pyrolysis were diatomite acidified by an ‘atomic implantation method’ and nano-sized porous Al-SBA-15, as well as strongly acidic zeolite HY and HZSM-5.

Catalysts were characterized by FE-SEM, TEM, XRD, IR, N$_2$ adsorption/desorption, DTA/TGA and NH$_3$-TPD.

The obtained results revealed that a similar bio-oil yield (liquid product) of 44–48% can be reached by pyrolysis in the presence of solid acid catalysts at 450 °C compared to that of pyrolysis without catalysts at 550 °C. This result revealed the significant application potential of nanoporous Al-SBA-15 catalyst, as indicated by the fact that the same liquid product yield could be obtained but at a much lower pyrolysis temperature (100 °C), saving energy consumption.

**Table 3. Product yield from pyrolysis without and with catalyst at 450 and 550 °C.**

| Pyrolysis | Solid (wt%) | Gas (wt%) | Liquid (wt%) | (total liquid product) |
|----------|-------------|-----------|--------------|------------------------|
| Without catalyst at 550 °C | 29.7 | 22.0 | 48.3 |
| With Al-SBA-15 catalyst at 550 °C | 29.3 | 26.2 | 44.5 |
| With Al-SBA-15 catalyst at 450 °C | 30.0 | 21.5 | 48.5 |

**References**

[1] Demirbas A H and Arin G 2002 Energy Sources 24 471
[2] Demirbas A H 2007 Energy. Convers. Manage. 48 2386
[3] Pütün A E, Apaydin E and Pütün E 2004 Energy 29 2171
[4] Lindula N W A, Mithulananthan N, Ongsakul X, Widjaya C and Henson R 2007 Renew. Energy. 32 1441
[5] Truong N H 2005 Current status of biomass utilization in Vietnam Biomass-Asia Workshop (Tokyo-Tsukuba, Japan, 19–21 January 2005) p 19
[6] Tran Huu Thuc 2006 General statistic office Statistical Yearbook of Vietnam (Vietnam: Statistical Publishing House)
[7] Sun R C, Tonkinson J and Mao F C 2001 J. Appl. Polym. Sci. 79 719
[8] Bridgenater A V and Grassi G 1991 A Review of Biomass Pyrolysis and Pyrolysis Technologies (London: Elsevier Applied Science)
[9] Probststein R F and Hicks R E 1982 Synthetic Fuels (New York: McGraw-Hill)
[10] Encina J M, Gonzalez J F and Gonzalez J 2000 Fuel Process. Tech. 63 209
[11] McKendry P 2002 Bioresource Technol. 83 47
[12] Islam M N and Beg M R A 2004 Bioresource Technol. 92 181
[13] Huber G W and Dumesic J A 2006 Catal. Today 111 119
[14] Williams P T and Ngrandan N 2000 Energy 25 493
[15] Sulman E M et al 2007 Chem. Eng. J. 134 162
[16] Liu Y and Pinnavaia T J 2002 J. Mater. Chem. 122 3179
[17] Liu Y and Pinnavaia T J 2004 J. Mater. Chem. 14 3416
[18] Adam J, Antonakou E, Lappas A, Stocker M, Nilsen M H, Bouzga A, Hustad J E and Oye G 2006 Micropor. Mesopor. Mater. 96 93
[19] Iliopoulou E F, Antonakou E V, Karakoulia S A, Vasalos I A, Lappas A A and Triantafillidis K S 2007 Chem. Eng. J. 134 51
[20] Antonakou E, Lappas A, Nilsen M H, Bouzga A and Stocker M 2006 Fuel 85 2202
[21] Triantafillidis K S, Iliopoulou E F, Antonakou E V, Lappas A A, Wang H and Pinnavaia T J 2007 Micropor. Mesopor. Mater. 99 132
[22] Zhao D, Feng J, Melosh Q N, Fredrickson G H, Chmelka B F and Stucky G D 1998 Science 279 548
[23] Yue Y, Gedeon A, Bonardet J L, Melosh N, D’Espinoise J B and Fraitssard J 1999 Chem. Commun. 1967