

Transesterification of Sunflower Oil Using Heterogeneous Catalyst Derived From Date Seeds of South Algeria.

**M. Khelafi^{1,2*}, S . Kalloum⁴, A. Boulal¹, N. Mansir³, Y. Bakache¹,
Y.H. Taufiq-Yap³**

¹Unité de Recherche en Energies Renouvelables en Milieu Saharien, URERMS, Centre de Développement des Energies Renouvelables, CDER, 01000, Adrar, Algeria

²UnivOuargla, Fac. Faculté des sciences appliquées, Dépt.Génie des Procédés, Ouargla 30 000, Algeria

³Catalysis Science and Technology Research Centre, Faculty of Science, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia

⁴Laboratoire d'énergie, environnement et système d'information, Université Ahmed Deraya, Adrar, Algerie

Abstract : Date Seeds (DS) were transformed into catalyst by calcining them at various temperatures. The produced catalyst was fully characterized by SEM, XRF, and BET analyses. The basicity of the catalyst was determined using CO₂-TPD technique.

The catalytic efficiency of the prepared catalyst was tested in the transesterification of sunflower oil with methanol. The effect of calcination temperature on the yield of Fatty Acid Methyl Ester (FAME) was investigated. In addition the transesterification process was optimised. In this study, the effect of FFA (Free Fatty Acid) on FAME yield was also investigated. The results show that the produced catalyst from date seeds is a good catalyst for biodiesel production reaction. The maximum biodiesel yield reached about 96.7% under the optimal conditions.

Keywords : Biodiesel ,transesterification, vegetable oil, heterogeneous catalyst, date seeds.

1. Introduction

Biodiesel is alternative fuel which produces low emissions of CO₂. It is renewable, bio-degradable, non-flammable, non-toxic, and free from sulfur¹. Many of studies have been investigated to produce biodiesel with different kinds of vegetable oils, such as sunflower oil², palm oil³, soybean oil⁴, rapeseed oil⁵ castor seed oil and cooking oil, as raw materials. Biodiesel can be easily produced through transesterification of oil using basic or acidic catalysts⁶. Homogeneous or heterogeneous catalysts can be used for biodiesel production. The use of homogeneous catalyst such as NaOH, KOH and CH₃ONa⁷ to produce biodiesel, possess major drawbacks specially in disposing the products via neutralization, and washing with a large volume of water⁸, these problems can be solved by using heterogeneous catalyst. These types of Catalysts are generally classified into base heterogeneous catalyst and acid heterogeneous catalyst and their sub classification are listed in the flow chart (Fig. 1)⁹. The solid base catalyst is found to be more active when compared to acid catalyst. There are several solid base catalysts studied for transesterification reaction such as magnesium oxide (MgO), calcium oxide (CaO), barium oxide (BaO), strontium oxide, titanium oxide, zinc oxide, mixed oxides catalysts and hydrotalcites¹⁰. solid base catalyst can be prepared also from Waste Material such as eggshell, Danlin Zeng and al.¹¹ reported that soybean oil was converted to biodiesel and achieved 99.1 wt% at the temperature of 65 °C in

2 h using 2 wt% of catalyst, derived from eggshell, and Methanol to oil molar ratio of 12:1. Another work realized by Osman NurSyazwani and al.¹ where they used Angel Wing Shell as source of catalyst for transesterification, and they reported that the calcined Angel Wing Shell at 900 °C was chosen as the best catalyst where it showed highest FAME yield (84.11%) at oil to methanol molar ratio 1:150 and catalyst loading of 9 wt.% in 1 h reaction time. In the present work Date Seed (DS) is used as source of heterogeneous catalyst for biodiesel production, The Algerian Sahara cities are considered as producing dates areas. According to the Agriculture Service Department, oasis dates cover an area of 165 thousand hectare with a number of 18 million palm and a production of 913,663 Qx of dates of different varieties per year (A SD2016), The seeds of these dates are considered as an unexploited byproduct, the purpose of our work is to value this significant amount of date seed and transform it into a catalyst for the transesterification reaction of vegetable oils in view of producing biodiesel.

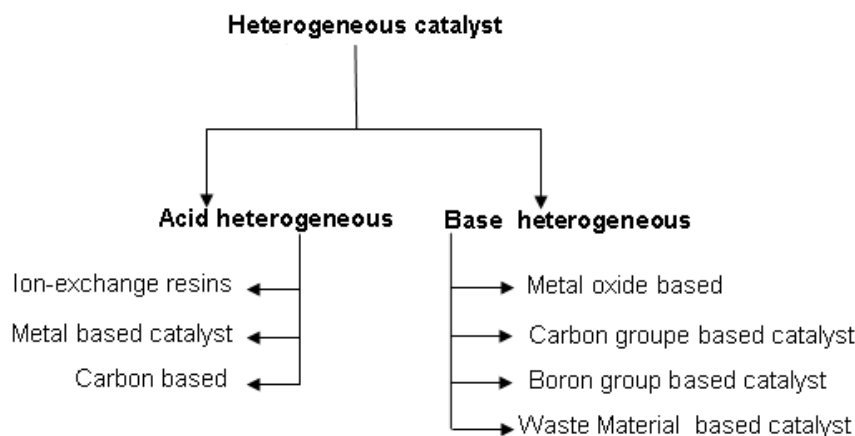


Fig.1 Classification of heterogeneous catalyst [9]

2 . Experimental

2.1. Material:

2.1.1 Vegetal substrate:

Phoenix dactylifera, commonly known as **date** or **date palm**, is a flowering plant species in the palm family, *Arecaceae*, cultivated for its edible sweet fruit. The date or fruit of date palm is generally elongated, oblong or rounded. It is composed of a seed, of a hard consistency, surrounded by a pulp. Date seed has an elongated shape and is of variable size. By weight, it represents 7 to 30% of that of the date. It is composed of a white albumen, hard and meat, protected by a cellulosic envelope of brown colour (fig.1)¹².



Fig.2: Fruit of date palm (b) and its seeds (a)

2.1.2. Chemical products

Sunflower oil was purchased in a local shopping store. The acid value and saponification value of this oil were 0.2 mg KOH/g and 195 mg KOH/g.

Analytical grade methanol 96% and 99.7%, HCl, K₂CO₃, Na₂SO₄, KOH were purchased from SIGMA-ALDRICH.

2.2. Methods:

2.2.1. Fatty acid compositions of sunflower oil

The fatty acid profiles of sunflower oil were evaluated using gas chromatography method. Prior to the injection, transmethylation was performed according to method described by Khanitta Ruttarattanamongko and all (2014)¹³. Gas chromatography analysis was performed on Thermo Scientific Trace 1300 Gas Chromatography, equipped with a flame ionization detector (FID) and connected to a polar BP-20 capillary column; 30 m in length and 0.5 mm internal diameter was employed. Helium was used as the carrier gas with a flow rate of 1.5 ml min⁻¹. The oven temperature was set at 120°C and rise up to 230°C with the heating rate at 5°C min⁻¹. Temperature for injector and detector were set at 250°C and 280°C, respectively. Injector split ratio was set at 50:1. The flow rates of air and hydrogen gas were set at 450 ml min⁻¹ and 40 ml min⁻¹, respectively. Obtained peaks were identified by comparison to the retention times of reference standards. Results are summarized in table1.

Table1:fatty acid compositions of sunflower oil

| Fatty acid | Relative composition (%) |
|------------|--------------------------|
| C16 | 6.0 |
| C18:0 | 3.0 |
| C18:1 | 15.2 |
| C18:2 | 74.3 |
| Others | 1.5 |

2.2.2. Catalyst preparation

Date Seeds (DS) were washed with distilled water then dried in an oven at 105°C for 24 hours. After drying, seeds were calcined in a muffle furnace at different temperatures (500, 600, 700, 800, 900°C) for 2 hours, with the ramp at 5°C/min.

2.2.3. Catalyst characterization:

The quantitative composition of the catalyst was determined by XRF spectroscopy using Firmware Version, XOS [HD MOBILE 1.2.6 IOP M2 10WPS S7 4SS].

Morphology of catalyst was investigated by using JEOLJSM-6400 Scanning Electron Microscopy (SEM).

CO₂ -TPD was used to evaluate the basicity of our catalyst, this experiment was carried out using a Thermo Finnigan TPD/R/O 1100 Series apparatus equipped with a thermal conductivity detector (TCD), the chemisorption of CO₂ was carried out by a CO₂ flow rate of 30 ml min⁻¹ for 1 h. The excess of CO₂ was then flushed with helium with flow rate 30 ml min⁻¹ for 30 min. Subsequently, desorption of CO₂ was proceed under helium as carrier gas from 50°C to 900°C with a ramp of 10°C min⁻¹ and soak for 10 min. Brunauer–Emmett–Teller (BET) surface area was measured using Micromeritics 3Flex analyzer.

2.2.4. Transesterification of Sunflower oil

The transesterification of sunflower oil was carried out in a round bottom flask equipped with a water cooled reflux condenser using methanol and calcined DS as catalyst, the system was heated by oil bath under given conditions: temperature (45 – 95 °C), time (0.5 –2 h), methanol/oil molar ratio (3/1–21/1),

catalyst dosage (1 – 7 wt%) and magnetic stirring (400 rpm). After reaction, solid catalyst was separated by centrifugation and the residual methanol was separated from the liquid product. The mass of the final product, i.e. biodiesel was measured for the determination of yield according to Eq. (1) ²⁵.

$$FAME \text{ Yield (\%)} = (\text{Weight of biodiesel} \div \text{Weight of oil}) \times 100 \quad (1)$$

Different parameters of produced biodiesel were measured: The flash point was determined by following method EN ISO 3679. The density at 15°C was measured according to ASTM method D4052 by using Densito30px Density Meter (METTLER TOLEDO), and the viscosity at 40°C was measured according to method EN ISO 3104. Cetane number was determined according to ASTM D976.

3. Results and Discussion

3.1. Catalyst characterization

3.1.1. Scanning electron microscopy (SEM)

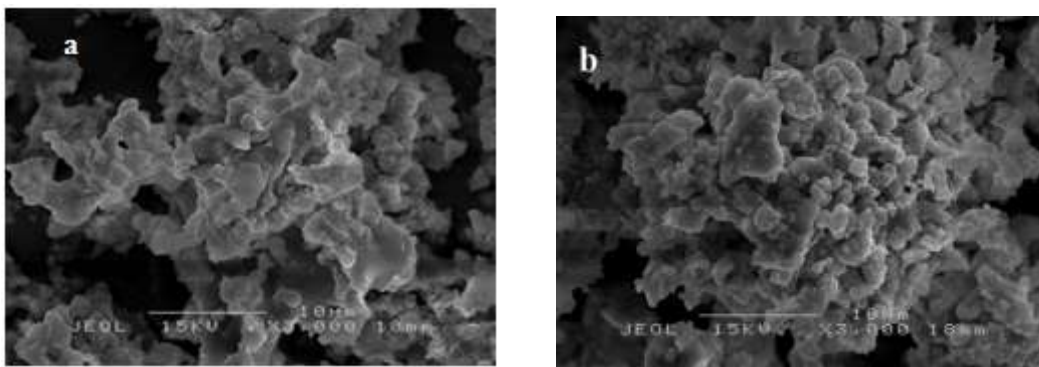


Fig.3. SEM of Date Seeds (DS) calcined at (a) 800°C and (b) 900°C.

Fig.3. (a) and (b) showed the SEM micrographs of the two catalysts. Catalysts calcined at 800°C and 900°C consisted of particles in diameter of 0.5 to 4 µm, The tow catalysts were irregular in shape, and some of them bonded together as aggregate, the catalyst calcined at 900°C showed large aggregated particles, which may be formed by sintering¹⁴.

3.1.2. BET analysis of the catalyst

As shown in Table 2, DS calcined at 900°C (DS 900) presented lower specific surface area and larger average pore sizes than DS calcined at 800°C (DS 800). This result indicated that when calcination temperature exceed 900°C it led to the decreases of the specific surface areas and increases of pore sizes of the catalyst, which were probably due to the sintering of DS 900 confirmed by the SEM results. With the increase of calcinations temperature from 800°C to 900°C, the BET specific surface decreased from 2.9481 to 1.9272 m².g⁻¹, and the average pore size increased from 2,138.6559 Å to 2,896.4043 Å.

Table 2: BET surface areas and average pore diameter of DS calcined at 800 °C and 900°C

| Parameter | DS 800 | DS 900 |
|----------------------------------|--------------------------------------|--------------------------------------|
| BET Surface Area | 2.948 m ² g ⁻¹ | 1.927 m ² g ⁻¹ |
| Adsorption average pore diameter | 2,138.65 Å | 2,896.40 Å |
| Desorption average pore diameter | 2,346.31 Å | 2,927.01 Å |

3.1.3. TPD-CO₂ analyses

Basic strength of the catalyst (DS 800 and DS 900) profile is shown in Fig. 4, DS 800 catalyst shows tow CO₂ desorption peaks at 620 °C and 450 °C attributed to desorption of CO₂ from the strong basic sites, another peak is observed at 160 °C attributed to desorption of CO₂ from the weak basic sites. When the

calcinations temperature is increased to 900 ° C, a decrease in the intensity of the peaks is observed with a low shift towards lower temperature values corresponding to a low basic strength.

Table 3 : XRF results for DS calcined at 800° C and 900°C

| Oxydes | DS 900(%) | DS 800(%) |
|--------------------------------|-----------|-----------|
| K ₂ O | 52.41 | 52.41 |
| Al ₂ O ₃ | 30.02 | 30.07 |
| Ca O | 5.55 | 5.49 |
| SiO ₂ | 3.03 | 3.01 |
| Fe ₂ O ₃ | 0.71 | 0.71 |
| CuO | 0.08 | 0.08 |
| MnO | 0.07 | 0.07 |
| Sr O | 0.11 | 0.10 |
| ZnO | 0.80 | 0.83 |
| Na ₂ O | 1.01 | 1.00 |
| C | 6.20 | 6.22 |
| Others ^a | 0.01 | 0.01 |

3.1.3. XRF analysis

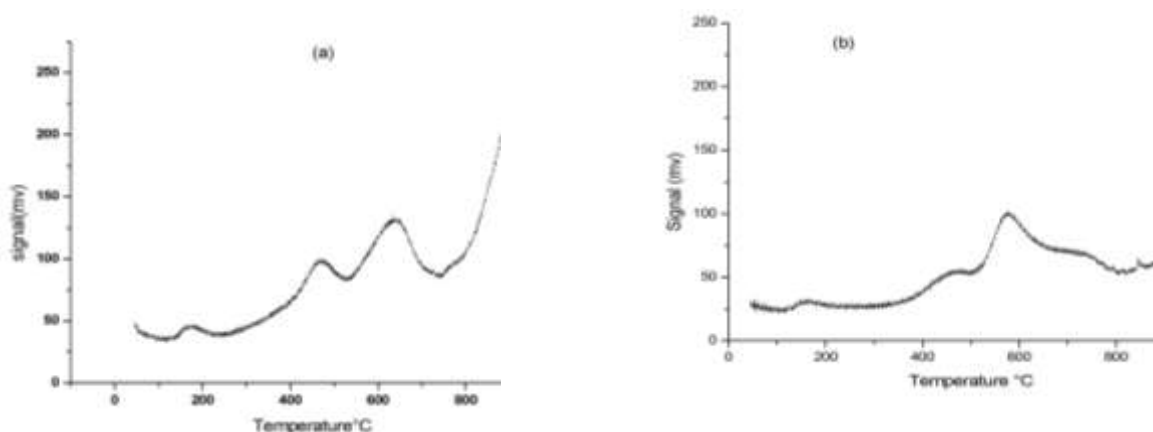


Fig.4. TPD-CO₂ of (a) DS 800 and (b) DS 900

^a**Others include:** BaO, Bi₂O₃, CdO, Co₃O₄, Cr₂O₃, NiO, PbO, TiO₂.

The mineralogical composition of the calcined DS is very complex due to vaporization, melting, crystallization, vitrification, condensation and precipitation, which occur during the high temperature combustion of organic products¹⁵.

DS was found to consist of a mixture of metal oxides and some organic compounds. As depicted in **Table 3**, K₂O and Al₂O₃ are the main composition of DS and they are highly basic, which explains the high basic strength reported earlier (TPD-CO₂ analysis).

The mineralogical composition of the DS calcined at 800°C is almost identical to that of the DS calcined at 900°C.

3.2. Transesterification reaction:

3.2.1. Effect of calcination temperature:

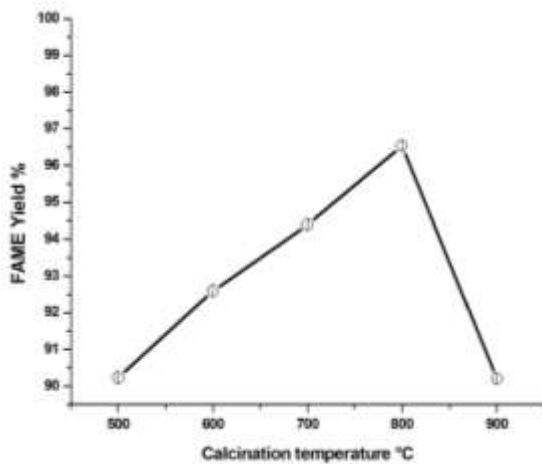


Fig.5. Effect of calcination temperature on the biodiesel yield using DS as catalyst with methanol to oil ratio 9/1, catalyst loading 3%, reaction time 1h, stirring rate 400 r.mn⁻¹, reaction temperature 65°C.

The catalytic activity of the calcined Date Seeds (DS) was investigated by varying temperature from 500°C to 900°C. As shown in figure 5, it could be seen that the best FAME yield (96.64%) had been obtained for a calcination temperature of 800°C, while at 900°C the FAME yield decrease from 96.64 to 90.21%. In association with the CO₂-TPD results, we can observe that the catalyst calcined at 800°C has a strong basicity than the catalyst calcined at 900°C. In accordance to Liu and all¹⁶ the stronger basicity was favourable for activating the methanol to form methoxide group. In addition, the decrease in catalytic activity can be contributed to the lower surface area of the DS calcined at 900 °C, which is illustrated by BET analysis.

3.2.2. Effect of reaction temperature

Reaction temperature is an important factor in the transesterification reaction. The effect of reaction temperature on FAME yield is shown in figure 6, as the temperature rose from 45 to 65 °C, the biodiesel yield increased. However, when the temperature was beyond 65 °C, the biodiesel yield decreased. At lower reaction temperature less than 65°C, the much decreased catalytic activities of the catalysts was due to the higher mass transfer resistance and solubility limitations^{16,17} At high temperature (more than 65°C) methanol kept boiling and caused the reaction to move backwards, decreasing the biodiesel yield¹⁸. The maximum biodiesel yield was 96.75% obtained at 65°C.

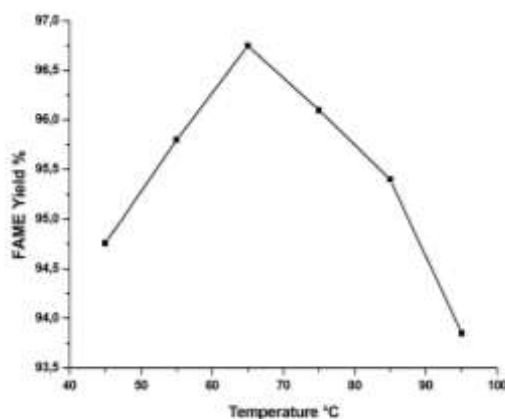


Fig.6. Effect of reaction temperature on FAME yield using DS calcined at 800°C with methanol to oil ratio 9/1, catalyst loading 3%, reaction time 1h, stirring rate 400 r.min⁻¹.

3.2.3. Effect of catalyst loading on biodiesel yield

The amount of catalyst to sunflower oil was studied ranging from 1.0 to 7.0 wt.%. Carried out under the fixed methanol-to-oil molar ratio of 9:1 at 65°C for 1h. The yield of FAME increased with the amount of the catalyst, and reached a maximum of 96.1% when 3 wt.% of catalyst was used. However, when the amount further increased to 7.0 wt.%, the biodiesel yield decrease to 92.36% (fig.7). This is mainly due the formation of multiphase mash under fast stirring and this would turn in resist stirring, causing to decrease the catalyst dispersion and consequently reduced the FAME yield production¹⁹. The same statements were also addressed by previous studies^{20,21}. Accordingly, 3.0 wt.% of catalyst dosage was suitable to obtain higher FAME yield.

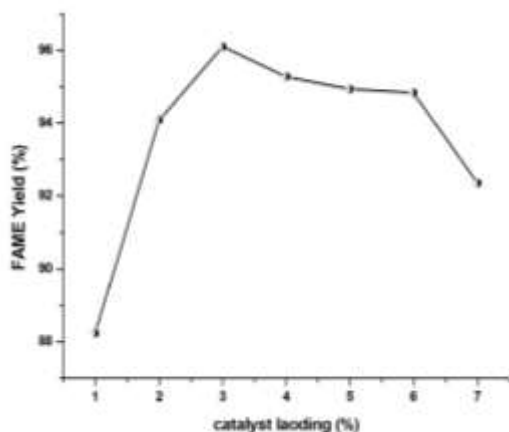


Fig.7. Effect of catalyst loading on FAME yield, calcination temperature 800 °C, reaction time 1 hour, temperature 65°C, methanol /oil ratio 9/1, stirring rate 400 r.mn⁻¹.

3.2.4. Effect of molar ratio methanol /oil

Fig. 8 shows the influence of the molar ratio of methanol to oil on biodiesel yield over DS calcined at 800°C. As the molar ratio of methanol to oil rose from 3/1 to 9/1, the density and viscosity of the reaction mixture was reduced and mixing was more efficient, contributing to the faster mass transfer and better availability of the catalytically active centers to the reacting molecules, as a result the biodiesel yield increased sharply²². A further increase of molar ratio of methanol to oil made weak increase of biodiesel yield. When the molar ratio of methanol/oil was over 9/1, we observe a decrease in biodiesel yield, because the excessive methanol made it difficult to separate the biodiesel from glycerol. The maximum yield (96.51%) was obtained for a molar ratio of 9/1.

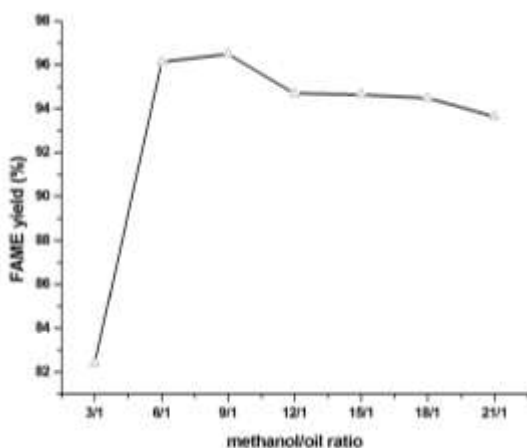


Fig.8. Effect of molar ratio oil/methanol on FAME yield, calcination temperature 800 °C, reaction time 1 hour, temperature 65°C, catalyst loading 3%, stirring rate 400r.mn⁻¹.

3.2.5. Effect of reaction time :

The effect of reaction time varying from 0.5 to 2 h on biodiesel yield was also investigated. At 1 h of reaction time, the nearly biodiesel yield was observed to be about 96.5 %. With further increase in reaction time, there was no obvious increase in the biodiesel yield. Hence, the suitable reaction time for biodiesel production was 1 h. fig.9.

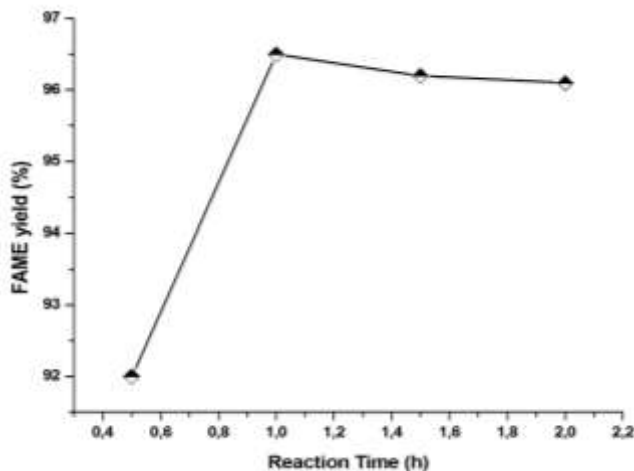


Fig.9. Effect of reaction time on FAME yield ,calcination temperature 800 °C, reaction time 1 hour, temperature 65°C, catalyst loading 3%, stirring rate 400 r.min⁻¹.

3.2.6. Effect of FFA

The base catalyzed reaction is reported to be very sensitive to the content of Free Fatty Acids (FFA), which should not exceed a certain limit recommended to avoid deactivation of catalyst²³. Zlatica and al. reviewed the literature and found that acid value of the feedstock for alkaline transesterification has to be reduced to less than 2 mg KOH/g (i.e. 1%)²⁴. To study the effect of FFA on the biodiesel yield, in the presence of the DS catalyst, we prepared three oil samples with different acid value (AV). The transesterification of these samples was carried out using different catalyst loading. The evolution of FAME yields for each sample is shown in figure 10. In this figure, it can be seen that the yield of biodiesel decreases with the increase of the acid value (from 90% to 76.7% when AV increases from 2 to 6 mg KOH.g⁻¹ at catalyst loading 3%) . On the other hand, increasing the catalyst loading improves the yield even at high values of acid number (from 76.7% to 92% when catalyst loading increases from 3% to 7% at AV 6 mg KOH.g⁻¹). This phenomenon can be explained according to the figure 11. which shows that the presence of FFA reduces the active surface area of the catalyst.

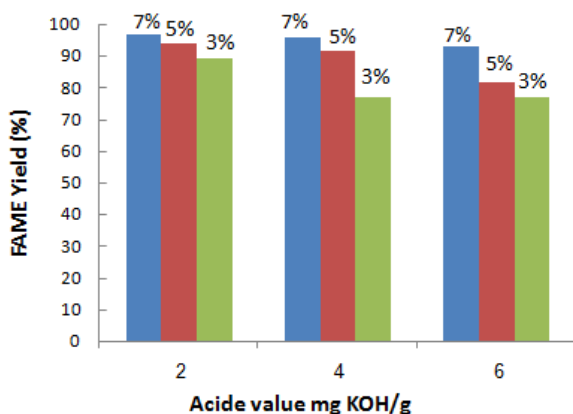


Fig.10.Effect of FFA on FAME yield at different catalyst loading, calcinations temperature 800 °C, reaction time 1 hour, reaction temperature 65°C, methanol / oil ratio 9/1, stirring rate 400 r.mn⁻¹.

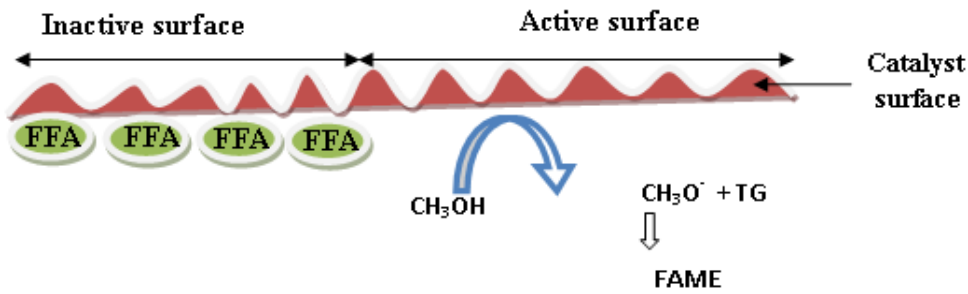


Fig.11.Demonstrative diagram of FFA effect on the catalyst efficiency. TG: Triglyceride

3.2.7. Physical properties of produced biodiesel

Table 4: Physical properties of produced biodiesel

| Property | Value | EN Standard | ASTM Standard |
|---|-------|-------------|---------------|
| Density at 15°C (Kg.m ⁻³) | 880 | 860-900 | - |
| Kinematic Viscosity at 40°C (mm ² .s ⁻¹) | 4.41 | 3.5-5.0 | 1.9-6.0 |
| Flash point (°C) | 140 | min 120 | min 130 |
| Cetane number CN | 49.6 | >51 | >47 |

The physical properties of produced biodiesel are tabulated in Table 4, kinematic viscosity, density, flash point and CN are within the limits specified by the European Standard EN 14214²⁵. The measured kinematic viscosity at 40 °C was slightly below the upper limit of 6.0 mm²/s. The measured density at 15 °C was slightly above the lower limit of 860 kg/ m³. The flash point of the biodiesel was 140 °C. The high flash point value ensures that the fuel is safe in terms of storage and transportation. the cetane number was predicted as 49.6.

4. Conclusion :

The results of this study revealed that the catalyst synthesized with the seeds date had a prominent catalytic activity in the transesterification of sunflower oil with methanol for biodiesel production. Utilization of these material reduces the catalyst cost because it can be prepared by just calcining seeds date at 800°C for 2h. The optimal catalytic reaction conditions were considered to be 9:1 molar ratio of methanol/oil, 65°C reaction temperature, 1hour reaction time and 3% catalyst loading. Under such a condition, the yield of biodiesel reached 96.7%. Additionally, The negative effect of FFA on biodiesel production can be reduced by increasing the catalyst loading which conduct to increase the active surface area of this catalyst.

Acknowledgement :

This work was financially supported by Reserch Unit in Renewable Energies in Saharan Medium in Adrar city –Algeria-. The authors also appreciate the technical support from catalysis science and Technology Research Centre Faculty of Science University Putra Malaysia.

References

1. Osman NurSyazwania, Umer Rashid, Yun HinTaufiq Yap. Low-cost solid catalyst derived from waste *Cyrtopleuracostata* (Angel Wing Shell) for biodiesel production using microalgae oil. *Energy Conversion and Management* 2015;101:749–756.
2. G. Vicente, M. Martínez, J. Aracil, A. Esteban. Kinetics of sunflower oil methanolysis. *Ind. Eng. Chem. Res.* 2005; 44: 5447–5454.
3. D. Darnoko, M. Cheryan. Kinetics of palm oil transesterification in a batch reactor. *J. Am. Oil. Chem. Soc.* 2000; 77: 1263–1267.

4. H. Nouredini, D. Zhu. Kinetics of transesterification of soybean oil. *J. Am. Oil. Chem. Soc.* 1997; 74: 1457–1463.
5. D. Kusdiana, S. Saka. Kinetics of transesterification in rapeseed oil to biodiesel fuel as treated in supercritical methanol, *Fuel* 2001; 80: 693–698.
6. María Laura Pisarello, Carlos A. Querin. Catalyst consumption during one and two steps transesterification of crude soybean oils. *Chemical Engineering Journal* 2013; 234: 276–283.
7. Z. Helwani, M.R. Othman, N. Aziz, J. Kim, W.J.N. Fernando. Solid heterogeneous catalysts for transesterification of triglycerides with methanol: a review. *Applied Catalysis A: General* 2009; 363: 1–10.
8. Feng-Jiao Li ,Hui-QuanLi, Li-Guo Wang , Yan Cao. Waste carbide slag as a solid base catalyst for effective synthesis of biodiesel via transesterification of soybean oil with methanol. *Fuel Processing Technology*.2015; 131: 421–429.
9. K. Ramachandran, T. Suganya, N. Nagendra Gandhi, S. Renganathan "Recent developments for biodiesel production by ultrasonic assist transesterification using different heterogeneous catalyst: A review. *Renewable and Sustainable Energy Reviews* 2013; 22: 410–418.
10. Borges ME, D'iaz L. Recent developments on heterogeneous catalysts for biodiesel production by oil esterification and transesterification reactions: a review. *Renewable and Sustainable Energy Reviews* 2012;6:2839–49.
11. DanlinZeng, Qi Zhang, Shiyuan Chen, Shenglan Liu, Yang Chen, YongshengTian, Guanghui Wang. Preparation and characterization of a strong solid base from waste eggshell for biodiesel production. *Journal of Environmental Chemical Engineering* 2015; 3: 560–564.
12. Espiard, E. Introduction à la transformation industrielle des fruits. Ed. Lavoisier 2002; pp 147 - 155.
13. KhanittaRuttarattanamongkol, Susanne Siebenhandl-Ehn, Matthias Schreiner, Angelik M. Petrasch. Pilot-scale supercritical carbon dioxide extraction, physico-chemical properties and profile characterization of *Moringaoleifera* seed oil in comparison with conventional extraction methods. *Industrial Crops and Products*2014; 58: 68–77.
14. Mengxing Su, RuYang , Min Li. Biodiesel production from hempseed oil using alkaline earth metal oxides supporting copper oxide as bi-functional catalysts for transesterification and selective hydrogenation. *Fuel* 2013;103: 398–407.
15. Peng-Lim Boeya, Shangeetha Ganesana, GaantyPragas Maniamb, Melati Khairuddeana. Catalysts derived from waste sources in the production of biodiesel using waste cooking oil. *Catalysis Today*2012; 190: 117 –121.
16. X. Liu, H.He, Y. Wang, S. Zhu, X. Piao. Transesterification of soybean oil to biodiesel using CaO as a solid base catalyst. *Fuel* 2008; 87: 216–221.
17. Boro J, Konwar LJ, Thakur AJ, Deka D. Ba doped CaO derived from waste shells of *T striatula* (TS-CaO) as heterogeneous catalyst for biodiesel production. *Fuel* 2014;129:182–7.
18. GuanyiChen ,Rui Shan , Shangyao Li , Jiafu Shi. A biomimetic silicification approach to synthesize CaO–SiO₂ catalyst for the transesterification of palm oil into biodiesel. *Fuel* 2015;153:48–55.
19. SiowHwaTeo ,Aminul Islam , TalaYusaf , Yun HinTaufiq-Yap. Transesterification of *Nannochloropsisoculata* microalga's oil to biodiesel using calcium methoxide catalyst. *Energy* 2014; 78: 63-71.
20. Zhenqiang Yang, WenleiXie. Soybean oil transesterification over zinc oxide modified with alkali earth metals. *Fuel Processing Technology* 2007; 88: 631–638.
21. Feng-Jiao Li ,Hui-QuanLi, Li-Guo Wang , Yan Cao "Waste carbide slag as a solid base catalyst for effective synthesis of biodiesel via transesterification of soybean oil with methanol" *Fuel Processing Technology* 2015; 131:421–429.
22. Marija R. Miladinovic´ , Jugoslav B. Krstic´ ,Marija B. Tasic´ ,Olivera S. Stamenkovic´ ,Vlada B. Veljkovic.A kinetic study of quicklime-catalyzed sunflower oil methanolysis. *Chemical Engineering Research and Design* 2014; 92: 1740–1752.
23. Y.C. Sharma, B. Singh, S.N. Upadhyay. Advancements in development and characterization of biodiesel: A review. *Fuel* 2008; 87: 2355–2373.
24. Zlatica J. Predojevic´. The production of biodiesel from waste frying oils: A comparison of different purification steps. *Fuel* 2008; 87: 3522–3528.

25. Wilson Wei Sheng Hoa, HoonKiatNga, Suyin Ganb, Sang Huey Tan. Evaluation of palm oil mill fly ash supported calcium oxide as a heterogeneous base catalyst in biodiesel synthesis from crude palm oil. *Energy Conversion and Management* 2014; 88:1167–1178.
