



Catalytic Pyrolysis of Soybean Oil in Presence of Al-MCM-41 Type Catalysts

LONGCHAO GAO, FENGWEN YU*, WEIJIN WANG, GUODONG ZHANG and JIANBING JI

College of Chemical Engineering and Materials Science, Zhejiang University of Technology, Zhejiang Province Key Laboratory of Biofuel, Hangzhou 310032, P.R. China

*Corresponding author: Tel/Fax: +86 571 88320598; E-mail: yufw@zjut.edu.cn

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The catalysts Al-MCM-41 with different Si/Al ratios (Si/Al = 0, 20, 40, 60, 80, 100) were synthesized hydrothermally, the catalytic activity of the catalysts was studied from the pyrolysis of soybean oil in terms of the yield and composition of the pyrolysis products. The pyrolytic oil was examined by gas chromatograph-mass spectrometry and elemental analysis. Some fuel properties of the bio-fuel were also studied according to China GB methods. The results showed that the bio-fuel obtained from the soybean oil pyrolysis in the presence of Al-MCM-41(80) catalyst has a good agreement with the specification in China.

Keywords: Soybean oil, Catalytic, Pyrolysis, Al-MCM-41, Bio-fuel.

INTRODUCTION

The production of bio-fuels has been studied extensively owing to the limited fossil fuels and increasing energy consumptions. Bio-fuels are liquid or gaseous fuels for the transport sector that are predominantly produced from biomass. Bio-fuels can be produced from a variety of bio-feedstocks. Vegetable oils are becoming a promising alternative to bio-fuel because they are renewable in nature and can be produced locally through environmentally friendly ways¹. Vegetable oils can be converted to useful products by blending², micro-emulsion, transesterification³ and pyrolysis methods⁴.

Pyrolysis is advantageous for its lower processing costs, compatibility with infrastructure, engines and fuel standards and feedstock flexibility. The potential for direct substitution of the pyrolytic bio-oil for petroleum and chemical feedstock may be limited due to the high viscosity, high oxygen content and especially the thermal instability of bio-oil². Improved results were obtained with catalytic pyrolysis.

Various catalysts have been used in the process. The mesoporous materials are known for their ability to crack compounds of high molecular weight, MCM-41 is found to be more favorable for the catalytic pyrolysis of vegetable oil because of its larger pore size which is much closer to the molecule size of the hydrocarbon fuels. However, the nature of MCM-41 with weak acid intensity, poor ion-exchange ability and hydrothermal stability, has limited their further application in the cracking process⁵. The incorporation of Al in the silica framework has been implemented in order to

increase the acidity and catalytic activity of the mesoporous silica molecular sieves. The thermal and hydrothermal stability as well as selectivity towards organic liquid products has been enhanced⁶.

In the present study, the mesoporous aluminosilicate Al-MCM-41 materials (Si/Al = 0, 20, 40, 60, 80, 100) were tested as catalysts for the catalytic pyrolysis of soybean oil in comparison to a siliceous MCM-41 sample and non-catalytic pyrolysis. All the pyrolysis experiments were studied in terms of the yield of the bio-fuel as well as the composition of the products. In addition, some physico-chemical properties of the bio-fuel were also reported in this research.

EXPERIMENTAL

Soybean oil was chosen as the raw material in the pyrolysis experiment since it is an abundant source of triglyceride. The oil was obtained from commercial sources without further purification. The fatty acid composition was: palmitic acid (12.5 %); stearic acid (2.9 %); oleic acid (34.8 %); linoleic acid (49.2 %) and others (0.6 %). The soybean oil contains 84 % unsaturated and 16 % saturated fatty acids. To determine the C, H and O contents of the starting material, an elemental analysis was performed on a Vario MACRO cube Elemental Analyzer. It principally consists of 76 wt % C, 11 wt % H and 13 wt % O.

Catalysts: The catalysts Al-MCM-41 (Si/Al = 0, 20, 40, 60, 80, 100) were prepared according to the method reported in the literature⁷. The catalysts were synthesized according to the molar ratios: SiO₂:Al₂O₃ = 0, 20, 40, 60, 80, 100; SiO₂:

CTAB = 0.2; SiO₂:H₂O = 140. Prior to experiment, all the catalysts were pelleted, crushed and sieved to give the particle size of 0.28-1.00 mm. The hexagonal structure of the catalysts was confirmed by X-ray diffraction. It was recorded by a PANalytical powder diffractometer using CuK_α radiation (40 kV, 40 mA) in the range of 0.5-10°.

Experiment procedure: Fig. 1 shows the simplified diagram of the continuous system used in this study for the pyrolysis of soybean oil. The pyrolysis experiments were performed in a stainless steel (#316) tubular reactor with a length of 60 cm and an internal diameter of 10 mm. Prior to experiment, the reactor was filled with nitrogen to remove any oxygen. Then it was heated by an electric furnace with the temperature been detected by a thermocouple. Once the temperature inside has reached a steady state, the soybean oil was injected into the reactor through a peristaltic pump drop by drop. The soybean oil was pyrolyzed and vaporized in the reactor. Then, the vapour passed through the catalyst bed resulting in a catalytic reaction. Subsequently, the vapour entered into a cooling system. Two phases were obtained in the condenser, the aqueous and the organic. The aqueous fraction was separated by a syringe and the organic was collected for further analysis. The residue in the reactor was weighed to give the coke yield. The quality of gas fraction was calculated by the difference of mass balance.

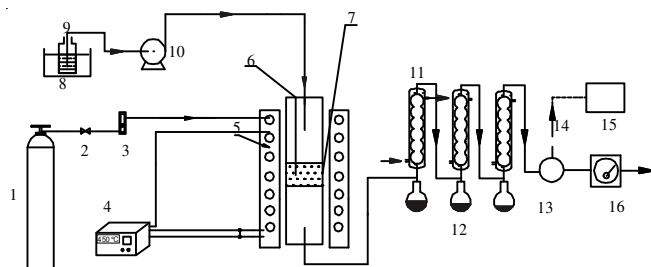


Fig. 1. Schematic diagram of the pyrolysis unit. 1. Nitrogen cylinder; 2. Valve; 3. Flow meter; 4. Temperature controller; 5. Furnace; 6. Thermocouple; 7. Catalyst bed; 8. Preheater; 9. Oil tank; 10. Oil pump; 11. Condenser; 12. Liquid collector; 13. Surge flask; 14. Sampler; 15. Gas chromatograph; 16. Wet type flow meter

Product analysis: The composition of the purified product was determined by the gas chromatograph-mass spectrometry (GC7890A-MS5975C). Samples were injected with a split ratio of 20:1 at 280 °C. A capillary column HP-5 (30 m × 0.25 mm × 0.25 μm) was used, the temperature started at 50 °C (5 min), increased with the gradient of 3 °C min⁻¹ up to 280 °C (5 min). All the peaks were determined with help of NIST library.

The carbon and hydrogen contents of the products were determined on a vario MACRO cube Elemental Analyzer and the oxygen content was given by mass balance.

The initial liquid product obtained from the pyrolysis process was normally dark in colour because of some tar component in it. Considering this, the liquid products first were submitted to a simple vacuum (100 Pa) distillation system to obtain purified products which divided into three categories according to the distillation temperature of fossil fuel: (a) green gasoline (distillation temperature < 50 °C); (b) green diesel (50 < distillation temperature < 150 °C) and (c) tar (distillation

temperature > 150 °C). The sum of green gasoline and green diesel was defined as bio-fuel in this work.

In order to study the potential use of the bio-fuel, some fuel properties were carried out by standardized procedures: Density according to GB/T19147-2003, viscosity according to GB/T265-1988 on a viscosity determination device; Heating value according to GB/T384 on an oxygen bomb calorimeter.

RESULTS AND DISCUSSION

Characterization of the catalysts: The XRD patterns of MCM-41 and Al-MCM-41 with different Si/Al ratios were studied by low angle X-ray powder diffractions.

Fig. 2 showed the XRD pattern of MCM-41 with strongest intensive peaks, it exhibited a strong peak in the 2θ range 1.8-2.2 due to 100 plane reflection lines and two small weak peaks in the 2θ range 3.5-4.2 due to 110 and 200 plane reflections. All these indicated the formation of a well ordered mesoporous material and these peaks are generally indexed according to the hexagonal regularity of MCM-41. Besides, the appearance of the above peaks in Al-MCM-41 with different Si/Al ratios suggested that the hexagonal array of mesopores in MCM-41 was sustained after the incorporation of Al in the framework. However, in comparison to the XRD pattern of the pure silicon MCM-41, the insertion of Al ions in the samples resulted in a partial destruction of the hexagonal ordering, as can be seen from the reduction in peak intensity and broadening of 100 peak of Al-MCM-41 samples. In addition, the hexagonal array of mesopores was destructed more serious with higher aluminium content as can be seen from the lower peak intensity.

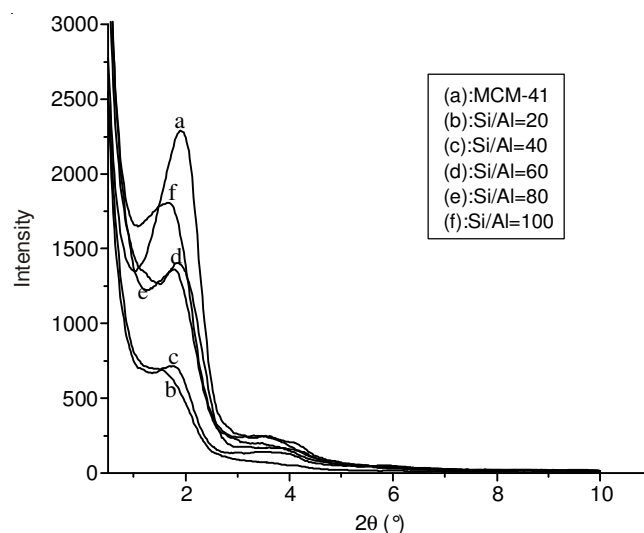


Fig. 2. Powder X-ray diffractograms of different catalysts

Product yields: The catalytic pyrolysis of soybean oil were conducted at the constant conditions: temperature 450 °C, weight hourly space velocity (WHSV) 6h⁻¹ and reaction time of 4 h under an atmospheric pressure. Meanwhile, for the comparison purpose, the pyrolysis experiment in the absence of catalyst and the presence of pure silica MCM-41 were also investigated under the same conditions.

The products distribution of the pyrolysis experiments were summarized in Table-1. As can be seen from the Table-1, it was unexpected to find that the yield of the pyrolysis

liquid decreased with the addition of catalysts. The liquid yield which was 94.7 % without any catalysts represented the maximum value. While the catalyzed pyrolysis has decreased the liquid yield, such as it showed a 4.8 % decline in the presence of MCM-41. From the study of the pyrolysis liquid, the high yield of liquid product in the non-catalytic experiment was mainly attributed by the high content of tar in it. When in the presence of catalysts, the heavy component may suffer a secondary decomposition. The production of bio-fuel, coke, gas were enhanced through the decomposition of tar component.

In view of the bio-fuel production, the yields of green gasoline and green diesel fraction of catalytic pyrolysis method are higher compared to that of non-catalytic pyrolysis. The yield of bio-fuel was enhanced significantly from 49.8 % of non-catalytic to 57.4 % in the presence of Al-MCM-41(60).

Moreover, the yield of water and gas product increased in the presence of catalyst. It has been reported before, the oxygen in the pyrolysis materials would be removed in the form of water, CO and CO₂. The higher yield of water and gaseous products always means the lower oxygen content in the liquid product. The assumption was in agreement with the elemental analysis results, as the 11.7 % oxygen content in the non-catalytic pyrolysis liquid decreased to 9.3 % in the presence of Al-MCM-41(60). A problem worthy to be pointed out here is that whether the bio-fuel could be applied is often associated with its oxygen content, the presence of oxygen lowers the heating value. And it would also be responsible for the weakness of stability. Thus the deoxygenated effect of the catalysts would be favored.

The distribution of pyrolysis products also changed significantly as the change of Si/Al ratios of the catalysts. The Si/Al affected the selectivity for the gas, water, coke, bio-fuel and tar component. In terms of the bio-oil, the selectivity increased from 52.2 to 57.4 % then decreased to 54.9 % as the Si/Al ratios increased from 20 to 60 then to 100. The Al-MCM-41(60) and Al-MCM-41(80) gave the higher yield of the bio-fuel among the investigated catalysts. The selectivity for the green gasoline fraction increased from 8.1 to 13.4 % with the Si/Al ratio increase from 20 to 60. When the ratio further increased, the yield increased slowly. In terms of the selectivity for the green diesel fraction, the results were almost constant at 42-44 %. It was turned out that the change of the Si/Al ratios has little effect on the selectivity on the green diesel fraction. Afterwards, when the Si/Al ratio was low, the catalytic activity was low, it was probably due to the destruction of the hexagonal array of mesopores, When the Si/Al ratio of MCM-41

increased, the acidity of these catalysts would decrease, this would due to the lack of active center in the catalyst. Thus there is a proper Si/Al ratio to get the best catalytic activity.

Chemical composition: For a detailed knowledge of the products, the composition of pyrolytic liquid product was analyzed by GC-MS. More than 100 compounds have been detected in the liquid product. For comparative purpose, the chromatograms for the products without any catalysts and with Al-MCM-41(60) were given in Fig. 3.

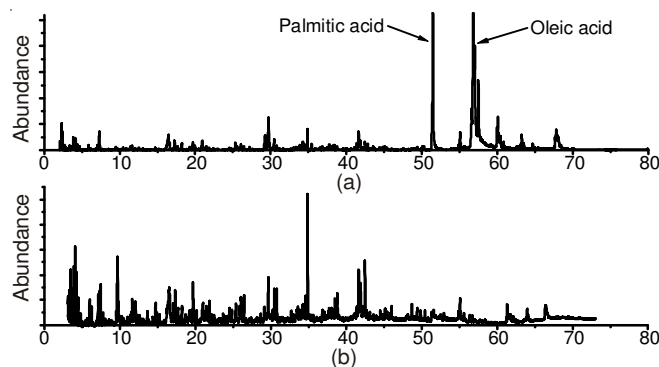


Fig. 3. Chromatograms for the pyrolytic oil of soybean oil: (a) blank, (b) Al-MCM-41(60)

The analysis of pyrolytic oil by GC-MS showed that the soybean oil were pyrolyzed into alkanes, alkenes, aromatics and various oxygenated compounds including alcohols, aldehydes, ketones and fatty acids.

As can be seen from Fig. 3(a), there was a great amount of fatty acids produced in the non-catalytic pyrolysis experiment. The two strong peaks represented palmitic acid and oleic acid respectively, which were the main contents in the soybean oil. It could be concluded that the soybean oil was first pyrolyzed into fatty acids and then the fatty acids undergo through radical reactions, such as deoxygenation, dehydrogenation, condensation, dehydration and aromatization. And it was agreed by former researches⁶. For the blank experiment, the secondary cracking reaction was not complete, resulting in large amounts of fatty acids. A problem worthy to be pointed out here is that the fatty acids have a negative effect on the heating value, cold filter plugging point and freezing point of the bio-fuel⁸. It was undesirable material in the pyrolysis product.

The strongest catalytic effect of the results presented in Fig. 3(b) was the significant reduction of the fatty acids peaks, that is, there was a greater decomposition of the fatty acids in

TABLE-1
PRODUCTS DISTRIBUTION OF THE CATALYTIC PYROLYSIS OF SOYBEAN OIL OVER Al-MCM-41 WITH DIFFERENT Si/Al RATIOS (% BY MASS)

Item	None	MCM-41	Si/Al = 20	Si/Al = 40	Si/Al = 60	Si/Al = 80	Si/Al = 100
Green gasoline	7.1	9.9	8.1	10.7	13.4	13.5	13
Green diesel	42.7	44.3	44.1	43.2	44	43.1	41.9
Tar	44.2	33.9	34.5	35	29.1	31	33.7
Water	0.7	1.8	2.5	1.6	2.7	3.5	1.3
Coke	0.4	0.4	1.6	1.8	1.8	1.9	1.1
Gas	4.9	9.7	9.2	7.7	9	7	9
Total liquid	94.7	89.9	89.2	90.5	89.2	91.1	89.9
Bio-fuel*	49.8	54.2	52.2	53.9	57.4	56.6	54.9

*Bio-fuel is the sum of green gasoline and green diesel.

the presence of Al-MCM-41(60). Meanwhile, the acidity of the pyrolytic oil would decrease as the decomposition of the fatty acids. Furthermore, an increase was also found in the short-chain compounds peaks, for this, it was possible to obtain hydrocarbons with chains similar to those present in fossil fuel.

Fuel properties: The properties are important for a bio-fuel which can be utilized in furnace and engines. For example, density, viscosity and heating value are known to be key properties for combustions. Thus the properties of pyrolytic oil were studied. The results of green diesel fraction get from the Al-MCM-41(60) catalyzed pyrolysis experiment were given and compared with the fuel properties specified in China

According the results shown in Table-2, the green diesel from the pyrolysis experiment presented properties comparable to the specification of diesel fuel in China. The density and viscosity have shown an acceptable value, except the heating value was a little below the standard. This indicated that it is possible to use the products as an alternative for the fossil fuel.

Physico-chemical property	Green diesel	Diesel fuel specification in China
Density, 20 °C (kg m ⁻³)	860	840-860
Viscosity, 20 °C (mm ² s ⁻¹)	5.8	3.0-8.0
Heating value (MJ kg ⁻¹)	43	≥ 45

Conclusion

The catalytic pyrolysis of soybean oil over the synthesized Al-MCM-41 type catalysts were studied in this work. The main conclusions from this work can be given as follows.

- The pyrolysis of soybean oil was strongly affected by the catalysts used. The catalytic activity of the Al-MCM-41

catalyst varied with the Si/Al ratios and the highest bio-fuel yield (57.4 wt %) was obtained with Al-MCM-41(60).

- The Al-MCM-41(60) catalyst promoted the secondary decomposition of the fatty acids formed in the first cracking phase. The acidity of the pyrolytic oil was decreased, short-chain compounds with similar chains to those present in fossil fuel were obtained.

- From the physico-chemical properties of the green diesel, it showed a good agreement with the fuel specification in China. There was a good prospect to serve as an alternative for the fossil fuel.

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