Biodiesel production by esterification /transesterification of jatropha oil over sulfated zircona

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Abstract

Transesterification of jatropha curcas oil (JCO) with high acidity (8.4%),using methanol over sulfated zirconia as heterogeneous acid catalyst was investigated. Sulfated zirconia was directly synthesized by solvent – free method (S-ZrO$_2$) at 600°C for 5 h, and characterized by various physicochemical techniques. The surface areas and pore volume were 9.71716 m^2/g and 5.20631x 10^{-3}cm^3/g respectively. This catalyst exhibits excellent activity in esterification / transesterification of (JCO).

The alcoholysis conversion of JCO under optimized conditions (65°C,16 h , 1:40 MR oil to methanol and 12.5% wt of catalyst) was 92 .33%.While under subcritical methanolysis (200°C, 21 bars) was 95.6% after 1h.

Generally oils containing high level of FFA cannot be directly esterified using base catalysts currently employed.

Kinetic data on the transesterification reaction were achieved by conducting the reaction at various reaction times, catalyst dose and molar ratio.

The experimental data was interpreted with a 1storder reaction. The reaction was represented fairly well by pseudo homogeneous 1st order reaction and the kinetic parameters were obtained. A good agreement between the experimental data and the model were observed.

Keywords:-Jatropha oil, Biodiesel, Methanolysis, Sulfated Zirconia, Kinetic parameters.

1. Introduction

The mono alkyl esters produced by transesterification of vegetable oils with alcohol are known as biodiesel fuel (BF). Most of BF is currently made using alkaline catalyst because the transesterification reaction by homogeneous acid catalysts is much slower than that by alkaline catalysts. [1-4]The alkaline catalyst shows high performance for obtaining vegetable oils with high quality, but a question often arises when the oils contain significant amount of free fatty acids

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(FFAs) which cannot be converted to biodiesel but a lot of soap. Soap production is undesirable because it reduces the ester yields and makes the recovery of the glycerol considerable more difficult, due to the formation of emulsions.[5]

To avoid these undesirable saponification reactions, heterogeneous acid catalysts could be used. They enable the transesterification of vegetable oils or animal fats with high contents of free fatty acids, such as deep – frying oils from restaurants and food processing. Heterogeneous acid catalysts can be filtered and recycled, there by simplifying the step of biodiesel purification.[6,7]

The conventional process of producing biodiesel or fatty acid methyl ester (FAME) involves oil extraction, purification and transesterification. The cost of oil contributed over 70% of the total cost of FAME product when refined oil was used. [8-10]

Oils from jatropha seeds give valuable products with features that have high oxidative stability compared to soybean oil, low viscosity compared with castor oil and better cooling characteristics of palm oil. [11]

In recent years, a search for different catalyst for a sustainable transesterification process has been done. Recently, heterogeneous catalyst such as metal oxides, carbonates, zeolites and hetero poly acids have also been investigated for biodiesel production.

Heterogeneous catalysts have the general advantages of being reusable and easy to separate from reaction products. In addition they are in general much more tolerant to water and FFAs in the feedstock. Therefore it does not lead to soap formation. However, heterogeneous catalyzed transesterification requires relatively elevated temperatures and pressures than those for homogeneous catalysts. Moreover are of the main problems with heterogeneous catalyst is their deactivation with time owing to many possible phenomena, such as poisoning, cooking, sintering and leaching.[12,13]

Strong acid or bases – both homogeneous and heterogeneous – catalyze the transesterification reaction. Since the base catalyzed transesterification of vegetable oils proceeds faster than the acid – catalyzed reaction and alkaline catalysts are less corrosive than acid compounds, industrial processes usually favor basic catalyst, such as alkaline hydroxides. [14]

Heterogeneous acid catalysts are developed to solve the problems associated with homogeneous catalysts. The main advantages of these catalysts are easy separation, reusability and more environmentally friendly. [15] These catalysts can also promote simultaneously transesterification of triglyceride and esterification of FFAs that causes cheaper product cost.[16]

Sulphated zirconia (S-ZrO$_2$) is classified as heterogeneous supper acid catalyst. It has recently received considerable attention as a promising catalyst for

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industrial processes due to its strong acid properties. [17] It is also has higher acid strength than other heterogeneous catalyst. [18]This catalyst has been successfully used in esterification of palmitic acid in sunflower oil with methanol at 60°C and esterification of refined soybean oil with methanol at 35 - 60°C[19].

There are several reports on the kinetics of FFAs esterification in presence of triglyceride using different heterogeneous acid – catalysts. Various models were proposed for this system either to explain the phenomenon. Eley – Ridal (ER) model as represented the adsorption phenomenon was a superior model for esterification of high FFA (≈50%) in the presence of soybean oil.[20] Langmuir – Hinshewood – Hougen Watson (LHHW) model is characterized by increasing number of parameters to describe esterification of FFAs in waste cooking oils.[21] Pseudo homogeneous second order reversible (PH) model applied for several esterification reactions of FFA in the presence of triglycerides. [22, 23]

In this study, (JCO) is used as the source for biodiesel production. Jatropha trees have a high resistance to hot and dry climate. JCO is available locally and it is non edible vegetable oil due to its toxicity. The utilization of non – edible and renewable crops such as Jatropha in biofuels production is crucial to minimize the utilization of edible food crops (corn, soya, palm, etc) as it is expected to create a short supply of food for human consumption.

The aim of the present work is to investigate the performance of sulfated zirconia as a heterogeneous catalyst in the transesterification of vegetable oils and simultaneous esterification of fatty acids with methanol.

2. Materials and Methods
2.1. Materials

JCO was extracted from jatropha seeds using commercial hexane. The seeds have been obtained from Ministry of Agriculture from Luxor farm, EGYPT.

The individual acid compositions of JCO is measured by gas chromatography are show in table (1). [24]

Table (1) Fatty acid composition of JCO

Fatty acid	Composition (%wt)
Palmitic (16:0)	18.22
Stearic (18:0)	5.14
Oleic (18:1)	28.45
Linoleic (18:2)	48.18

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Extracted JCO was subjected to some tests and characteristics are illustrated in table (2).[24]

Table (2) Characteristics of JCO

Parameter	Value
Viscosity	46.8 m Pas
Density	0.91 kg/L
Acidity	8.4%*

*High acidity content is due to long storage time.

- Zirconia (IV) oxide chloride octahydrate purity ≥ 99.5% from India – Art 6568.
- Ammonium sulfate. Purity ≥ 99% from El- Nasr Co., Adwic, EGYPT.
- Sodium hydroxide, purity 99% from El – Nasr Co., EGYPT.
- Toluene rectified 99% packed under nitrogen from Loba Chemica Co.
- Iso propanol 99.5% from Alpha Chemica Co.
- Phenol phethalein indicator (1%).
- Methanol: pure reagent – El Nasr Co., Adwic, EGYPT.
- Potassium hydroxide extra pure from El – Nasr Co., EGYPT

2.2. Catalyst preparation and characterization

The solvent – free method of sulfated zirconia designated as S-ZrO_2 was prepared by Sun – et al. [25] $ZrOCl_2$. $8H_2O$ and $(NH_4)_2SO_4$ in a molar ratio of 1:6 were ground in an agate mortar for 20 min at room temperature , let the mixture for 18 h in open air, then the sample was calcined at 600°C for 5h.

- The strictional information of the catalyst was carried out by XRD pattern, the surface morphologies of the catalyst was studied by scanning – electron microscope (SEM), specific surface area was calculated by BET method

2.3. Determination of acid value and acidity for JCO

2.3.1. Acidity determination (visual titration)

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The acidity is an expression of the content of free percentage fatty acid as content of dominant of chosen fatty acid. In case of JCO it expressed as oleic acid (Mwt. 282).

In visual titration the desired amount (1:1 v/v) of oil dissolved in 125 ml of the solvent mixture, isopropanol and toluene (1% v/v), 2 ml of Phenol Phethaleine was used as indicator and the solution was titrated with 0.025mol/ L NaOH. The percent acidity (%AD) of JCO was calculated by equation (1) as follows :[26]

$$\%AD = \frac{C\ NaOH \times V\ NaOH \times M}{W \times 1000} \quad (1)$$

Where: C NaOH = the concentration of NaOH (g/l), V NaOH= the titration volume of NaOH (ml), M= the molecular weight of oleic acid (282g) and

W = weight of sample (g).

2.4. Experimental set – up

Experimental work is carried out on a bench scale reactor and a floor- stand reactor under pressure.

2.4.1. Bench – scale reactor

The esterification / transesterification of JCO with low moderate weight alcohol (methanol) carried out in a round glass reactor (250 ml) placed in adjusted water bath. The glass reactor is provided with reflux condenser, magnetic stirrer thermometer and a funnel for methyl alcohol addition.

2.4.2. Stand floor reactor under pressure

The reactor includes a stainless steel 316vessel (3.7Lcapacity), pressure gauge and a heating jacket provided with mechanical stirrer. The temperature and pressure inside the reactor were also controllable through proportional integral derivative panel (PID) after that, the percentage conversion of FFAs can be calculated by equation (2).[27]

$$X = \left(1 - \frac{AD}{AD_o}\right) \times 100 \quad (2)$$

Where X is the conversion of FFA, AD_0 is the initial acidity before the reaction and AD the acidity calculated after the reaction

2.5. Reaction Procedure

2.5.1. Normal heterogeneous reaction at 65°C

50 g oil was added to 12.5% w/w S-ZrO$_2$ and stirred at 500 rpm for 20 min using magnetic stirrer. Then raising the temperature to the desired temperature (65±5 °C). Subsequently methanol was added drop wise through the funnel over the condenser, after certain reaction time, the reaction mixture was filtered and transferred to a separating funnel. Two liquid phase layers were appeared.

2.5.2. Subcritical heterogeneous methanolysis technique (120 - 200°C)
The reaction vessel was charged with 500 gm oil and 12.5% w/w S-ZrO$_2$, stirred at 500 rpm for 20 min. at ambient temperature. Esterification transesterification reaction was performed by adjusting temperature controller to the desired temperature and while heating the reaction mixture, the pressure was elevated with the rise in temperature. At the end of reaction time, the reaction mixture was filtered then allowed to settle in a separating funnel.
Excess methanol was recovered under vacuum at 80°C from the two layers using rotavapor.

2.6. Kinetic studies

Kinetic studies are reported to observe the effect of operating conditions on the final conversion in batch esterification / transesterification reaction and to obtain the chemical engineering data for full scale design.

3. Results and Discussion

3.1. Catalyst Characterization

The acid catalyst (S-ZrO$_2$) is prepared by the solvent free method and characterized by various physicochemical techniques.

3.1.1 X-Ray diffraction (XRD)

XRD of the sulfated zirconia is shown in Fig. 1. which illustrated that sulfated zirconia calcined at 600 °C is an amorphous material and shows peaks assigned to both the tetragonal and the monoclinic peak of zirconia and exhibits poor crystanility for this mixture.
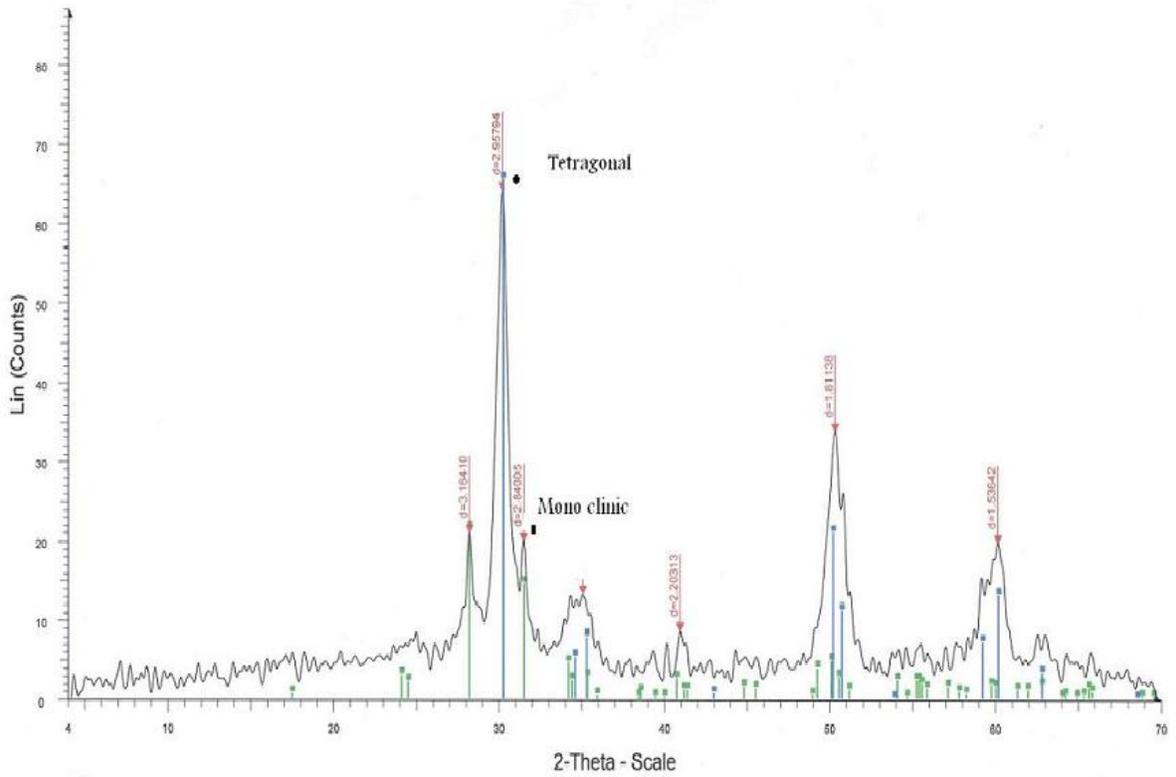
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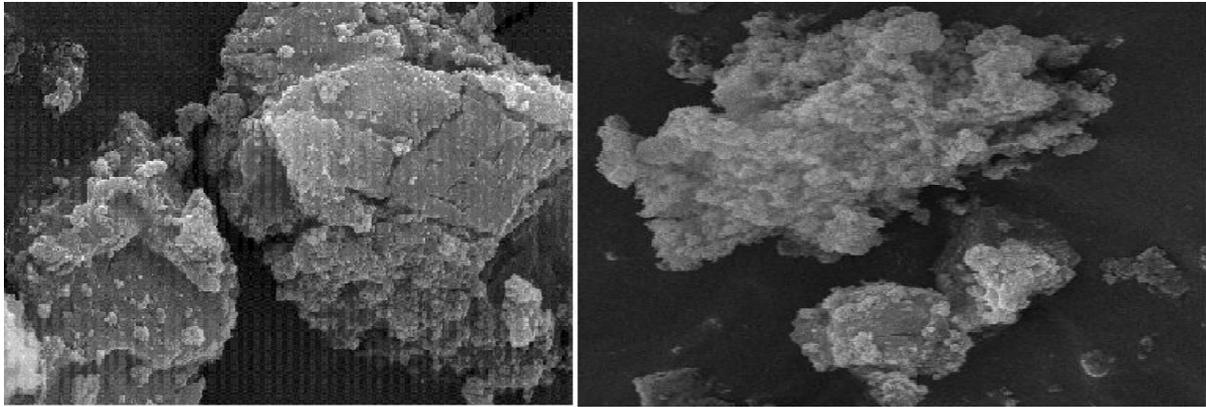www.ijiset.com

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Fig.1. XRD of the sulfated zirconia

3.1.2 The surface area measurement and pore volume

Surface area and pore volume were found (9.71716 m^2/g and 5.20631×10^{-3} cm^3/g) which indicated that the higher activity of (S-ZrO$_2$) related to the type of highly charged species of SO_4^{2-} ions. It has reported that the sulfur species on sulfated zirconia very complex [28]. However the tetragonal phase of sulfate zirconia is an important factor for the formation of Broneste acid [29].

Our experiments confirm that the amorphous (S-ZrO$_2$) has much higher quantity of acid sites that are active for the transesterification of vegetable oil.

3.1.3 The scan electron microscope (SEM)

SEM images shown in Fig. 2. Illustrated irregular shape but the grains became similar to each other Fig 2.a and sintered Fig. 2.b .Also, the surface of the catalyst exhibited considerable surface shinning due to the presence of highly charged species of sulfated ions.

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Fig.2. Scan Electron Microscope (SEM) of sulfated zirconia

3.2. Experimental Results

The esterification / transesterification of JCO are conducted under subcritical conditions and at atmospheric pressure.

3.2.1. Reaction under subcritical conditions

Under subcritical conditions the effect of temperature, catalyst dose and oil to alcohol molar ratio were investigated.

3.2.1.a Effect of reaction temperature

The reaction temperature was varied in the range of 120 - 200°C, the molar ratio of alcohol to oil was 20M, the amount of catalyst used was 5% (w/w of oil/ and the stirring speed was set at ≈500rpm for 1hour. The results obtained are shown in Fig.3.
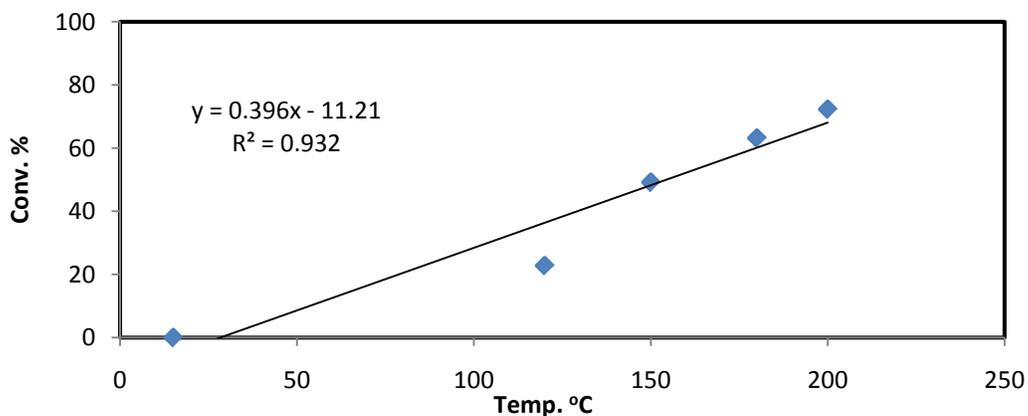

Fig.3. Effect of temperature on JCO conversion to FAME at molar ratio 1:20 oil : alcohol, 5% wt catalyst , 500rpm for 1h.

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Fig.3. Effect of temperature on JCO conversion to FAME at molar ratio 1:20 oil: alcohol, 5% wt. catalyst, 500rpm for 1 h.

It can be seen that higher percentage of conversion was obtained at higher temperature. Hence it can be concluded that 200°C can be considered as the optimum economic temperature (72.33% conversion).

The catalytic activity of (S-ZrO$_2$) was highly dependent on the reaction temperature between 120 – 200 °C and the fatty acid methyl ester (FAME) yield increased with increasing temperature.

3.2.1.b Effect of catalyst amount

For this case we consider the optimal reaction conditions to be 12.5% wt of S-ZrO$_2$ catalyst with respect to jatropha oil at 200°C for 1h the reaction was carried out with a molar ratio of alcohol to oil of 12:1, 500 rpm and the results are shown in Fig.4.
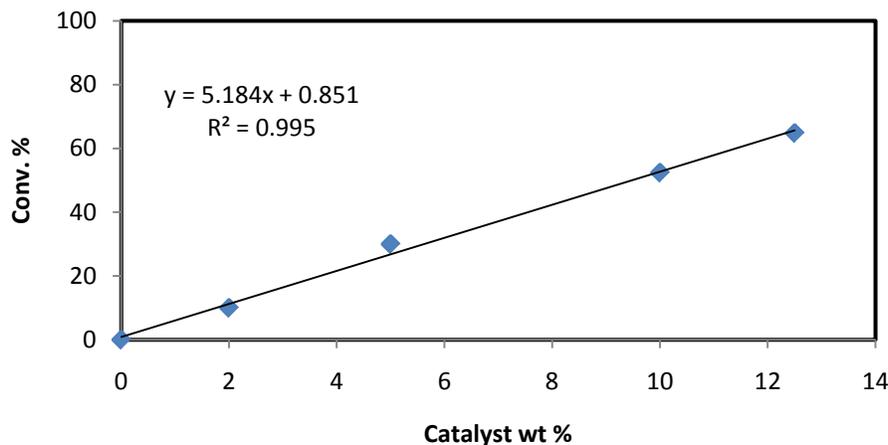

Fig.4. Effect of catalyst dose on JCO conversion to FAME at molar ratio 1:12 , 200°C, 500rpm for 1h.

It is clear that the reaction conversion% was highly dependent on catalyst dose at high catalyst amount (12.5% wt of oil) the conversion was higher (64.8%). We can reach higher conversion value (92.33%) at higher molar ratio (1:20). But further experiments showed that increasing molar ratio decreases catalyst dose and increases oil conversion as mentioned in section 3.2.1d

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3.2.1.c Effect of the amount of alcohol

Alcohol to oil molar ratio was studied at constant temperature (200°C), 5% wt catalyst and 500 rpm for 1 hour. The molar ratio of methanol to raw mix was varied between 12 and 40. Fig.5. shows the oil conversion plot at different alcohol amount.

From the results shown in the figure it is obvious that increasing alcohol to oil molar ratio increases the oil conversion till 88%. Higher conversion can be reached when the catalyst dose increases.
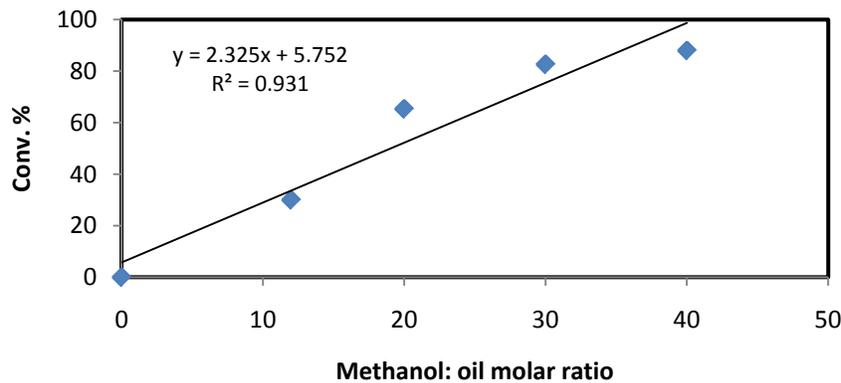

y = 2.325x + 5.752
R^2 = 0.931

Fig.5. Effect of oil : alcohol molar ratio on JCO conversion to FAME at 5% wt catalyst , 200°C, 500rpm for 1h.

3.2.1. d Experimental results at optimum reaction conditions under pressure

Best results obtained at the experimental operating conditions are applied in a final experiment from which the dependence of the conversion of JCO reached 95.6% .Results are illustrated in table (3).

Table (3) Conversion of JCO at optimum conditions

Temp. °C	Molar ratio Oil: Methanol	Catalyst % w/w	Time h	Conversion %
200	1 : 50	5	1	95.6

3.2.2. Transesterification of JCO at atmospheric conditions

Transesterification of JCO at different levels of catalyst dose, molar ratio of methanol to oil and various reaction times are studied.

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3.2.2. a Effect of time at different alcohol to oil molar ratio

The reaction was carried out at a constant temperature of about 70°C and with stirring at 500 rpm and 12.5% wt of sulfated zirconia as catalyst. The molar ratio of methanol to oil was varied between 20 and 50 and results are shown in Fig.6.
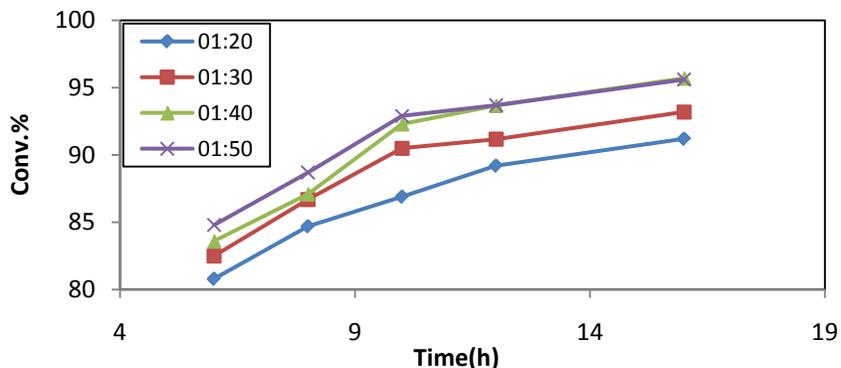

Fig.6. Effect of time on JCO conversion at 70°C , 500 rpm, 12.5 wt% catalyst at different methanol to oil molar ratio

It is clear that the reaction rate and final conversion increased with the increasing of molar ratio of oil to methanol .It also be noted that higher molar ratio from 1 :40 to 1 :50 (at time from 12 to 16 h) resulted in no significant increases in reaction rate and final conversion.

3.2.2. b Effect of time at different catalyst doses.

Effect of varying the amount of catalyst were studied at the reaction conditions of 40M (methanol: oil), T=70°C, agitation speed of 500 rpm and the catalyst amount varied from 10 to 15% wt of oil were used.

Fig.7. showed that catalyst quantity of 12.5% (w/w) was enough to ensure the higher conversion of JCO (94%) after 12 h.
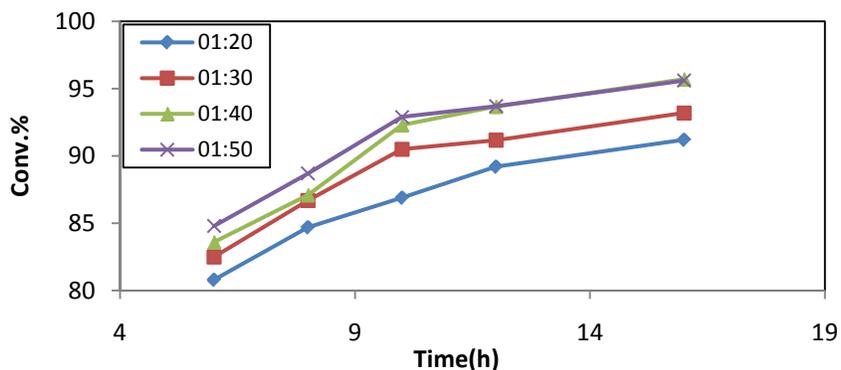

Fig.7. Effect of time on JCO conversion at 70°C , 500 rpm and 40 oil to methanol molar ratio at different catalyst doses.

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The increase of catalyst dose to 15% improves the conversion by about 1% but create a difficulty in separation of glycerol from FAME.
Increasing catalyst dose or time of reaction above that no significant increases in oil conversion are observed.

3.3. Estimation of kinetic reaction parameters

To determine the reaction order by integral method, the following simplifying assumption are made

1- Presence of excess methanol reactant minimizes the reversibility of the reaction.
2- Solid catalyst is in very fine powder form so, the reaction mixture is assumed homogeneous
3- The reaction mixture was under reflux keeping constant volume during the whole reaction time.
4- Reaction temperature is constant.

In addition, stirring rate is sufficient to overcome the diffusion limitation of reactive species-catalyst.

Therefore the performance of pseudo – homogeneous reaction can be considered to correlate the esterification of jatropha oil with methanol using sulfated zirconia as a catalyst and represented by equation (3)

A (oil) + B (methanol) $\longrightarrow$ C (methyl est.) + D (glycerin)   (3)
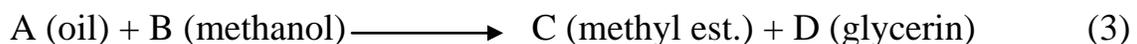
The concentration of methanol being in excess does not influence the global reaction which is finally represented by equation (4) which is in accordance with previous studies. [30, 31]

$$A(oil) \rightarrow product\ (C + D)   (4)$$

Therefore, the rate constant can be calculated from equation (5)

$$r_A = -\frac{dC_A}{dt}\ (5)$$

Separating and integrating we obtain

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$$-\int_{C_0}^{C_A} d\frac{C_A}{C_O} = k \int_0^t dt$$

The rate constant in linear from is represented as$= kt$

$$-ln\frac{C_A}{C_{A_0}} = kt \quad (6)$$

WhereC_{A_0}= initial concentration of Amole / L, C_A= concentration of A, mole/L $= C_{A_0}$- X(reactant) and k = Kinetic parameter of the reaction .

Hence, for determining the order of reaction a plot of – In C_A/C_{A0} against time at different molar ratio and catalyst doses were drawn in Fig. 8 and Fig. 9.
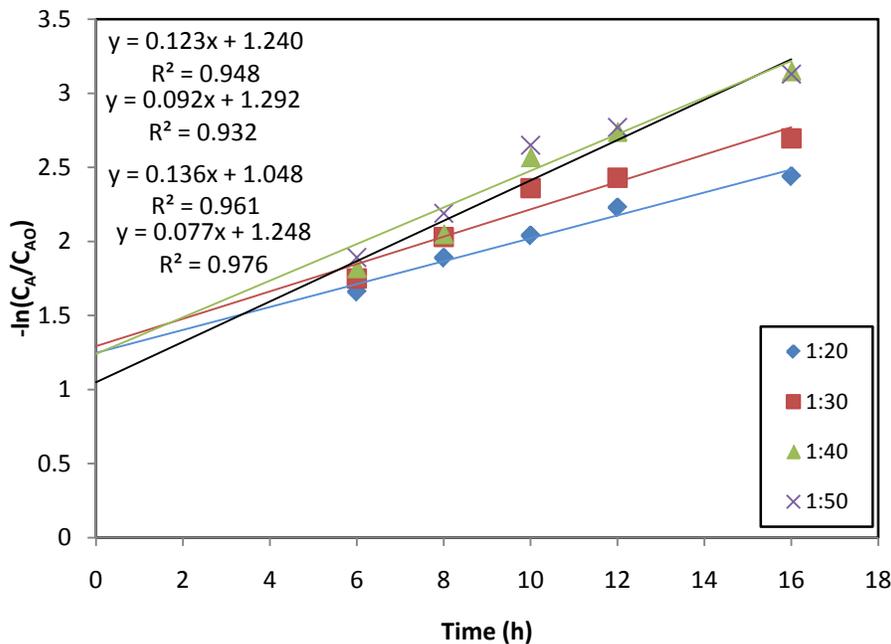

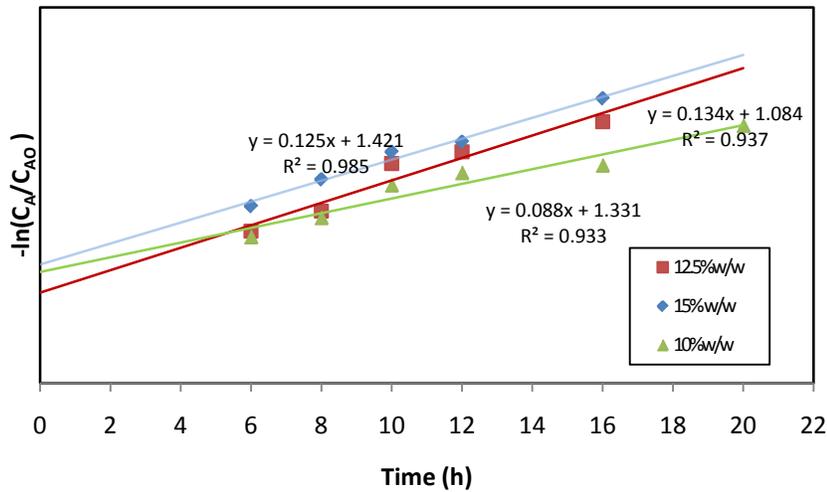Fig. 8.-lnC$_A$/C$_{Ao}$ versus time at different molar ratios

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Fig. 9. -ln (C$_A$ /C$_{AO}$) versus time a different catalyst dose

As shown from the figures, all straight lines gave good linear correlations in the range of 0.93 to 0.99. It is clear that the proposed kinetic parameters appropriating for this reaction. The values of reaction rate parameters in tables (4, 5), different molar ratios and catalyst concentrations are shown in tables (3&4).

Table (4) Estimated reaction rate kinetic parameters (k at different molar ratios

Molar ratio	k(h^{-1})
1:20	0.0773
1:30	0.0924
1:40	0.1236
1:50	0.1363

Table (5) Estimated reaction rate kinetic parameters (k) at different weight of catalyst

Catalyst dose (%w/w)	k(h^{-1})
10	0.088
12.5	0.1255
15	0.1344

It is clear that the triglyceride proceeded faster when the molar ratio and weight of catalyst increased because the reaction rate constants were improved as the molar ratio and weight of catalyst increased.

Conclusions

- Sulfated zirconia – synthesized by solvent – free method (S‑ZrO$_2$) is not only active for the transesterification of triglyceride but also for esterification of free fatty acids, allowing an excellent overall yield of about 96% for simultaneous esterification of oleic acid and transesterification of (JCO).
- Experiments from present study confirm that the amorphous sulfated zirconia has much higher quantity of acid sites that are active for the transesterification and that the tetragonal phase of this catalyst is an important factor for the formation of acid sites.
- The conversion of JCO catalyzed by (S‑ZrO$_2$) under optimized subcritical conditions (200°C, 5 % wt of catalyst and oil: alcohol molar ratio 1:50) reached 95.6% after 1 h reaction time
- Optimal parameters used to obtain the best conversion were molar ratio oil : methanol 1:40, catalyst dose 12.5% w/w of oil, 70°C, and stirring speed 500 rpm to reach 92.33 % JCO conversion after 16 hours reaction time.
- The estimated kinetic rate parameter of JCO was 0.13h^{-1}at the optimum conditions and the reaction is represented finally well by pseudo – homogeneous 1st order kinetic model.

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References

1- Canakci, J. Gerpen, V., Trans ASAE 42 (5): 1203 – 1210(1999).
2- Schwab, A.W., M.O.Bagby, B.Freedman, Fuel 66(10) :1372-1378 (1987).
3- Liu. K., JAOCS 71(11): 1179-1187(1994).

IJISET - International Journal of Innovative Science, Engineering & Technology, Vol. 1 Issue 7, September 2014.

www.ijiset.com

ISSN 2348 – 7968

4- Freedman, B., R.O.Butterfield., E.H.Pryde, JAOCS 63(10) : 1375-1380(1986).

5- Vicente, G., Martinez, M.,Aracil, J., "Integrated biodiesel production : a comparison of different homogeneous catalysts systems". Bioresource Technol. 92(3): 297-305(2004).

6- Lopez, D.E., Goodwin, J.G., Bruce, D.A., Lotero, E., "Transesterification of triacetin with methanol on solid acid and base catalyst". Appl.Catal. A 295: 97-105(2005).

7- Camila Martins Garcia, Sergio Teixeira, Leticia LedoMarciniuk, Ulf Schuchardt, "Transesterification of soybean oil catalyzed by sulfated zirconia". Bioresource Technology 99: 6608-6613(2008).

8- Holmberg, W.C.; Peeples, J.E. "Biodiesel: A Technology, performance and Regulatory Overview". National SoyDiesel Development Board: Jefferson City, MO(1994).

9- Bender, M. "Economic Feasibility Review for Community – Scale Farmer Cooperatives for Biodiesel". Bioresour. Technol, 70,81(1999).

10- Haas, M.J.;McAloon, A.J.;Yee, W.C.;Foglia, T.A. "A process Model to Estimate Biodiesel production Costs". Bioresour. Technol 97,671(2006).

11- Noor HafizahArbain , JumatSalimon. "The Effect of Various Acid Catalyst on the Esterification of JatrophaCurcas oil based Trimethylolpropane Ester as Biolubricant base stock". E-Journal of Chemistry 8(S1): S33-S40 (2011).

12- Schuchardt, U., Sercheli, R., Vargas, R.M., "Transesterification of vegetable oils: a review". J.Brazil Chem. Soc9 :100-210 (1998).

13- A.A.Refaat, Int.J.Environ. Sci. Tech. 7:183-213(2010).

14- A.Sivasamy, K.Y.Cheah, P. Fornasiero, F. Kemusuor, S.Zinoviev, S.Miertus, Chem. Sus. Chem. 2:278-300(2009).

15- Kulkarni MG, Gopinath R, Meher LC, Dalai AK.,"Solid acid catalyzed biodieselproduction by simultaneous esterification and transesterification". Green Chem.8:1056-62(2006).

16- Vyas AP, Verma JL, Subrahmanyam N.,"A review on FAME production processes".Fuel89:1-9(2010).

IJISET - International Journal of Innovative Science, Engineering & Technology, Vol. 1 Issue 7, September 2014.

www.ijiset.com

ISSN 2348 – 7968

17- Yadav GD, Nair JJ.,"Sufated zirconia and its modified versions as promisingcatalysts for industrial processes". MicroporMesoporMater33:1-48(1999).

18- Brei VV.,"Superacids based on zirconium dioxide". TheorExpChem41:165-75(2005).

19- Ni J, Meunier FC.,"Esterification of free fatty acids in sunflower oil over solid acidcatalysts using batch and fixed bed-reactors". ApplCatal A: Gen333:122-30(2007).

20- R.K. Balasubramanian, J.P. Obbard,"Esterification of free fatty acids usingsulfated zirconia". In: A. Sayigh, editor, World Renewable Energy Congress:239-42(2008).

21- Meng-yu G, Deng P, Li M, En Y, Jianbing H.,"The kinetics of the esterification offree fatty acids in waste cooking oil using $Fe_2(SO_4)_3$/C catalyst". Chinese J. Chem. Eng.17:83-7(2009).

22- Tesser R, Serio MD, Guida M, Nastasi M, Santacesaria E.,"Kinetics of oleic acidesterification with methanol in the presence of triglycerides". Ind. Eng. Chem. Res.44:7978-82(2005).

23- Su CH, Fu CC, Gomas J, Chu IM, Wu WT.,"A heterogeneous acid-catalyzedprocess for biodiesel production from enzyme hydrolyzed fatty acids". AICHE J.54:327-36(2008).

24- Hawash S., N.Kamal and G. El Diwani, "Egyptian jatropha oil extraction for biodiesel production".AFINIDAD LXV:536(2008).

25- Sun Y, Ma S, Du Y, Yang J. et al., "Solvent – free preparation of nanosized sulfated zirconia with bronsted acidic sites from a simple calcinations". J phys Chem. B 109:2567- 72 (2005).

26- Mario J.D Carneiro, Mario A.Feres Junior and OswaldoE.S.Godinho."Determination of the acidity of oils using paraformaldehyde as a thermometric end – point indicator".J,Braz. Chem. Soc. 13(5): 692 – 694 (2002).

IJISET - International Journal of Innovative Science, Engineering & Technology, Vol. 1 Issue 7, September 2014.
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27- Dussadee R., Adam P.H., Anusith T., and Penjit S., " Kinetic of myristic acid esterification with methanol in the presence of triglycerides over sulfated zirconia". Renewable Energy 36:2679-2686(2011).

28- Yadav, G.D., Kirthivasan, N. "Single – pot synthesis of methyl tertbutyl ether from tert- butyl alcohol and methanol – dodecatungstophosphoric acid supported on clay as an efficient catalyst". J. Chem. Soc.,Chem.Commum. 2,203-204(1995).

29- Sun,Y.,Ma,S.,Du, Y., Yuan, L., Wang, S.,Yang,J.,Deng,F.,Xiao,F.s. "Solvent –free preparation of nanosized sulfated zirconia with Bronsted acidic sites from a simple calcinations". J. Phys. Chem. B 109,2567-2572(2005).

30- Tiwari P., Kumar R., and Garg S., "Transesterification, modeling and simulation of batch kinetics of non edible vegetable oils for biodiesel production fuels and petrochemicals". Hilton. San Francisco (2006).

31- Debk , "Optimization for engineering design prentice". Hali of India.New Delhi (2003).