



Biodiesel Synthesis from Vegetable Oil Deodorizer Distillate Over Mesoporous Superacid Oxo-Phosphated Sulfated Zirconia Catalyst

Hong Khanh Dieu Nguyen^{1*} and Phong Van Pham²

1. Hanoi University of Science and Technology, **VIETNAM**

2. Vietnam National Oil and Gas Group, **VIETNAM**

Email: dieuhongprof@gmail.com

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ABSTRACT

Mesoporous oxo-phosphated sulfated zirconia (m-PSZ) were applied for converting vegetable oil deodorizer distillate to biodiesel in one-step reaction. The catalyst possessed mesopores, high surface area and strong acid sites while the feedstock contained mainly free fatty acids. Many investigations were established for finding the most suitable conditions of the biodiesel synthesis process. Some techniques including XRD, TEM, BET and GC-MS were used for characterizing the catalysts properties and chemical composition of the biodiesel product.

Keywords: Mesoporous, zirconia, oxo-phosphate, deodorizer distillate.

INTRODUCTION

Biodiesel was an environmentally friendly fuel as it was made from renewable resources and CO₂ balance. It was derived from the esterification of free fatty acids or the transesterification of triglycerides with methanol or ethanol. The base catalyzed process suffered from some limitations of feedstock, especially the acid value must be lower than 1 avoiding the saponification during the alcoholysis [1, 2]. Therefore, in case of rich free fatty acid feedstocks, the solid acid catalysts were preferable [3]. Recently, there have developed various solid acids for the esterification of long chain fatty acids including sulfonated carbonized sugar [4], sulfated zirconia [5] and organosulfonic acid mesoporous silica [6]. However, the activities of most of these catalysts were still low in comparison with sulfuric acid. It was desirable to further develop good solid acid catalyst with high catalytic activity and stability for both esterification of fatty acids and transesterification of triglycerides. There were several considerations in the development of a strong solid acid for the purpose. First, the catalyst needed to be highly dispersed in order to bring out a large number of active acid sites. Second, mesoporosity in the catalyst would be able to accommodate the relatively larger molecules of fatty acid. Finally, the catalyst required to be water-tolerant since water is a byproduct of the esterification process.

Mesoporous sulfated zirconia (m-SZ) was also a kind of the metal oxide derived mesostructured material exhibiting its high surface area, superacid sites, and it was a good potential for widening applications of the traditional zirconia based acid materials. The major problem for synthesizing the m-SZ material still

belonged to its low thermal stability leading to collapse the mesopores during the template removal at high temperature. One of the best solution for improving the thermal stability of the m-SZ material was to change its surface state through the oxophosphate process. In which, the oxophosphate groups could be used to lock the –OH groups attached on the zirconium sites; therefore the zirconium site could ensure its oxidation state during the calcination, and the catalyst could be assigned as m-PSZ catalyst. In a previous paper, both m-SZ and m-PSZ catalyst were synthesized through condensation method in alkaline solution followed by oxo-phosphated process [7].

Vegetable oil deodorizer distillate was one of the cheapest feedstock which could be used for biodiesel synthesis. The drawback of this feedstock was its very high acid value limiting its applications when using the traditional base catalysts because of the saponification. The problem could be solved by using a suitable solid acid. The m-PSZ catalyst exhibited superacid property, high surface area and good thermal stability which could play an important role in the conversion of free fatty acids and triglycerides in the deodorizer distillate to biodiesel in an one-step reaction.

MATERIALS AND METHODS

Chemicals: Zirconyl chloride ($ZrOCl_2 \cdot 8H_2O$), cetyltrimethylammonium bromide (CTAB), sulfuric acid (H_2SO_4), ammonia solution were all purchased from Merck and used as received; deodorizer distillate collected from the Cailan Vegetable Refinery in Quang Ninh province, Vietnam was pretreated by heating up to $120^\circ C$ for 2 h to complete water removal before used; distilled water was prepared in our own laboratory.

Preparation of m-PSZ catalyst: The m-PSZ catalyst was prepared in previous paper [7], in which the synthesized m-SZ material was sinked into 20 mL solution of H_3PO_4 1M in combination with well stirring. The mixture was maintained for 24 h at ambient temperature; then the precipitate was filtered and dried at $110^\circ C$ overnight. This dried powder was then calcinated at $450^\circ C$ for 6 h to obtain mesoporous oxophosphated sulfated zirconia (m-PSZ). Characterizations of the m-PSZ catalyst were also established in the paper [7] including powder XRD, TG-DTA, BET, TEM, and NH_3 -TPD pointing out its mesoporous structure, strong acid sites and high surface area.

Conversion of vegetable oil deodorizer distillate to biodiesel over the m-PSZ catalyst: The deodorizer distillate feedstock with volume of 40mL was transferred to an autoclave reactor supported magnetic stirrer and heater. A precise mass of the m-PSZ catalyst was then carefully measured and homogeneously mixed with the feedstock before closing the reactor. The temperature was risen to a defined temperature and lasted for a suitable period of time. The stirring speed was also surveyed for maintaining the good mixing of all chemical components in order to completely convert the feedstock to methyl esters under auto-pressurized condition. After the reaction completed a decantation was applied to separate upper liquid phase including biodiesel and excess methanol for further purification. The purification was performed by rinsing the liquid with hot water for a certain time followed by drying the raw biodiesel at $120^\circ C$ for 2 h to obtain refined biodiesel. The biodiesel yield was calculated by the yield – kinetic viscosity relation obtained from the paper [8]. The yield – kinetic viscosity equation was described as $Y = -6.00X + 129.20$ [8], in which Y was the biodiesel yield, and X was the kinetic viscosity of the refined biodiesel at $40^\circ C$. Some procedures for testing reusability of the catalyst was also proposed in the 3.4 part. The chemical composition of the refined biodiesel at the highest yield was determined by GC-MS, and some properties of the refined biodiesel were determined to illustrate the applicability of this process in the biodiesel synthesis.

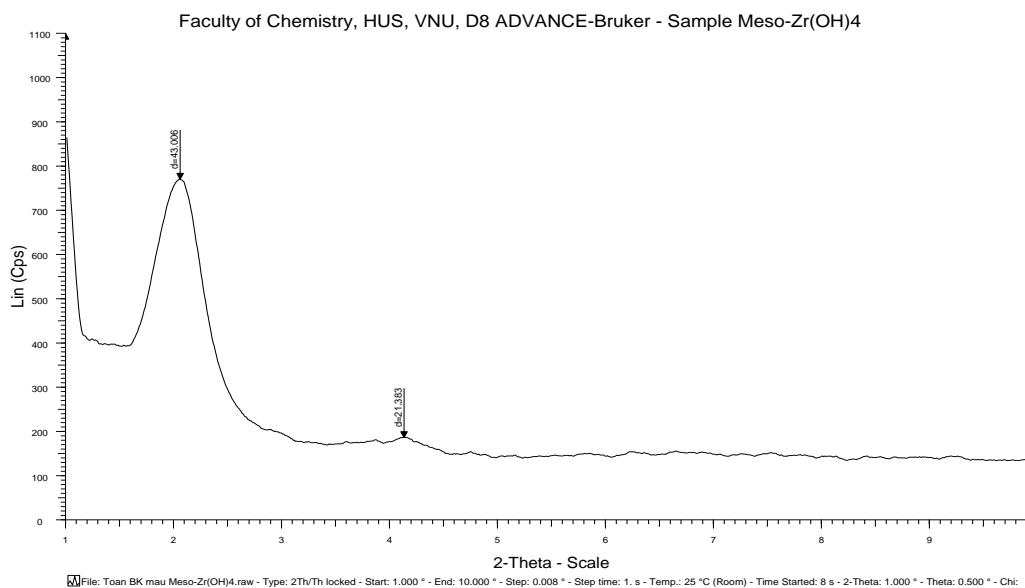
RESULTS AND DISCUSSION

Characterizations of the m-PSZ catalyst: A series of the m-PSZ catalysts properties were described in table 1. These results were collected from our previous publishes.

Table 1. The properties of the m-PSZ catalyst

No.	Properties	Methods	Values
1	Bulk density	ASTM D 6683	0.3586
2	Surface area, m ² /g	BET	629.6
3	Concentrated pore diameter, Å	BJH	38.06
4	Structure	XRD	Amorphous
5	Superacid desorbed temperature, °C	NH ₃ -TPD	506.9
6	Superacid sites, mmol/g	NH ₃ -TPD	0.51
7	Thermal stability, °C	TG-DTA	~550

The m-PSZ catalyst existed in amorphous phase providing the ordered mesoporous structure with very high surface area of 629.6 m² g⁻¹. The concentrated pore diameter belonged to the mesoporous group, and it was large enough for enhancing the diffusion of the free fatty acids and triglycerides in the deodorizer distillate to the strong acid active sites located on the catalysts surface. Beside the m-PSZ catalyst exhibited considerable thermal stability in comparison to the m-SZ catalyst [7, 9] leading to protect the meso-walls from the collapse during the calcination for template removal. The acidity of the m-PSZ catalyst observed from the Table 1 showed its very strong superacid sites with the desorbed temperature of 506.9°C during NH₃-TPD establishment, and the amount of superacid sites was very high. These properties clearly pointed out that the m-PSZ catalyst was a potential candidate to be applied in the biodiesel synthesis. Some characterizations of the m-PSZ catalyst including XRD, BET and BJH were also displayed in figure 1 and figure 2.



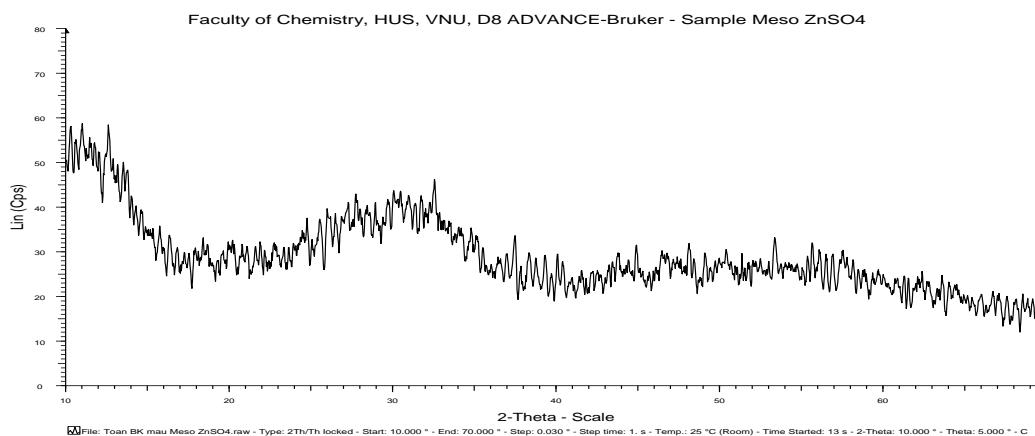


Figure 1. Small and wide angle powder XRD patterns of the m-PSZ catalyst

The appearances of finger print peaks at positions of $2\theta = \sim 2^\circ$ and $\sim 4^\circ$ in the small angle XRD pattern clearly confirmed the ordered mesoporous structure of the m-PSZ catalyst, and the absences of crystalline peaks in the wide angle XRD pattern also illustrated the amorphous existence of the catalyst as mentioned above.

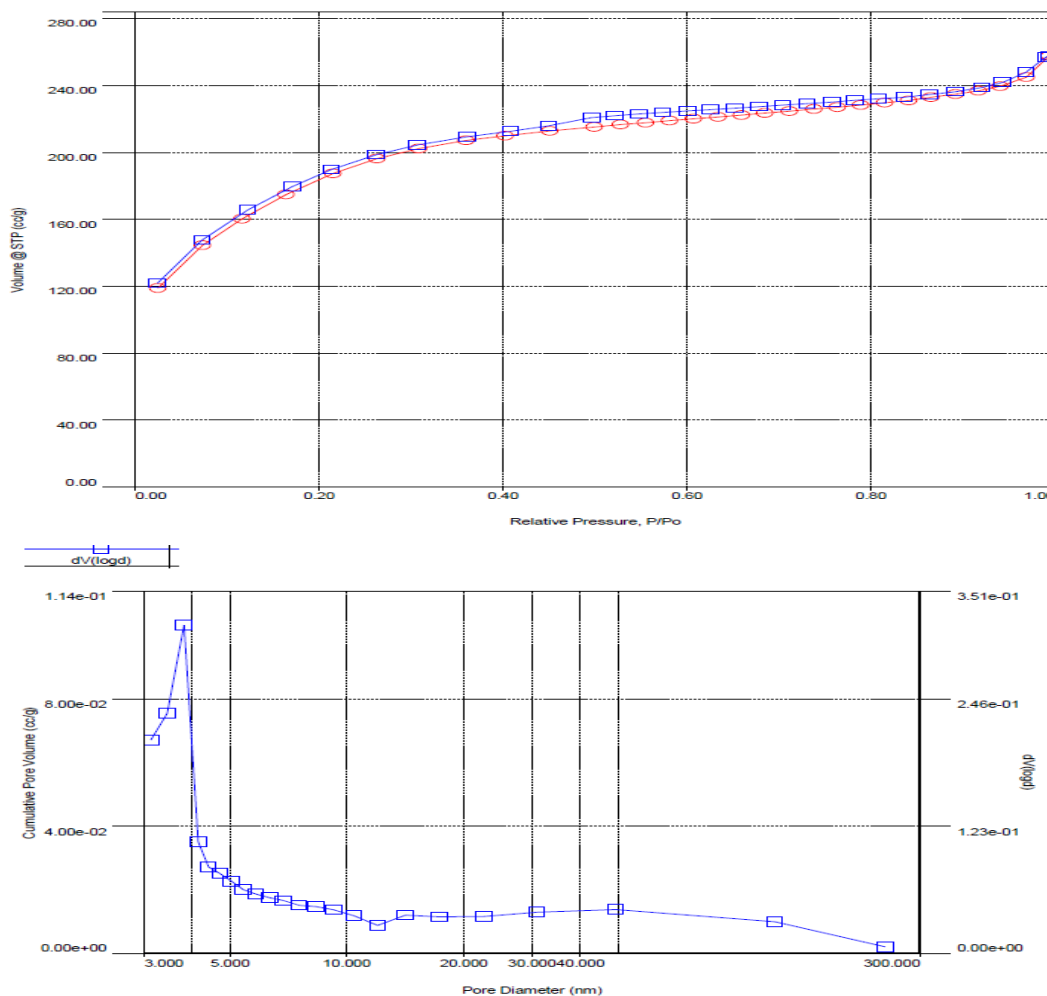


Figure 2 Adsorption – desorption isotherm and pore distribution diagram

The hysteresis appeared in relative pressure ranged from 0.4 to 0.9 because of the capillary condensation of the nitrogen vapor in the technique procedure. This phenomenon also demonstrated the mesoporous structure of the m-PSZ catalyst. The BJH analysis confirmed the concentrated pore diameter with a sharp and intensive peak at $\sim 38\text{\AA}$. Morphology of the catalyst could be observed through TEM images because of their clear exhibition of mesoporous channels in each catalysts particle. Figure 3 pictured this ability.

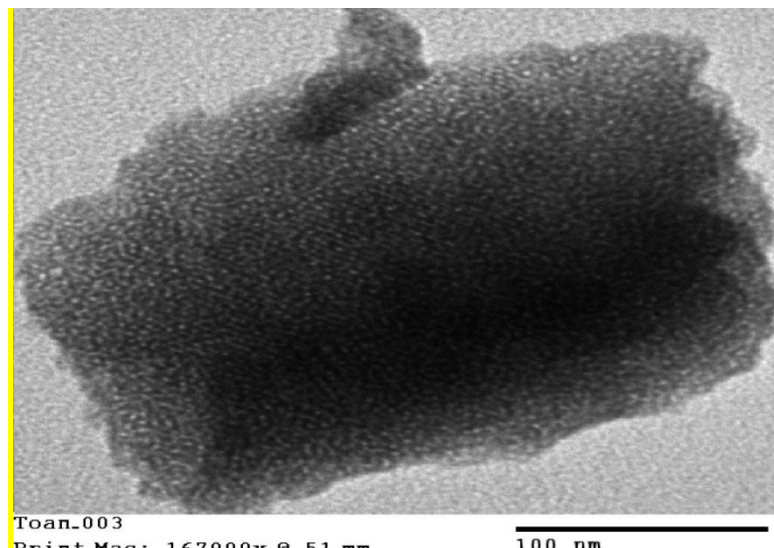


Figure 3 TEM image of the catalyst

The TEM image clearly showed a tightly porous distribution in each catalysts particle with one direction proving that their degree of order was good. This observation was well fitted with the results obtained from the XRD and BET techniques. Therefore, that was surely to confirm that the mesoporous system in the catalyst was well prepared through the chosen method of preparation. The high degree of order of the mesosystem also considerably provided the catalyst the ability of enhancing the diffusion of reagents in the biodiesel synthesis.

Some properties of the vegetable oil deodorizer distillate: Table 2 described some major properties of the vegetable oil deodorizer distillate. The properties were all determined by using ASTM and EU standards.

Table 2. The specifications of the vegetable oil deodorizer distillate

No.	Properties	Methods	Values
1	Density at 25°C	D 1298	0.92
2	Pouring point, °C	D 97	5
3	Saponification value, mg KOH/g	D 464	193
4	Acid number, mgKOH/g	D 664	124
5	Iodine number, g I ₂ /100g	EN 1411	36.28
6	Water content, mg/kg	D 95	670
7	Residue content, mg/kg	EN 12622	452

The special property of the deodorizer distillate was the very high value of free fatty acid with acid number of 124. Therefore that was impossible to convert this feedstock to biodiesel over the basic catalysts because of the saponification reactions [7]. The m-PSZ catalyst possessed superacid sites providing a very effective way to convert constantly esterification and trans-esterification of the free fatty acids and the triglycerides to biodiesel.

Beside, many other properties of the deodorizer distillate were the same trends as that of the vegetable oils or animal fats, so the applications of that kind of feedstock in the biodiesel synthesis were very suitable.

Investigation of the biodiesel synthesis: Many parameters were surveyed in the biodiesel synthesis such as temperature, period of time, catalyst dosage, volume ratio of methanol/feedstock and stirring speed. The biodiesel synthesis process was gradually optimized through each survey by fixing the obtained parameter in the previous procedure and varying the rest parameters through each next reaction. The first parameter was temperature ranged from 80°C, 100°C, 120°C, 130°C and 140°C during fixing the time of 3 h, methanol/feedstock volume ratio of 1/1, catalyst dosage of 4% and stirring speed of 400 rpm. The results were described in table 3.

Table 3. Effect of temperature on biodiesel yield

Temperature, °C	80	100	120	130	140	150
Biodiesel yield, %	70.4	82.3	89.6	92.2	90.0	86.2

The best value of temperature was 130°C when the biodiesel yield reached peak of 92.2%. Below this temperature, the biodiesel yield was lower because of the lack of the kinetic energy [7]. At the temperature higher than 130°C, the biodiesel yield was also lower than that at 130°C. The reason was assigned for the byproduct generations or the increase of velocity of the inverse reactions instead of esterifications and transesterifications [8]. Therefore, the temperature of 130°C was chosen for surveying the other parameters.

The second investigated parameter was the reaction time at 130°C. The fixed parameters included methanol/feedstock volume ratio of 1/1, catalyst dosage of 4% and stirring speed of 400 rpm. The reaction time was ranged from 1, 2, 3, 4, 5 and 6 h. The results were briefed in table 4.

Table 4. Effect of reaction time on biodiesel yield

Reaction time, h	1	2	3	4	5	6
Biodiesel yield, %	73.2	85.8	92.2	94.5	94.6	94.6

The reasonable phenomenon was that when raising the reaction time, the biodiesel yield also rised, but the biodiesel yield could not be risen by raising the reaction time to a very high value because of the kinetic limitations of the biodiesel synthesis. On the other hand, it could be said that the reaction gradually approached the balance state [8]. The biodiesel yield reached the highest value when the reaction time was 5 h, but the yield at 4 h was very the same. Therefore, the reaction time of 4 h was chosen for further investigation of the effect of catalyst dosage on the biodiesel synthesis.

The m-PSZ catalyst dosages were varied from 2, 3, 4, 5 and 6% based on the feedstocks weight. The fixed conditions included temperature of 130°C, reaction time of 4 h, methanol/feedstock volume ratio of 1/1 and stirring speed of 400 rpm. The results were showed up in table 5.

Table 5. Effect of catalyst dosage on biodiesel yield

Catalyst dosage, %	2	3	4	5	6
Biodiesel yield, %	80.1	90.1	94.5	95.5	95.5

The catalyst dosage also played a major effect on the biodiesel yield, and the principle was the same as the effect of the reaction time. In the former reaction, the catalyst dosage was 4% with the very high value of the biodiesel yield, but it could be applied with the higher weight (5%) for enhancing the biodiesel synthesis. At this catalyst dosage, the biodiesel yield could reach 95.5%.

For the methanol/feedstock volume ratio investigations, some fixed conditions consisted of temperature of 130°C, reaction time of 4 h, and catalyst dosage of 5% wt and stirring speed of 400 rpm. The same survey

was also implemented with the stirring speed when keeping the best methanol/feedstock volume ratio and changing the stirring speed from 100, 200, 300, 400, 500 and 600 rpm. The same behavior of the effects was observed, and finally we chose the most suitable methanol/feedstock volume ratio and stirring speed of 1.5/1 and 500 rpm. The detail parameter investigations were described in table 6 and table 7.

Table 6. Effect of methanol/feedstock volume ratio on biodiesel yield

Methanol/feedstock volume ratio	0.5/1	1/1	1.5/1	2/1	2.5/1	3/1
Biodiesel yield, %	90.6	95.5	95.8	95.8	95.8	95.8

Table 7. Effect of stirring speed on biodiesel yield

Stirring speed, rpm	100	200	300	400	500	600
Biodiesel yield, %	87.6	92.2	94.0	95.8	96.3	96.3

On the whole, the highest biodiesel yield could be optimized to 96.3%, a very high value demonstrating the extremely good catalysts activity, at conditions such as temperature of 130°C, reaction time of 4 h, catalyst dosage of 5% wt, methanol/feedstock volume ratio of 1.5/1 and stirring speed of 500 rpm.

Chemical composition of the refined biodiesel was determined by GC-MS method, and the results showed that there were many fatty acid methyl esters varying from C₈ to C₂₀; in which the C₁₆:0, C₁₈:2, C₁₈:1 and C₁₈:0 mixture accounted for the main content of the product (Table 8). These compositions represented the mixture of much kind of vegetable oils in the feedstock. The total content of the methyl esters in the refined biodiesel also reached 97.83% which was higher than the required content for biodiesel blending according to the ASTM D 6751. Some properties of the biodiesel were also collected in table 9 pointed out that the product could be useful in the blending with commercial diesel fuel.

Table 8. Chemical composition of the refined biodiesel

No.	Name of acids	Simple formula	Content, %
1	Octanoic	C8:0	0.09
2	Decanoic	C10:0	0.14
3	Dodecanoic	C12:0	0.88
4	Tetradecanoic	C14:0	2.07
5	Pentadecanoic	C15:0	0.13
6	Hexadecanoic	C16:0	38.91
7	Heptadecanoic	C17:0	0.49
8	10,13-octadecadienoic	C18:2	33.55
9	9-octadecenoic	C18:1	11.28
10	Octadecanoic	C18:0	6.19
11	9, 12-octadecadienoic	C18:2	0.50
12	11-eicosenoic	C20:1	0.63
13	Eicosanoic	C20:0	0.97
Total, %			97.83

Table 9. Main specifications of the biodiesel

Specifications	Methods	Values	ASTM D 6751
Density at 15.5°C	D 1298	0.8671	-
Flash point, °C	D 93	168	130 min
Kinetic viscosity at 40°C, cSt	D 445	5.3	1.9-6.0
Methyl ester content, wt%	EN 14103d	97.83	96.5
Cloud point, °C	D 2500	4	-
Cetane index	J 313	56	47 min
Acid value, mg KOH/g	D 664	0.30	0.50 max
Carbon residue, wt%	D 4530	0.01	0.050 max
Sulphate ash, wt%	D 874	0.008	0.020 max
Water content, mg/kg	D 95	182	500 max
Alkali metal, mg/kg	D 2896	4	5 max
Oxidative stability at 110°C, hours	D 525	8	3 min

Reusability test of the m-PSZ catalyst: The m-PSZ catalyst was reused after each batch reaction by some following step by step procedures: completely settling the catalyst from the liquid phase, gradually withdrawing the liquid from the catalyst, introducing same amounts of feedstock and methanol into the flask containing catalyst and establishing the reaction at the same conditions as being investigated. The reactions were repeated continuously until the reaction yield was lower than 80%. The reusability curve of the m-PSZ catalyst plotted in figure 4 showed that the catalyst could be used for 9 recycles of reaction.

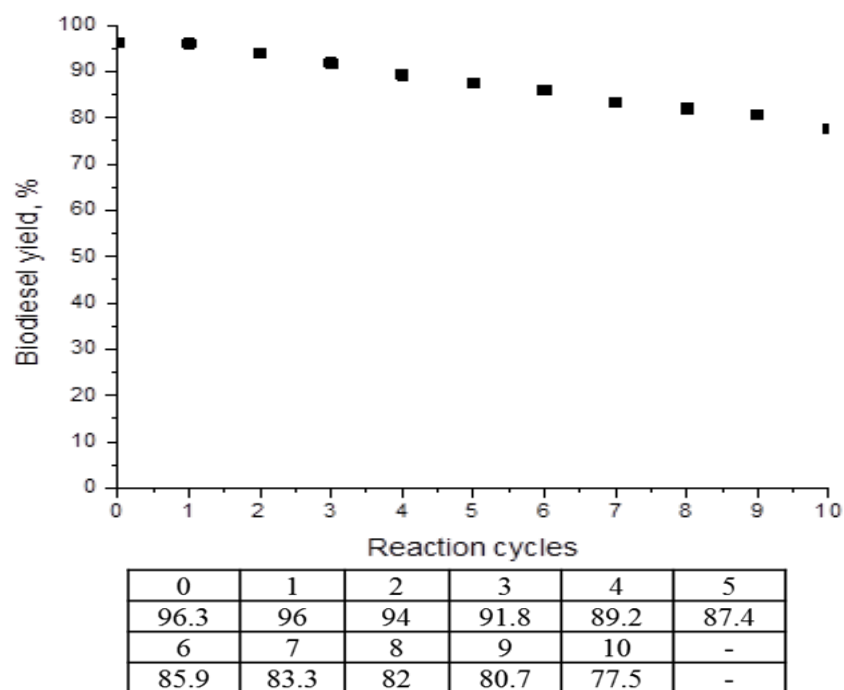


Figure 4. Reusability testing of the m-PSZ catalyst

APPLICATIONS

The biodiesel synthesis using vegetable oil deodorizer distillate over mesoporous oxo-phosphated sulfated zirconia (m-PSZ) showed a very high potential for applying this kind of catalyst in many other biodiesel production processes, especially in the conversion of rich free fatty acid oils and fats.

CONCLUSIONS

The m-PSZ catalyst possessed high surface area, strong acidity, mesoporous structure. The catalyst could play an important role in many applications using superacid catalyst, especially in biodiesel synthesis from the rich free fatty acid feedstocks.

The biodiesel synthesis using vegetable oil deodorizer distillate over mesoporous oxo-phosphated sulfated zirconia (m-PSZ) showed a very high potential for applying this kind of catalyst in many other biodiesel production processes, especially in the conversion of rich free fatty acid oils and fats. The refined biodiesel specifications met almost with the major specifications for biodiesel in commercial usage. The catalyst could be recycled for 9 times demonstrating its stability in the reaction media.

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AUTHOR ADDRESS

1. **Hong Khanh Dieu Nguyen**

Hanoi University of Science and Technology, Vietnam.

Email: dieuhongprof@gmail.com