

Production of Biodiesel Production from *Castor* Oil Using Modified Montmorillonite Clay

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IN THIS study, *castor* oil was used to produce biodiesel via transesterification reaction in present of methanol. The reaction was performed using novel modified montmorillonite catalyst (heterogeneous catalyst). The prepared catalysts were characterized by the HR-TEM, XRD, IR, and N₂-adsorption. The transesterification reaction was carried out using different oil /methanol molar ratios (1:3), (1:6), (1:9), and (1:12). Various amounts of catalyst were used ranged from 1 to 7 wt.% and reaction time from 1 to 5 hr in temperature range of 40 to 70°C. The optimized conditions of the transesterification reaction of *castor* oil were pointed at 12:1 methanol to oil molar ratio and 5 wt.% catalyst at 60 °C for 5 hr. The catalyst was reusable for 7 times. The fuels produced were characterized and found to have closed properties to conventional petroleum diesel.

Biodiesel is a mixture of fatty acid methyl esters (FAME) obtained from vegetable oil by the transesterification reaction. In recent years, many researchers were concentrated their effort to develop biodiesel from alternative and renewable sources to replace commercial petroleum products⁽¹⁾. Biodiesel has received increasing attention due to it's a renewable energy resource, less polluting, superior lubricity, high cetane number, high flash point and high biodegradability, and its natural resources opposed to conventional diesel⁽²⁾. The suitable properties of plant oils and animal fats (renewable and low sulfur, nitrogen and heavy metal content), which are made up of triglycerides with long chained fatty acid groups 16 to 24 carbon atoms in length, make them ideal sources for the production of biodiesel^(3,4). From a list of 75 plant species⁽⁵⁾ containing oil in their seeds or kernels, 26 species have potential sources for biodiesel production. Some examples of non-edible oil seed crops as palm⁽⁶⁾, cotton seeds oil⁽⁷⁾, *Jatropha* oil⁽⁸⁾, and waste cooking oil⁽⁹⁾ studied as feedstocks for production of biodiesel. Studies on *castor* oil suggested that their uniquely high content of ricinoleic acid, with a hydroxyl group, is the reason for *castor* oil with high viscosity and density. It is also characterized by its high stability and high hygroscopicity. Ability of *castor* oil to solubilize in alcohol, affects the transesterification reaction⁽¹⁰⁾. Heterogeneous catalysts are feasible economically due to the reusability of catalyst for both batch and continuous process and cost

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effective due to easy separation ^(11,12). Thus, the present study focuses on exploiting transesterification of *castor* oil as a source of biodiesel by using modified montmorillonite catalyst as heterogeneous catalyst. The optimization of transesterification reaction was studied including several reaction parameters. The obtained biodiesel was characterized and compared by the ASTM or EN standards.

Material and Methods

Materials used

Castor oil was extracted from its dried seeds. Chemicals used for the synthesis of catalyst and production of biodiesel were: montmorillonite, dodecyl amine, tetraethyl orthosilicate (TEOS), trimethoxy phenyl silane, 1, 2-dichloroethane, dichloromethane, chlorosulfonic acid, n-hexane, 2-propanol, methanol, were obtained in their analytical grade from ADWIC chemicals company, Egypt.

Extraction of castor oil

The oils were obtained by mechanically pressing of the dry seeds. The obtained virgin oils were centrifuged to remove the contaminated solids and water ⁽¹³⁾.

Synthesis of Montmorillonite (MMT) catalyst

Acidic MMT (5 g) is swelled in 250 ml distilled water for 2hr. Then, the swelled MMT and 13.5 g of dodecyl amine dissolved in 2-propanol (200 ml) were charged in 500 ml round flask under mechanical stirring for 2 hr. TEOS (50 ml) was then added to the reaction matrix and aged for 4 hr at room temperature. At the end of the reaction, a white precipitate was obtained. The product was filtered, washed by acidified distilled water, dried in oven at 75 °C, and finally air calcined at 600 °C for 5 hr. The product was denoted as Si-MMT.

Phenyl functionalized Si-MMT catalyst was synthesized by post grafting reaction using trimethoxyphenylsilane. Si-MMT (5 g) was dispersed in n-hexane (100 ml) for 30 min in 500 ml round flask and then trimethoxyphenylsilane (2.5 g) was added to reaction medium under stirring and refluxed for 6 hr. After cooling to room temperature, the precipitate was filtered off, washed by excess dichloromethane and finally dried under vacuum at 50 °C for 2 hr. The product was denoted as Si-MMT-Ph.

Si-MMT-Ph catalyst (6 g) was dispersed in 1,2-dichloroethane (100 ml) as a solvent and chlorosulfonic acid (3 g) were charged in added in 250 ml round flask at 0 °C and vigorously stirred for 12 hr at 50 °C. Then, the reaction medium was concentrated by evaporating the solvent using rotatory evaporator. The obtained precipitate was filtered off, washed several times by 1, 2-dichloroethane and dried in vacuum oven at 50 °C. The product was denoted as Si-MMT-Ph-SO₃H.

Tranesterification of oil

Tranesterification reaction of *castor* oil was carried out in a round bottom flask (250 ml). Generally, the transesterification reaction was preceded by mixing the methanol, oil and catalyst. Then, the matrix was heated in autoclave under stirring condition for the desired reaction time. At the end of the reaction, excess methanol was removed under reduced pressure. Then, the reaction matrix was allowed to cool to room temperature, centrifuged to separate the different phases. After centrifugation, three layers were separated: the upper phase is the obtained biodiesel; the middle phase which contains the produced glycerol, and the lower phase contained the catalyst in glycerol. The obtained biodiesel was collected and stored in refrigerator for further analysis.

Castor oil and biodiesel specifications

The following data were determined for *castor* oil: fatty acid composition, saponification value, iodine value, acid value, photometric color, water content, and oil percent in *castor* seeds. The characteristic specifications of the produced biodiesel including: kinematic viscosity (at 40 °C), iodine value, density, cetane number, pour point, cloud point, flash point, and fire point were determined. These properties were determined according to ASTM specifications^(14–21).

Results and Discussion

Catalyst characterization

XRD patterns of MMT, Si-MMT and MMT-Ph-SO₃H are shown in Fig. 1. The diffraction pattern of K10-MMT is indicative of a main contribution of the mineral family corresponding to a typical smectite MMT. Compared to the MMT sample, Si-MMT and MMT-Ph-SO₃H showed an obvious shift in 2θ values at 8.85° towards lower angles, and there is a slight decrease in the relative intensities of the XRD reflections of MMT. That supports the grafting of trimethoxyphenylsilane between MMT galleries.

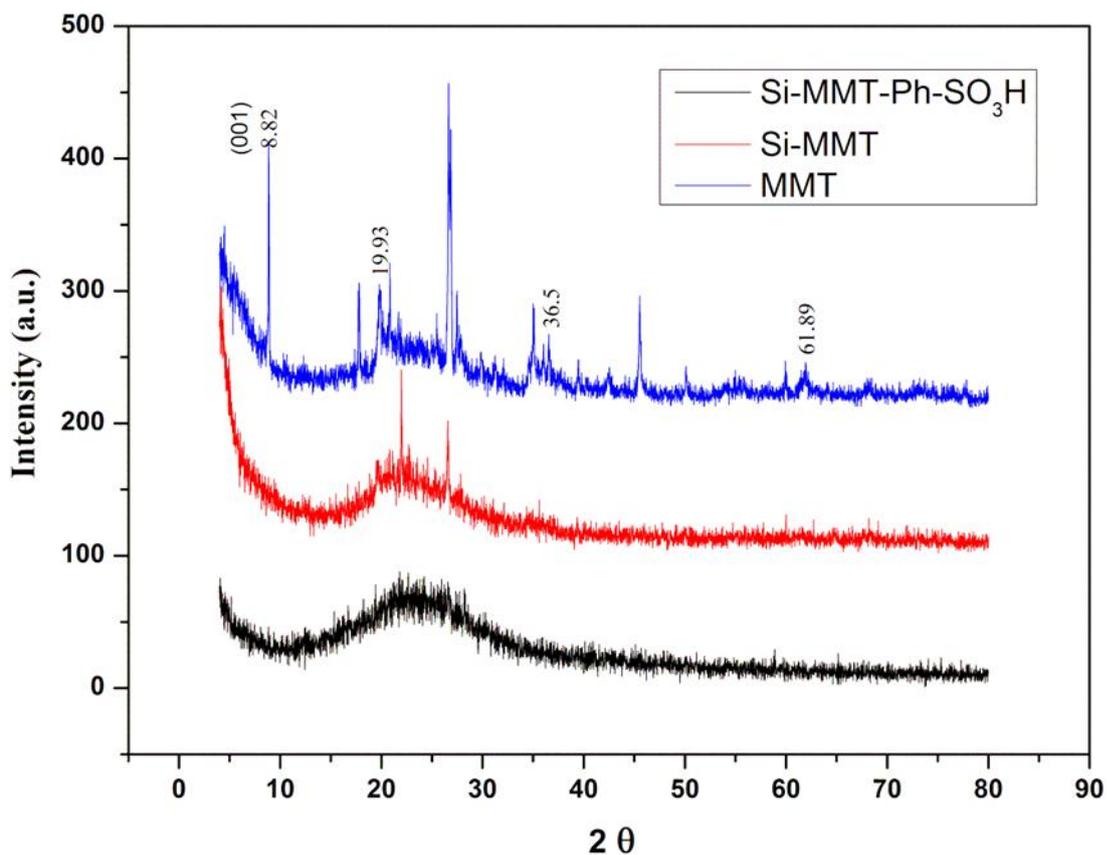


Fig. 1. XRD powder patterns of MMT, Si-MMT and SiMMT-Ph-SO₃H samples.

The HRTEM images of MMT, Si-MMT and MMT-Ph-SO₃H materials are shown in Fig. 2. The results showed that MMT is composed of stacking layers in agreement to the typical layered materials.

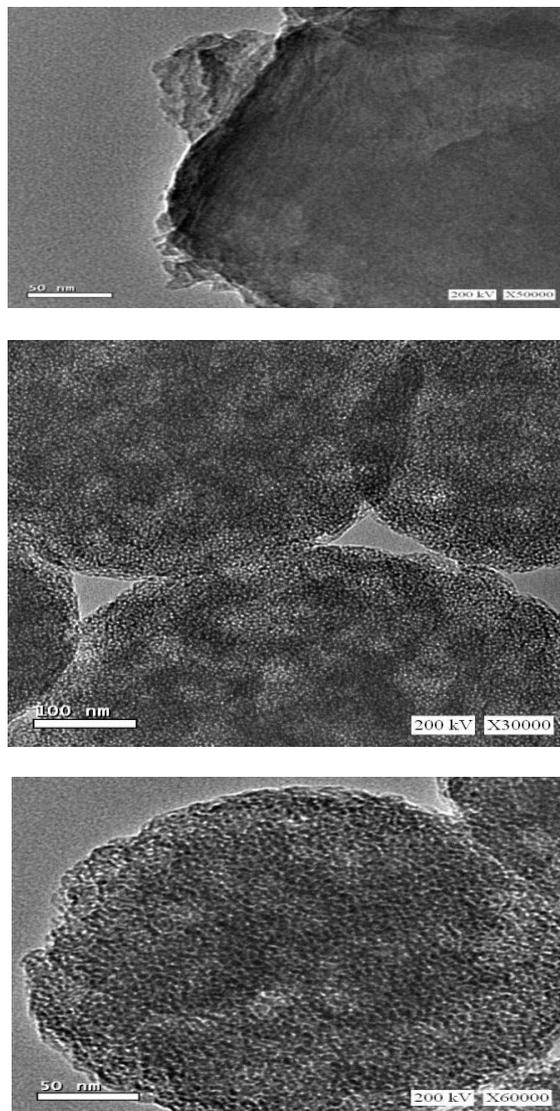


Fig. 2. HRTEM of MMT, Si-MMT and Si-MMT-Ph-SO₃H materials.

The BET isotherm curves of MMT, Si-MMT and MMT-Ph-SO₃H are shown in Fig. 3 and the data listed in Table 1. MMT shows Type IV isotherm with large H3 hysteresis loop illustrative of layered materials, in accordance with acid activated montmorillonite-based materials⁽²²⁾. The presence of H3 hysteresis loop indicates that MMT has an irregular porous structure.

TABLE 1. Surface properties of various samples prepared.

Sample	Surface area ($\text{m}^2 \text{g}^{-1}$)	(Pore radius (\AA))	Pore volume ($\text{cm}^3 \text{g}^{-1}$)
MMT	220	7.5, 14.7 & 24.5 (Board)	0.342
Si-MMT	795	17.2	0.96
MMT-Ph-SO ₃ H	260	17	0.39

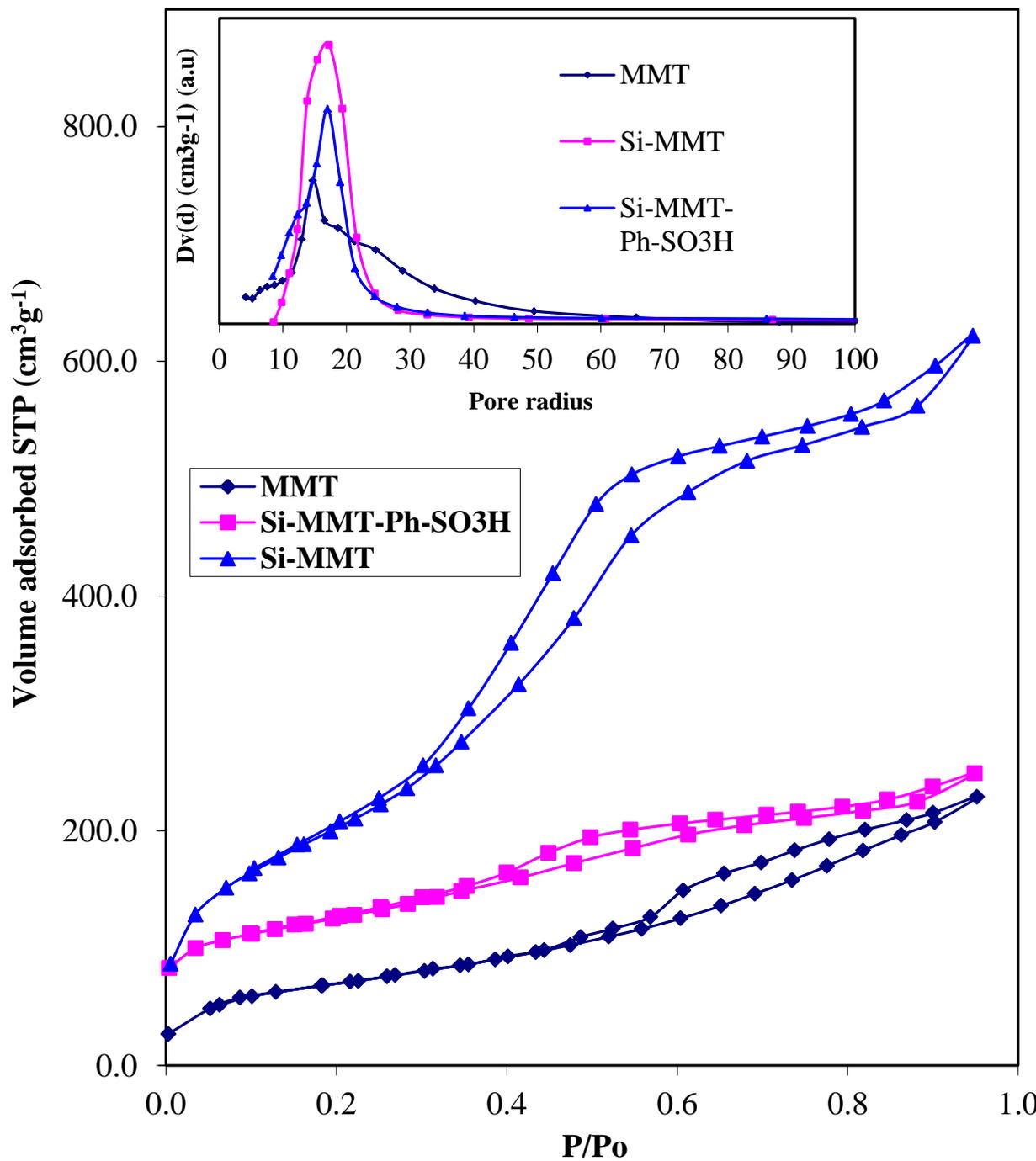


Fig. 3. Nitrogen adsorption isotherms and pore size distribution of MMT, Si-MMT and Si-MMT-Ph-SO₃H samples. Curves are plotted offset for clarify.

The FT-IR spectrum of the sample is shown in Fig. 4. The spectrum of Si-MMT is similar to pure MMT.

The Si-MMT-Ph-SO₃H showed broadband at 3100 cm⁻¹ is due to stretching –C=C, the band at 888 cm⁻¹ and 875 is resulted from phenyl moieties, indicates the presence of phenyl rings. Moreover, the asymmetric and symmetric stretching vibration bands at 1330, 1183 cm⁻¹ are represented SO₂ in SO₃H group are seen, indicating successful sulfonation.

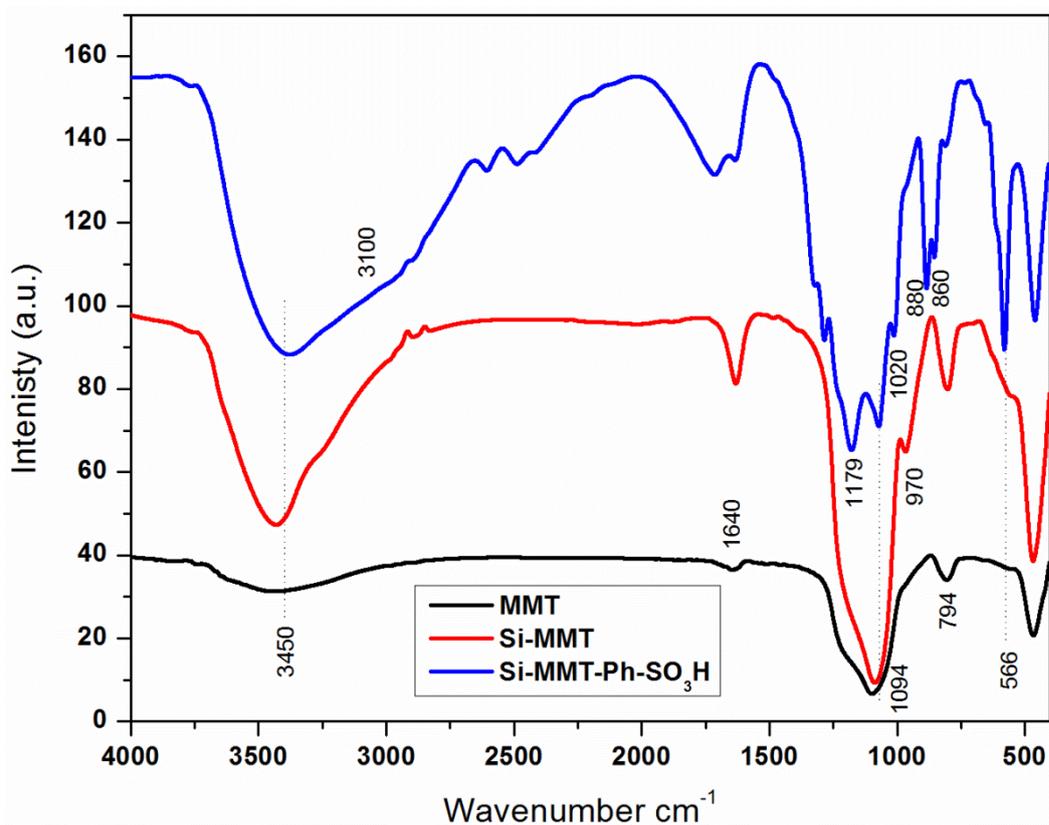


Fig. 4. FTIR spectra of MMT, Si-MMT and Si-MMT-Ph-SO₃H samples.

Optimization of transesterification reaction.

The catalytic activity of the synthesized catalyst montmorillonite (MMT) was evaluated for the transesterification reaction of *castor* oil at the identified reaction conditions, such as the reaction temperature of 60 °C, methanol to oil molar ratio of 12:1, reaction time of 300 min, agitator speed of 800 rpm and catalyst loading of 5 wt%. Catalyst shows the best catalytic performance in the transesterification reaction and provides the maximum biodiesel yield of 89.8 % in the 300 min.

The reaction parameters were varied to obtain the optimized transesterification reaction conditions in order to obtain the maximum yield from biodiesel with least economic cost reaction and provide the maximum biodiesel.

The studied reaction parameters were: - oil to methanol ratio, catalyst percent ratio, reaction time, and reaction temperature.

The transesterification reaction of *castor* oil was performed at 60 °C for 5 hr in the present of 5% catalyst ratio relative to oil at 800 rpm. While, reaction was performed at different oil-to-methanol ratio of: 1:3, 1:6, 1:9, 1:12, using Montmorillonite catalyst (MMT).

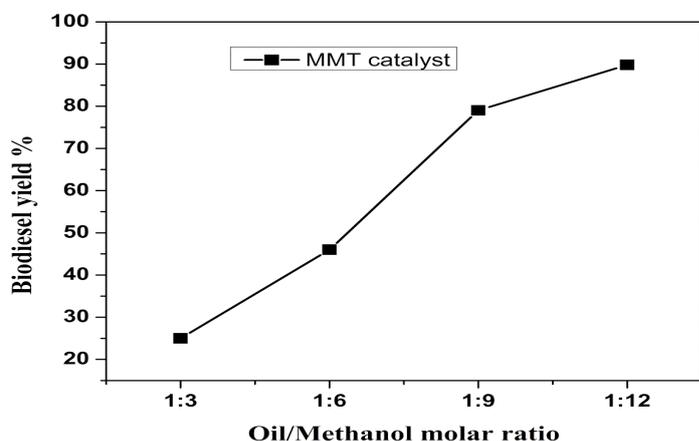


Fig. 5. Effect of Oil to methanol molar ratio on biodiesel yield in transesterification reaction of *castor* oil using 5 wt.% MMT catalyst at reaction temperature 60 °C, reaction time 300 min and stirring speed of 800 rpm.

From Fig. 5, it is clear that the gradual increase of oil to methanol ratio increases the conversion ratio of *castor* oil into their corresponding biodiesel.

The maximum conversion ratio of *castor* oil was 89.8% which obtained at 1:12 ratio of oil –to-methanol. The obtained results are in agreement with the reported results⁽²²⁻²⁵⁾.

The effect of the used catalysts concentration on the transesterification reaction of *castor* oil was varying by increasing the catalyst wt.% from 1% to 7%, relative to oil weight. The results of *castor* oil transesterification showed that the gradual increasing of the catalyst concentration is gradually increasing the yield percent of the biodiesel. The maximum yield obtained was 89.8% at 5% of MMT, respectively. Increasing the catalyst concentration more than 5% has no considerable effect on the yield percent (Fig. 6).

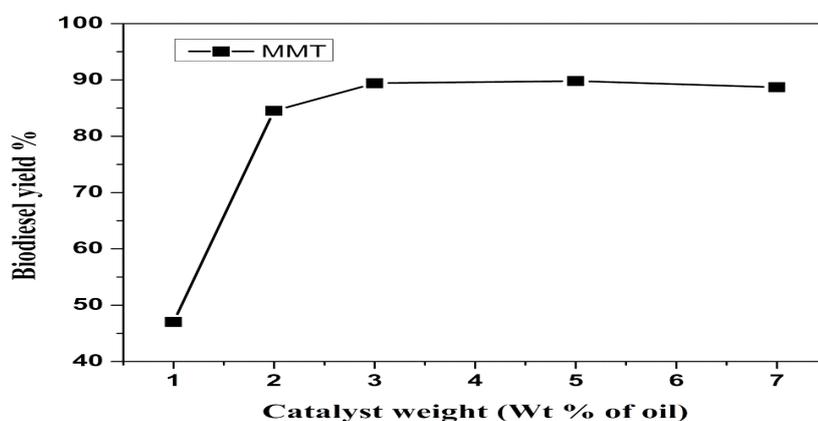


Fig. 6. Effect of catalyst amount on biodiesel yield in transesterification reaction of *castor* oil using oil to methanol molar ratio 1:12 at reaction temperature 60 °C, reaction time 300 min and stirring speed of 800 rpm.

The gradual increase of biodiesel yield % by increasing the catalyst concentration is attributed to the increase of catalytic active sites participated in the reaction.

From Fig. 6, the optimum catalyst concentration which is suitable for *castor* oil is 5 % relative to the weight of the used oil. These results are in good agreement with the published data reported on the use of heterogeneous catalysts in transesterification reaction of *castor* oil⁽²⁶⁻²⁸⁾.

The transesterification reaction of vegetable oils is catalyzed by the effect of temperature. Generally, increasing the reaction temperature leads to increase the reaction rate and the reaction yield. The influence of temperature increasing was studied at the following condition: - 5wt. % of catalyst, 1:12 oil to methanol ratio for 300 min at 800 rpm in case of *Castor* oil in a temperature range of (40-70 °C), and 5 wt.% of catalyst (Fig. 7).

The increase of reaction temperature increases the yield % of biodiesel. The maximum yield % was 89.8% MMT catalyst at 60 °C. While, increasing the reaction temperature above 60 °C to approximate 70 °C leads to decrease the biodiesel yield %. The maximum yield % was 86.4%. The obtained results are in parallel with the reported date ⁽²⁹⁻³¹⁾. From Fig. 7, it can be concluded that the optimum temperature of transesterification reaction for *castor* oil are 60 °C using the synthesized MMT catalyst.

The conversion of vegetable oils into biodiesel using heterogeneous catalysts was increased by increasing the time of reaction. At a certain time (maximum time), the yield % of biodiesel reached the maximum and no further increase can be obtained, Fig. 8. ⁽³²⁻³⁴⁾.

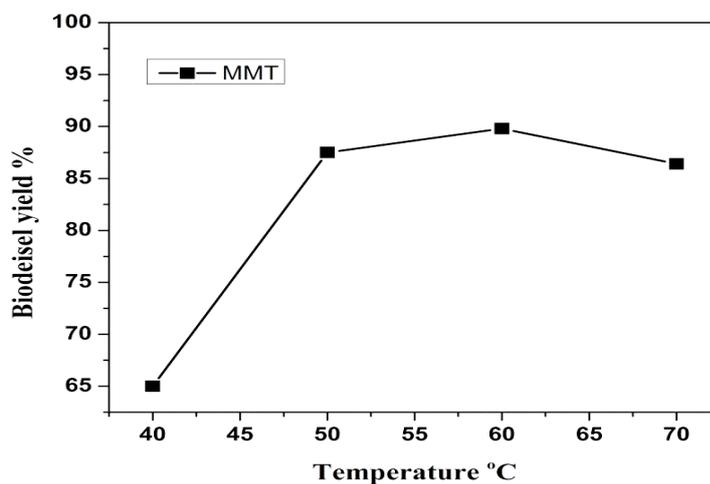


Fig. 7. Effect of temperature on biodiesel yield in transesterification reaction of *castor* oil using 5 wt.% MMT, oil to methanol molar ratio 1:12, reaction time 300 min and stirring speed of 800 rpm.

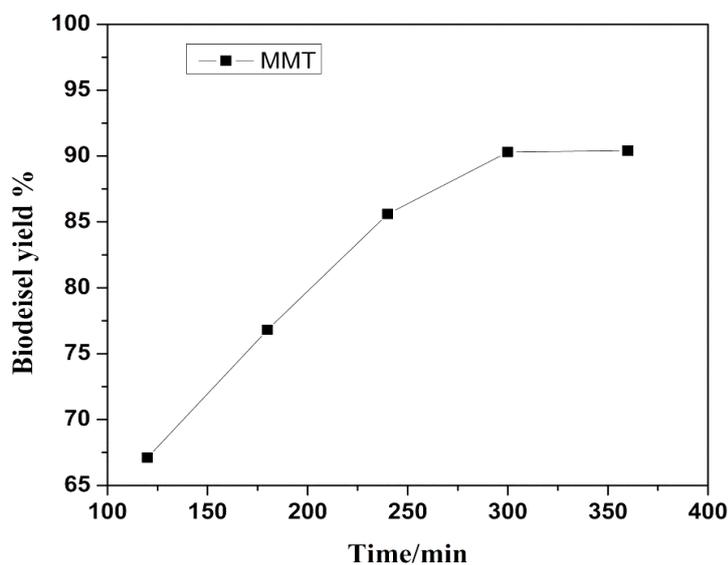


Fig. 8. Effect of reaction time on biodeisel yield in transesterification reaction of *castor* oil using 5wt.% MMT catalyst at reaction temperature 60°C, oil to methanol molar ratio 1:12 and stirring speed of 800 rpm.

It is clear that the increasing of the reaction time increases the yield % of the produced biodiesel. The maximum yield % was obtained after 300 min.

Normally, the reaction proceeded to the right side direction of biodiesel formation and at the longer time starts to reverse the product to the backward reaction of transesterification reaction⁽³⁵⁻⁴⁷⁾. That results in reduction of the biodiesel yield %^(38, 39). From Fig.8, the optimized time of transesterification reaction of *castor* oil at 300 min.

Catalyst reusability

The reusability is an important characteristic in using heterogeneous catalysts. That is due to the economic impact of the catalyst used decreases the whole cost of the operation.

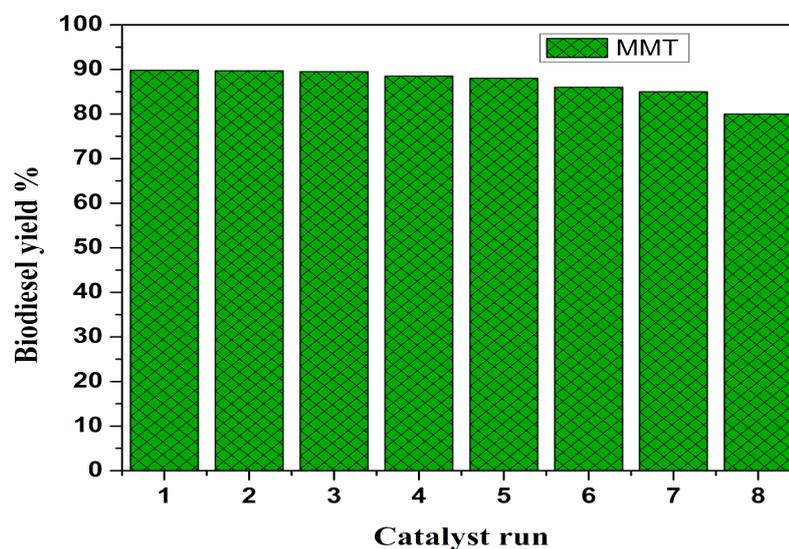


Fig. 9. Reusability profile of the MMT catalysts.

It is clear from Fig. 9, that the MMT catalysts have good reusability during the transesterification reactions of *castor* oil; the first trial gave biodiesel yielded 89.8%. Repeating the reaction using the same used catalyst after activation for two times gave identical products %. Further using of the catalyst after activation is gradually. Decreasing the yield % of the biodiesel to reach to 85 at the seventh round. Higher rounds showed a significant depression in the yield % of the biodiesel.

Physicochemical properties of the synthesized biodiesel

The physicochemical properties of the biodiesel were analyzed and compared to those reported in literature, and are found to be within the limits set by the ASTM D-6751 and the European Standard EN 14214 (Table 2).

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This shows that the *castor* oil used in this study has immense potential to be used in large scale biodiesel production using the modified montmorillonite clay.

Conclusion

- 1- Modified montmorillonite clay showed good activity in transesterification of *castor* oil.
- 2- *Castor* oil can be used as efficient and economic source of biodiesel.
- 3- Montmorillonite Modified clay has excellent reusability.

- 4- The fuel obtained the *castor* oil and synthesized catalyst has acceptable standard properties according to ASTM and EU standards.

TABLE 2.The physicochemical properties of the biodiesel.

Property	Test method	Test limits	Biodiesel Value
Specific gravity	ASTM-14214	0.860-0.900	0.9183
Kinematic viscosity at 40°C	ASTM D445	4.0 to 6.0	6.89
Flash point, °C	ASTM D93-94	100-170	176
Cloud point, °C	ASTM D2500-91	-3 to 15	-6
Pour point, °C	ASTM D97-93	-5 to 10	-18
Boiling point, °C		315-350	356
Cetane number	ASTM D613	48 - 65	54
Sulfur, wt%	ASTM D5453-93	0.0 - 0.0024	0.001

References

1. Issariyakul, T., Dalai, A. K. and Desai P., *Am Oil Chem J. Soc.* **88**, 391 (2012).
 2. Shashikant, V. G. and Hifjur, R., *Biomass Bioenergy.* **5**, 28 (2011).
 3. Krawczyk, T., Biodiesel- alternative fuel makes inroads but hurdles remains, *Inform.*, **7**, 801 (2005).
 4. Bridgewater, A. V. and Cottam, M.L., *Energy Fuel.* **6**, 113 (2010).
 5. Murphy, D. J., *Trends Biotechnolo.*, **14**, 206 (2012).
 6. Sang, O. Y., *Energy Sour Part A Recover Utile Environ Effects.* **25**, 859 (2003).
 7. Li, H., Yu P. and Shen, B., *Fuel Process Technol.* **90**, 1087 (2009).
 8. Biswas, S. and Sharm, D. K., *J Anal Appl Pyrolysis.*, **52**,110 (2014).
 9. Tang, X. and Wei, F., *Fluid Eng.*, **7**, 12 (2010).
 11. Hara, M., *Chem. Sus. Chem.*, **2**, 129 (2009).
 12. Berman, P., Nizri, S. and Wiesman, Z., *Biomass Bioenergy*, **35** , 2861 (2011).
 13. Aldrich handbook of fine chemical laboratory equipment, Sigma- Aldrich; (2003).
 14. Firestone, D., *Official Methods and Recommended Practices of the American Oil Chemists' Society.* 5th ed. AOCS Press; Champaign (Method Ca 5a-40)(2003).
 15. Firestone, D., *Official Methods and Recommended Practices of the American Oil Chemists' Society.* 5th ed. AOCS Press; Champaign (Method Ja 6a-40) (2003) .
- Egypt. J. Chem.* **59**, No. 6 (2016)

16. **Firestone, D.**, *Official Methods and Recommended Practices of the American Oil Chemists' Society*. 5th ed. AOCS Press; Champaign (Method Cd 3–25) (2003).
17. **Firestone, D.**, *Official Methods and Recommended Practices of the American Oil Chemists' Society*. 5th ed. AOCS Press; Champaign (Method Cc 7–25) (2003).
18. ASTM D 445. Standard test method for kinematic viscosity of petroleum products. West Conshohocken: American Society for Testing and Materials International; (2010).
19. ASTM D 93. Standard test method for flash point of petroleum products. West Conshohocken: American Society for Testing and Materials International; (2010).
20. ASTM D 2500. Standard test method for cloud point of petroleum products. West Conshohocken: American Society for Testing and Materials International; (2010).
21. ASTM D 97. Standard test method for pour point of petroleum products. West Conshohocken: American Society for Testing and Materials International; (2010)
22. **Mishra, T., Parida, K.M. and Mater, J.**, *Chem.* **7**, 147 (2012).
23. **Meher, L.C., Vidya S.S. and Dharmagadda S.N.N.**, *Bioresource Technol.* **7**, 97 (2006).
24. **Zhang, Y., Dube, M.A., Mclean, D.D. and Kates, M.**, *Bioresource Technol.* **90**, 229 (2015).
25. **Atadashi, I.M., Aroua, M.K., Abdul Aziz, A.R. and Sulaiman, N.M.N.**, *Journal of Industrial and Engineering Chemistry*, **19**, 14 (2013).
26. **Wang, X., Liu, X., Zhao, C., Ding, Y. and Xu, P.**, *Bioresource Technol.* **102**, 6352 (2011).
27. **Baskar, G. and Soumiya, S.**, *Renewable Energy*, **98**, 101 (2016).
28. **Chen, G. Y., Shan, R., Shi, J.F. and Yan, B.B.**, *Fuel Process Technol.* **133**, 8 (2015).
29. **Samart, C., Sreetongkittikul, P. and Sookman, C.**, *Fuel Processing Technology*, **90**, 922 (2009).
30. **Liu, X., He, H., Wang, Y., Zhu, S. and Piao, X.**, *Fuel.*, **87**, 216 (2014).
31. **Long, T., Deng, Y., Gan, S. and Chen, J.**, *Chinese Journal of Chemical.*, **87**, 210 (2009).
32. **Tyagi, B., Chudasama, C.D. and Jasra, R.V.**, *Spectrochim. Acta, Part A.*, **64**, 273 (2006).
33. **Santana, A., Maçaira, J. and Larrayoz, M.A.**, *Fuel Processing Technology*. **102**, 110 (2012).
34. **Taufiq-Yap, Y.H., Lee, H.V., Hussein, M.Z. and Yunus, R.**, *Biomass and Bioenergy*, **35**, 827 (2011).

35. Alamu, O.J., Waheed, M.A., Jekayinfa, S.O. and Akintola, T.A., *Agric EngInt: CIGR Ejournal IX* (2007).
36. Leung, D.Y.C. and Guo, Y., *Fuel Process Technol* **87**, 883 (2006).
37. Dennis, Y.C., Leung, Xuan, W.U. and Leung, M.K.H., *Applied Energy*. **87**, 1083 (2015).
38. Eevera, T., Rajendran, K. and Saradha, S., *Renew, Energy.*, **34**, 762 (2011).
39. Ma, F., Clements, L.D. and Hanna, M.A., *Trans Am Soc Agric Eng.*, **41**, 1261 (1998).

(Received 4/10/2016:
accepted 11/10/2016)

انتاج وقود الديزل الحيوى من زيت الخروع باستخدام المونتمورلنيت المحسن كنوع من انواع الطفله

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تتجه هذه الدراسه الى انتاج وقود الديزل الحيوى من زيت الخروع عن طريق تفاعل الاستره فى وجود الميثانول ويتم تحفيز هذا التفاعل باستخدام المونتمورلنيت المحسن كعامل مساعد غير متجانس . يتم قياس خواص الحفاز المحضر باستخدام بعض اجهزه التحليل الحديثه مثل:- جهاز قياس مساحه السطح-جهاز قياس البلورات لاشعه الحبيود السينيه- النافذ الالكترونى الضوئى- جهاز الاشعه تحت الحمراء اجراء عمليه الاستره لزيت الخروع باستخدام الحفاز المحضر، ويعتمد قياس كفاءه الحفازات المحضره على كميته وقود الديزل الحيوى الناتج من عمليه الاستره باستخدام هذه الحفازات. وللحصول على اعلى انتاجيه من وقود الديزل الحيوى يجب ان تقوم بتقييم الحفازات للحصول على الظروف المثلى لعمليه الاستره وكذلك دراسه بعض العوامل المؤثره على التفاعل وهى:-
 1- تعيين نسبة الكحول الى الزيت المستخدم التى تعطى اعلى انتاجيه من وقود الديزل الحيوى وبعد الدراسه تبين ان اقصى نسبة فى زيت الخروع هى 1:12
 2- وكانت النسبه الامثل لكميه الحفاز الى الزيت هى 5% - تعيين اقل نسبة من كميته الحفاز المستخدم الى الزيت للحصول على افضل انتاجيه.
 3- تعيين درجه الحراره التى تعطى اعلى كفاءه لانتاجيه وقود الديزل الحيوى وكانت افضل درجه حراره فى زيت الخروع هى 60 درجه سيلزيه.
 4- تعيين الوقت الامثل للتفاعل وكان افضل وقت للتفاعل فى الخروع 300 دقيقه.
 - اخيرا بدراسه الخواص الفيزيائيه لوقود الديزل الحيوى الناتج من زيت الخروع والجائز وفا تبين ان وقود الديزل الحيوى الناتج مطابق لمواصفات القياس العالميه