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Catalytic Co-Cracking of Used Cooking Oil Methyl Ester and Polystyrene Waste for Gasoline-Rich Biofuel Over Mesoporous Al-MCM-41 Catalyst

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***Abstract*—Used cooking oil and packaging foam are typical waste materials that are abundantly available as household and fast food restaurant waste with high energy content, thus representing potential feedstock for conversion into an alternative energy source. In this study, catalytic co-cracking was examined at 300°C in atmospheric pressure to generate fuel products with gasoline-like properties from a mixture of used cooking oil biodiesel and polystyrene pyrolysis oil. Mixture of ceramic powder and Al-MCM-41 was used as catalyst in comparison to a pristine mesoporous aluminosilicate material. The product distribution of produced biofuel wes analyzed by gas chromatography – mass spectrometry. Experimental results exhibit that catalytic co-cracking process generated up to 64,6 – 67,2% yield of liquid hydrocarbon. The product distribution and the quality of the resulting biofuel were significantly affected by Si/Al ratio of the catalyst. Pristine Al-MCM-41 with lower Si/Al ratio was more favored for the enrichment of gasoline range fraction (C_7–C_{12}) which give 88,98% yield, while Al-MCM-41/ceramic with higher Si/Al ratio only give 32,84% yield of gasoline fraction. Moreover, lower oxygenate compound with better stability of biofuel was also obtained using pristine Al-MCM-41 catalyst. The produced biofuel blend by both catalysts indicated promising physical properties including higher calorific value (53,2 and 52,4 MJ/kg) and higher-octane number (RON 99,8 and 95,5) than commercial gasoline.**

***Keywords*—Al-MCM-41, Catalytic Co-cracking, Liquid Hydrocarbon Product, Polystyrene, Used Cooking Oil Biodiesel.**

I. INTRODUCTION

RECENTLY, the demand for petroleum-based motor fuel like gasoline, diesel, and others has increased considerably due to rapid industrialization and increased population [1]. However, severe reliance on fossil fuel energy lead to depletion of fossil fuel reserves and environmental issues [2]. These negative side effect urge the researchers to develop alternative fuel which is renewable, efficient, and environment friendly. There are various kind of natural resources which considered as potential feedstock for biofuel such as lignocellulosic biomass, sugar/starch biomass, triglyceride biomass, and algae [3]. Among these, triglyceride based compound such as palm oil, sunflower oil, and other vegetables oil might become major alternative resources for production of sustainable bioenergy [4].

Table 1.
Physical characterization method

Parameters	Method
Density	ASTM D 4052
Viscosity	ASTM D 445
Caloric value	ASTM D 4809-13/IP12
RON	ASTM D 2699

Used cooking oil is considered as economically viable triglyceride-based feedstock for biofuel production due to their low cost and high availability [5]. According to The International Council on Transportation (ICCT), Indonesia has the potential of used cooking oil reaching 157 million liters from restaurants, hotel, and schools in urban areas, and more than 1,638 million liters from household waste. This amount is equivalent to 35% of annual biodiesel production in Indonesia. In addition, these feedstock are not competitive with human consumption or agriculture and their utilization can solve environmental issues associated with their disposal [6]. Thermochemical technologies such as catalytic pyrolysis can be used to convert biomass sources such as used cooking oil into bio-oil [7]. Used cooking oil is composed of triglyceride and fatty acid such as oleic acid, palmitic acid, etc., which can be cracked into hydrocarbons with shorter carbon chains and have conformity with the nature of fossil fuel [2]. However, high viscosity and low H/C_{eff} ratio of biomass feedstock cause a large amount of coke formation during cracking process which can reduce the yield of bio-oil [8-9].

Catalytic co-cracking process of biomass and plastic waste has gained more extensive attention in recent decade since it is one of the most promising route for biofuel production with high yield of bio-oil [10]. Plastic waste as co-feeding material can act as a hydrogen donor in the cracking process to enhance the quality and yield of bio-oil [11]. Synergistic effect between biomass and plastic waste co-feeding has been reported in several studies previously. Sajdak and Muzyka investigated the effect of using polypropylene plastic waste in the co-cracking of alder wood and pine wood [12]. The results showed that the addition of polypropylene waste increased the yield of liquid products by an average of approximately 14.3% for alder wood and 10.8% for pine wood in comparison with its pure biomass. Moreover, blending 30% of polypropylene waste had the largest impact on the calorific value of liquid products. Similar findings were reported for co-cracking of two different non-edible seed oil (Karanja and Niger seed) with polystyrene waste [13]. It revealed that co-cracking of polystyrene waste and seed oil not only enhanced the conversion of bio-oil, but also significantly affected the biofuel properties including higher calorific value, lower viscosity, and better acidity.

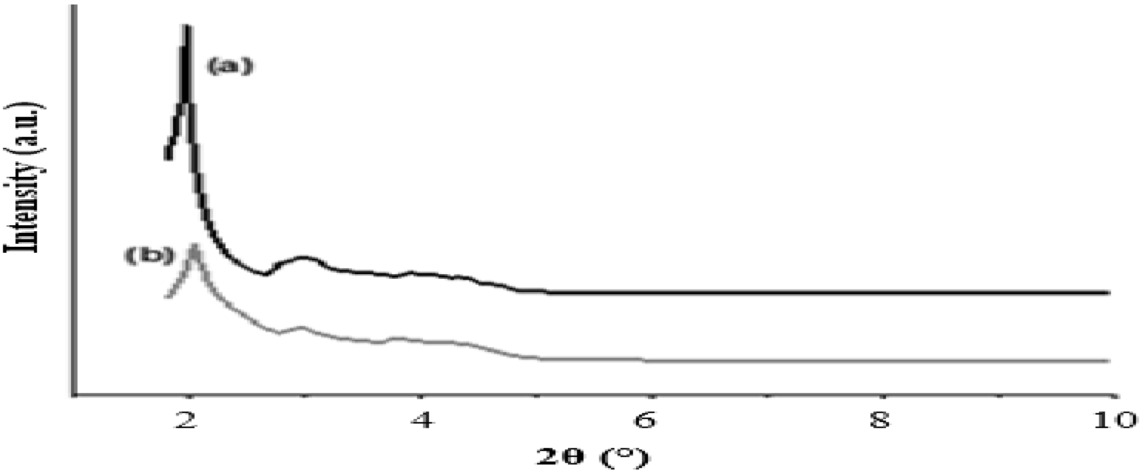
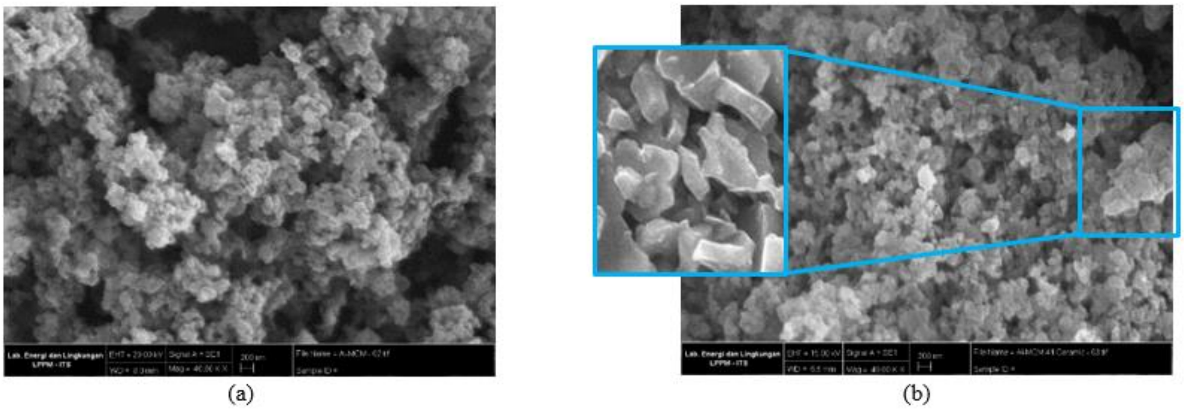


Figure 1. SAXRD diffractogram of (a) Al-MCM-41 and (b) Al-MCM-41/ceramic.


(a)

(b)

Figure 2. SEM image of (a) Al-MCM-41 catalyst and (b) Al-MCM-41/ceramic catalyst.

Proper catalyst might play a crucial role in conducting the cracking process selectively toward particular products. Zeolite catalysts such as ZSM-5 had been widely used in cracking process to produce lighter fractions of liquid hydrocarbon [14-17]. However, due to the small pore size of ZSM-5 (5.2 – 5.9Å), the large molecular size of oxygenate compound cannot enter the pore of ZSM-5 and cause deposition of coke on its surface [18]. The mesoporous catalyst, Al-MCM-41, appears to be less prone to deactivation and to give higher yield of bio-oil since it has specific porosity and acidic properties (large surface area, relatively large pore 30 - 40Å, and mild to moderate acidity). Chi et al. performed catalytic co-pyrolysis of polypropylene and cellulose using Al-MCM-41 catalyst at 650°C. Their results exhibited that the use of Al-MCM-41 can yielded 72.8% liquid hydrocarbon with the major products lie in the range between C_4 – C_7. Moreover, had shown that Al-MCM-41 or stage catalyst which composed of Al-MCM-41 with ZSM-5 give very high selectivity which could reach maximum yield 66.74% and 97.89% respectively toward gasoline-range products for catalytic cracking of beech wood [19].

In this study, catalytic co-cracking of used cooking oil methyl ester and polystyrene waste was conducted at 300°C with Al-MCM-41 catalyst to produce biofuel rich in gasoline range fraction. Pretreatment of used cooking oil by converting it into methyl esters through transesterification reaction was carried out to reduce the viscosity and acidity of the feedstock. The effect of physically mixing of the Al-MCM-41 with ceramic insulator spark plug on the yield and product distribution of the liquid hydrocarbon was evaluated. Furthermore, the physical properties of the resulting biofuel comprise of density, flash point, calorific value, and octane number (RON) were also investigated in the present study and compared with SNI 06:3506:2015.

II. METHOD

A. *Catalyst Preparation and Characterization*

Ceramic insulators from spark plug were grinded and sieved using mesh filter 100 to get a uniform size of ceramic powder. Al-MCM-41 catalysts which obtained from previous study by hydrothermal process were physically mixed with ceramic powder by mass ratio of 7:3 and then put in an oven at 120°C for an hour to remove the water vapors on its pore [20]. After being cooled, its characteristics was analyzed.

The BET surface area was measured by nitrogen adsorption using Tristar II 3020. Pore volume and pore size were calculated by the desorption branch based on BJH method [21]. Pyridine was used as probe molecule for the quantitative analysis of catalyst surface acidity by FTIR spectroscopy. XRD was carried out with Cu Kα radiation to examine the phase structure of catalyst. The surface

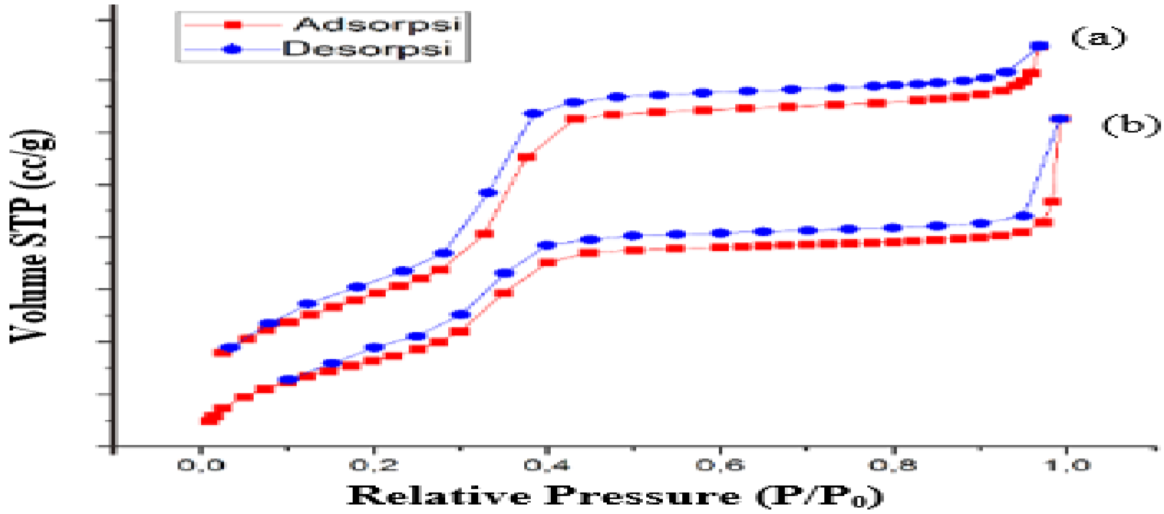


Figure 3. N_2 adsorption-desorption isotherm graph of (a) Al-MCM-41 and (b) Al-MCM-41/ceramic.

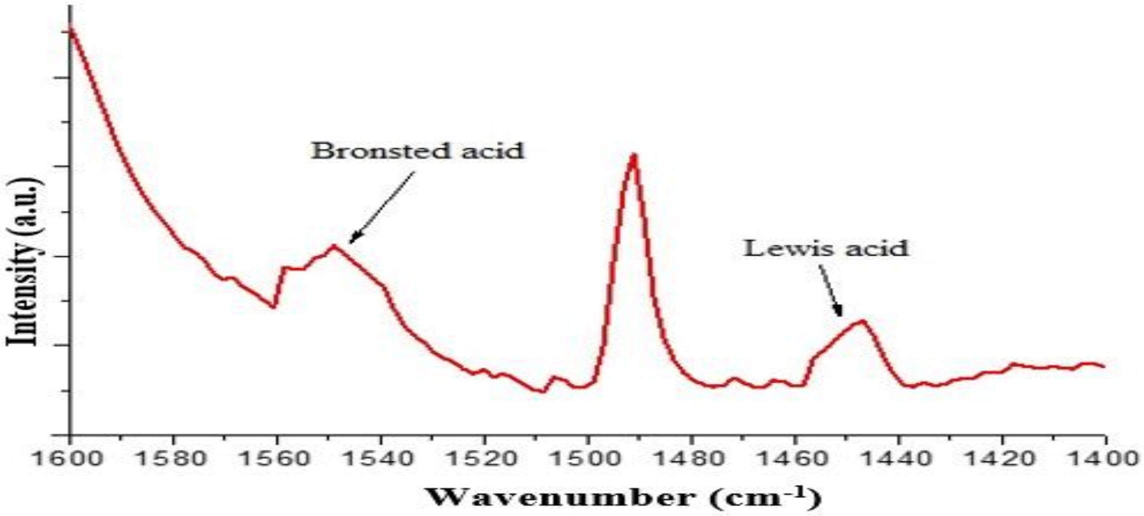


Figure 4. FTIR spectrogram for pyridine adsorption.

morphology was analyzed by scanning electron microscopy (SEM FEI Quanta 20F).

B. *Catalytic Co-Cracking Process*

Used cooking oil methyl ester was co-cracked with PS pyrolytic oil with volume ratio of 1:1 by means of 9 grams Al-MCM-41 and Al-MCM-41/ceramic catalysts. Initially, 500 mL of used cooking oil methyl ester was blended with 500 mL PS oil and stirred until evenly mixed. These mixtures then put into the chamber reactor and flushed with nitrogen gas flow. 9 grams of pellet catalyst was arranged in 2 stage with glass wool and placed in the catalyst holder to ensure that the vapor of the reaction product passed through the catalyst completely for further cracking reaction. Catalytic co-cracking process was conducted at 300°C under atmospheric pressure for 60 minutes of reaction time. White colored vapor which contains several types of hydrocarbon were tend to condense when it reaches the condenser as liquid hydrocarbon products and collected in the collecting flask.

C. *Product Analysis and Characterization*

In this study, product analysis was focused on the liquid hydrocarbon products (LHP) which consist of a varied number of components. The LHP was analyzed using GC-MS and its component grouped into gasoline range hydrocarbons ($C_7 – C_{12}$), above C_{12} hydrocarbons, and below C_7 hydrocarbons. The physical properties which comprises density, viscosity, calorific value, and research octane number (RON) were measured by the method as given in the Table 1.

III. RESULT AND DISCUSSION

A. *Catalyst Characterization*

The SAXRD pattern of the prepared catalysts are given in Figure 1. Al-MCM-41 shows a sharp peak in the range of 2θ = 1.86 - 2.42° and two broad peaks with low intensity in the range 2θ = 2.74 - 3.85° and 2θ = 3.89 - 4.87° which corresponds to the plane reflection of (100), (110), and (200) respectively [22] . These peaks are the characteristic peaks of highly ordered hexagonal arrangement of the mesopores. Physically mixing of alumina oxide ceramic powder from spark plug isolator waste material in the sample does not damage the hexagonal structure of MCM-41 since the

Table 2.
The acidity properties of the catalyst

Amount of acid (mmol/g)	Al-MCM-41	Al-MCM-41/ceramic
Lewis	0.0386	0.0311
Bronsted	0.0670	0.0342
Total acid site	0.1056	0.0653

Table 3.
Product yield from catalytic co-cracking of used cooking biodiesel and polystyrene waste

Catalyst	% Yield Liquid Hydrocarbon	% Yield Coke	% Yield Gas
Al-MCM-41	67.2	14.6	18.2
Al-MCM-41/ceramic	64.6	23.4	12.0

characteristic peaks are still persisted without any shifting. However, a decrease in intensity of the sharp peak is observed after addition of ceramic powder.

The morphology of the Al-MCM-41 and Al-MCM-41/ceramics catalysts were characterized using Scanning Electron Microscopy (SEM) shown in Figure 2. Based on SEM micrographs, it can be seen that the Al-MCM-41 and Al-MCM-41/ceramics catalysts show agglomeration of particles with hexagonal structures which are the characteristic of the MCM-41 material's morphology of. In addition, added alumina ceramic powder particles were shown by the agglomeration of particles in sheet form attached to Al-MCM-41 particles. Thus, it can be inferred that there was no structural damage from the Al-MCM-41 catalyst after mixing of alumina oxide ceramic powder because no significant differences in morphology were observed. Moreover, the EDX analysis shows that Si/Al ratio increase from 10 to 15 after addition of alumina ceramic powder.

Figure 3 shows the N_2 adsorption–desorption isothermal for the catalyst. The shape of isotherm of the two Al-MCM-41 and Al-MCM-41/ceramic samples are similar to those highly ordered MCM-41 mesoporous materials, revealing that the porous characteristics of the aluminosilicate samples have not been damaged to the extent that the XRD patterns indicated. Addition of alumina ceramic resulted in higher surface area and pore volumes. Its values increase from 419.93 to 490.665 m^2/g and 0.50 to 0.547 cc/g respectively. However, the total number of acid sites obtained from pyridine FTIR analysis decreases with the addition of alumina ceramic powder as given in Table 2. FTIR spectrogram of pyridine adsorption is shown in Figure 4.

B. Catalytic Co-cracking Process

The product yield (liquid, coke, and incondensable gas) in the catalytic co-cracking of used cooking oil biodiesel and polystyrene waste using both Al-MCM-41/ceramic and Al-MCM-41 catalyst are presented in Table 3. Moreover, the composition of liquid hydrocarbon product fractions is given in Figure 5. It can be clearly seen that the yield of liquid hydrocarbon products are comparable each other using either Al-MCM-41/ceramic or pristine Al-MCM-41. That result can be achieved because both catalysts have larger pore size in the range of mesopore which might facilitate the diffusion (enter, reformulate, and exit) of larger fragment from the major product of biomass and plastic waste pyrolytic gases in the catalyst particle for further catalytic cracking process. As a result, catalyst deactivation rate can be reduced and give higher yield of liquid hydrocarbon product.

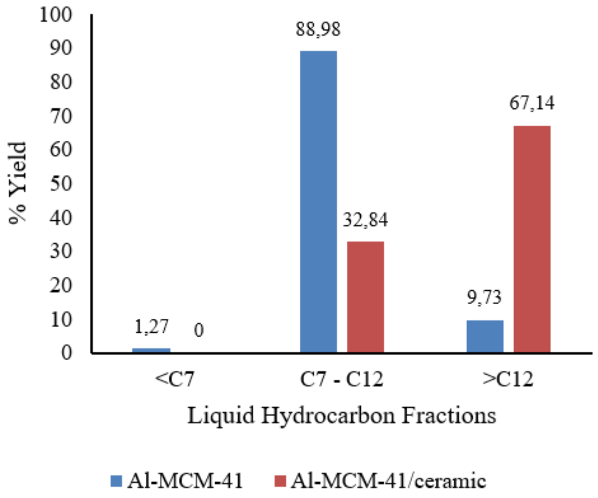


Figure 5. Composition of liquid hydrocarbon fraction.

The composition of liquid hydrocarbon product fraction was further analyzed using GC-MS. From the Figure 5, it can be revealed that Si/Al ratio has a significant effect toward the composition of liquid hydrocarbon fraction. Al-MCM-41 which possess lower Si/Al ratio produce more gasoline fraction (C_7 – C_{12} hydrocarbons) than Al-MCM-41/ceramic in which 88.98% yield is achieved. Meanwhile, Al-MCM-41/ceramic with higher Si/Al ratio give more products on larger hydrocarbon fraction ($>C_{12}$). It is known that Si/Al ratio affect the acidity of the MCM-41 catalyst as have been proved by the catalyst characterization in previous section. Consequently, lower Si/Al ratio reflect a higher acidity with more acidic active site which enhance the cracking reaction of feedstock toward gasoline range product.

A wide range of organic compounds was found in the liquid biofuel produced. Alkane, olefin, and aromatics hydrocarbons are desirable fractions since they possess high commercial value, while oxygenate compounds, such as acids and carbonyls, as well as heavy compounds is considered as undesirable compound. The large fraction of oxygenate compounds can bring some drawback toward the quality of biofuel, including corrosiveness, stability, and lower calorific value. From the Figure 6, we can see that Al-MCM-41 catalyst with lower Si/Al ratio also beneficial for the reduction of oxygenated compound and enhance the production of aromatics hydrocarbon. It seems that the presence of higher acidic active site of the Al-MCM-41 material can catalyzes more series of decarboxylation, decarbonylation, dehydration, and aromatization that convert the afore mentioned oxygenated compounds into alkane, olefin, and aromatics hydrocarbon.

C. Physical Characterization of Biofuel

Physical characterization result of the produced biofuel using Al-MCM-41 and Al-MCM-41/ceramic is compared with SNI 06:3506:2015 for gasoline quality standard in Indonesia and summarized in Table 4. It can be seen that the physical properties from both of the produced biofuel

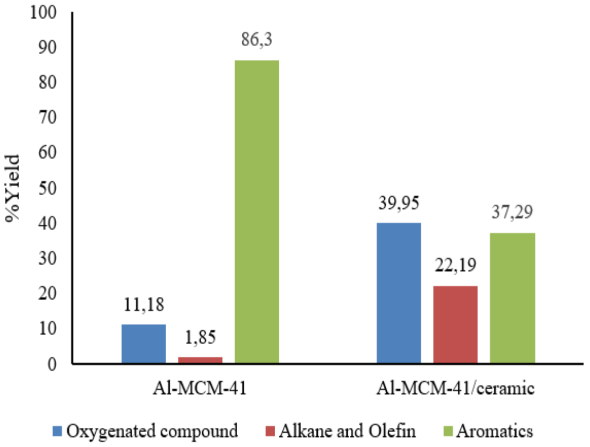


Figure 6. Distribution of liquid hydrocarbon product compound.

Table 4.
Physical properties of biofuel from catalytic co-cracking of used cooking oil biodiesel and polystyrene waste

Parameter	Al-MCM-41	Al-MCM-41/ceramic	SNI 06:3506:2015
Density (g/mL)	0.751	0.7304	0.75 – 0.77
Viscosity (cSt)	0.82	0.87	1.08
Calorific value (MJ/kg)	53.215	52.412	49.678
Octane number	99.8	95.5	88

variation are in accordance with gasoline quality standard, SNI 06:3506:2015. Biofuel produced using Al-MCM-41 catalyst shows a better quality in term of higher-octane number and higher calorific value. It can be attributed to the higher composition of gasoline fraction in the liquid hydrocarbon product from catalytic co-cracking of used cooking oil biodiesel and polystyrene waste using Al-MCM-41.

IV. CONCLUSION

Experimental results exhibit that catalytic co-cracking process of used cooking oil methyl ester and polystyrene waste generated up to 64,6 – 67,2% yield of liquid hydrocarbon using Al-MCM-41 and Al-MCM-41/ceramic catalyst respectively. The product distribution and the quality of the resulting biofuel were significantly affected by Si/Al ratio of the catalyst. Pristine Al-MCM-41 with lower Si/Al ratio was more favored for the enrichment of gasoline range fraction (C_7 – C_{12}) which give 88,98% yield, while Al-MCM-41/ceramic with higher Si/Al ratio only give 32,84% yield of gasoline fraction. Moreover, lower oxygenate compound with better stability of biofuel was also obtained using pristine Al-MCM-41 catalyst. The produced biofuel blend by both catalysts indicated promising physical properties including higher calorific value (53,2 and 52,4 MJ/kg) and higher-octane number (RON 99,8 and 95,5) than commercial gasoline.

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