

Transesterification of esterified mixed oil for biodiesel production

H.A. Farag¹, Azza El-Maghraby^{2,*}, Nahla A. Taha²

¹Chemical Engineering Department, Faculty of Engineering, Alexandria University, Egypt.

²Department of Fabrication Technology, Institute of Advanced technology and New Materials, City for Scientific Research and Technology Applications, Alexandria, Egypt.

Abstract

Biodiesel has become more attractive recently because of its environmental benefits and the fact that it is made from renewable resources. The most common way to produce biodiesel is through transesterification. In spite of the many advantages of biodiesel, it is not yet commercialized all over the world. The major problem is the cost of the raw material. Waste cooking oil is a promising alternative to vegetable oil due to its reduced cost. Biodiesel was prepared via the transesterification of the esterified mixed oil, waste home domestic oil and restaurant waste cooking oil with excess alcohol using potassium hydroxide as an alkaline catalyst. The effects of reaction temperature, time and alcohol to oil ratio, catalyst type and concentration on the conversion of diesel were examined. Comparison between the analytical methods used to measure the conversion of biodiesel was evaluated and the maximum conversion of approximately 98.6 using TGA analysis and 97.6% using GC were obtained. The biodiesel conversion s as measured by TGA and GC are found to be approximately the same as the linear fit between the two data series results for R^2 value of 0.9983.

Key words: Transesterification, Mixed oil, Biodiesel, Thermogravimetric analyzer

Full length article Received: 27-07-12

Accepted: 31-07-12

Available online: 31-07-12

*Corresponding Author, e-mail: maghrabyazza@yahoo.com

Tel: 0103087123

Fax: 03-4593414

1. Introduction

Due to the depletion of the world's petroleum reserves and high level emission of certain pollutants from conventional petroleum based fuels, there is a great demand for alternative sources to petroleum-based fuel, including diesel and gasoline fuels. One possible alternative to petroleum-based fuel is the biofuel. Biofuels are derived from renewable sources such as naturally occurring fats and oils, which may be obtained from variety of plants and animals [1,2]. Biodiesel, a clean renewable fuel, has recently been considered as the best candidate for a diesel fuel substitution because it can be used in any compression ignition engine without the need for modification [3]. Biodiesel has been defined as "the mono alkyl esters" of long chain fatty acids derived from renewable lipid feedstock, such as vegetable oils or animal fats. Biodiesel can be used as a substitute or an additive to diesel fuel. Compared to fossil-based diesel fuel, biodiesel possesses many advantages such as cleaner engine emissions, biodegradable, renewable and superior lubricating property [4]. In spite of the many advantages of biodiesel, it is not yet commercialized all over the world. The major problem is the cost of the raw material. Biodiesel obtained from neat

vegetable oil is costly compared to the petroleum diesel fuel. More than 95% of biodiesel production feed stocks come from edible oils since they are mainly produced in many regions and the properties of biodiesel produced from these oils are much suitable to be used as diesel fuel substitute [5]. However, it may cause some problems such as the competition with the edible oil market, which increases both the cost of edible oils and biodiesel [6]. In order to overcome these disadvantages, many researchers are interested in non-edible oils which are not suitable for human consumption because of the presence of some toxic components in the oils. Furthermore, nonedible oil crops can be grown in waste lands that are not suitable for food crops and the cost of cultivation is much lower because these crops can still sustain reasonably high conversion without intensive care [7,5] However, most non-edible oils contain high amounts of free fatty acids. Thus they may require multiple chemical steps or alternate approaches to produce biodiesel, which will increase the production cost [8-10]. Waste cooking oil is a promising alternative to vegetable oil due to its reduced raw material cost. Restaurant waste oils and rendered animal fats are less expensive than food grade [11]. Production of biodiesel from waste cooking oil is one

of the better ways to utilize them efficiently and economically. In literature, many reports are available on the use of waste cooking oil for biodiesel production [12-15]. A number of methods are currently available and have been adopted for the production of biodiesel fuel. There are four primary ways to produce biodiesel: direct use and blending of raw oils [16–20], micro-emulsions [21], thermal cracking [22–27], and transesterification [1]. The most commonly used method for converting oils to biodiesel is through the transesterification of vegetable oils, which forms the basis of the present paper.

The present work deals with the transesterification of a model acid mixed oil after esterification it to eliminate the problem of high amount of FFA. The conversion of biodiesel was investigated by altering a few parameters such as temperature, reaction time, catalyst amount, catalyst type and molar ratio of alcohol to oil. There are reported publications on this technology. After choosing the optimum conditions which give the highest conversion value, those are used to compare the model acid with, home domestic waste cooking oil and finally restaurant domestic waste cooking oil.

2. Materials and methods

2.1. Materials

1) **Model acid oil:** is a mixture of refined oil "50% sunflower oil+ 50% soybean oil" which prepared by mixing pure oleic acid and the oil (5 g of oleic acid and 95 g of refined oil) 8.5% FFA as oleic.

2) **Home domestic oil:** The used frying oil collected from the house domestic waste vegetable oil (used for 4-5 times at a cooking temperature of 120-130 °C) with acid value = 2mg/ g KOH .

3) **Restaurant domestic oil:** The used frying oil collected from popular fast- food restaurant as waste vegetable oil, the cooking temperature of the oils varied from 150-200 °C. The oils were kept at these temperatures nearly twelve hours , with acid value = 4.3 mg/ g KOH .

4) **Alcohol:** Anhydrous methanol (Fluka Co., Assay : > 99.8%.) was used, which is most commonly used because of its low cost (compared to other alcohols) .

5) **Potassium hydroxide:** Alkaline catalyst (ADWIC, El Nasr Pharmaceutical product Co., Assay: min 85%.)

2.2. Methods

[1] Transesterification of esterified oil:

Using esterified model acid oil according to method mentioned before [28], the reaction mixture was left for 1 hr, then pour and separate. 40 ml of upper layer are fed to the bench scale set-up (500 ml three neck flask) then heated to required temperature. Alcohols to oil with the different molar ratios were added then add potassium hydroxide catalyst with suitable amount as a solid form. The mixture was left for 1 hr at 65 ±1°C and 300 rpm. Excess alcohol was recovered by a rotary evaporator. The mixture was left to separate for 2 hrs. The lower layer of glycerol is drawn off and the upper layer of biodiesel is washed with hot distilled water (50±1°C) 3 times to remove any traces of catalyst and glycerol. The produced biodiesel was heated at 50±1°C for 2-3 hrs. to remove any remained amount of alcohol. Sodium sulfate anhydrous is added to biodiesel to remove any amount of water remaining after washing.

[2] Analytical Methods:

GC (17A Shimadzu-Japan) technique was used in analyzing the produced fatty acid methyl ester (biodiesel). Nitrogen was used as the carrier gas with the initial oven temperature at 35 °C held for 1.5 min and subsequently increased to 195 °C at 20 °C/min , temperature was raised to 205 °C at 3 °C/min. Temperature of the injector and detector were set at 215 °C. In each run, 0.5 µl of sample was injected into the column. The conversion of the transesterification reaction was calculated by the following equation:

$$\text{Relative conversion} = \frac{\text{SUM (Area of each fatty acid methyl ester)}}{\text{Total area of all fatty acids methylesters}}$$

TGA(60A- Shimadzu-Japan) analyses of the prepared biodiesel were completed with 5-15 mg of samples which was heated at a constant rate of 10 °C/min in an atmosphere of nitrogen at a constant purge rate of 20 ml /min into the pan. The temperature range employed was 25-500 °C. The conversion percentage was calculated from the following equation: [29]

$$\% \text{Conversion} = \frac{W - R}{W} \times 100\%$$

Where:

W = Original specimen mass, mg

R= mass at the end of decomposition temperature of the sample, mg

3. Results and Discussion:

3.1. Comparison between the two Analytical Methods

In the literature, the transesterification reactions were monitored by GC. Determination of the products by GC is not simple, difficult and time consuming because of the need for sample derivation or the use of special columns.[30-32] Instead , TGA instrument was used in the calculation of conversion of the transesterification reaction for production of biodiesel, as TGA can be used for the quantitative analysis of a mixture of materials [33,34]. Figure (1) shows the TGA of fatty acid methyl esters (Biodiesel) with optimum conditions and refined mixed oil (sunflower oil +soybean oil). There is a large temperature difference between the weight loss temperatures of these two compounds and this allows one to determine the conversion. The mass of the biodiesel starts to decrease approximately at 126 °C, and it continues its decrease until all the biodiesel present in the sample is vaporized at about 300 °C. Also the figure shows the derivative of each plot and the wide range between the degradation temperature of the two samples (Biodiesel and refined oil) is clearly shown as the set point of degradation for biodiesel is at 247 °C and for refined oil at 427.5 °C. Similarly, evaporation of refined mixed oil starts at approximately 320 °C.

Table 1. Determination of biodiesel conversion using TGA and GC for different molar ratio

Molar ratio	% Conversion using TGA	% Conversion using GC
3:1	61.68	62
6:1	90.65	91.1
7:1	94.07	93
8:1	95.64	95.3
10:1	98.02	97.6

Table 2. Calibration curve (Biodiesel % by weight obtained from TGA analysis and the actual biodiesel weight % in the standard sample).

Standard samples wt % (biodiesel)	TGA measured wt% (biodiesel)
20	21.8
50	48.8
75	71.8
95	88.3

Table 3. Comparison between using TGA &GC in biodiesel conversion calculation

Oil type	TGA	GC
Model acid oil	97.6	98.6
WCO1	96	97
WCO2	96.4	97.4

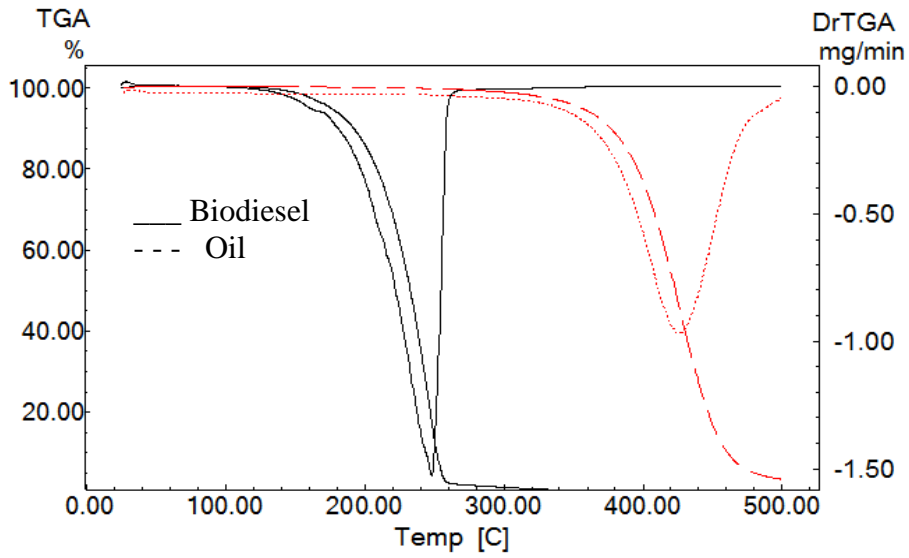


Fig. 1. TGA comparison between mixed oil and prepared biodiesel

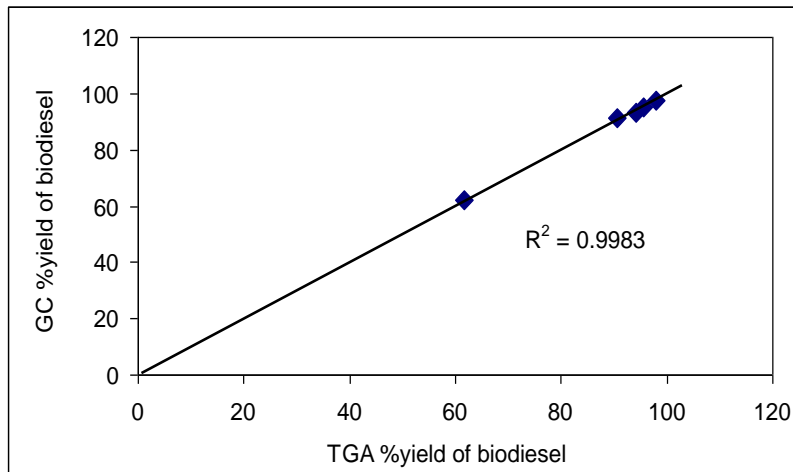


Fig. 2. TGA-GC relation

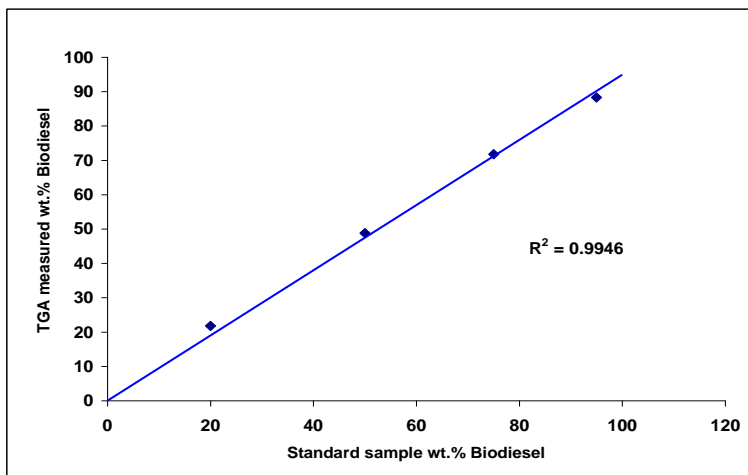


Fig. 3. Biodiesel % by weight obtained from TGA analysis vs the actual biodiesel weight % in the standard sample.

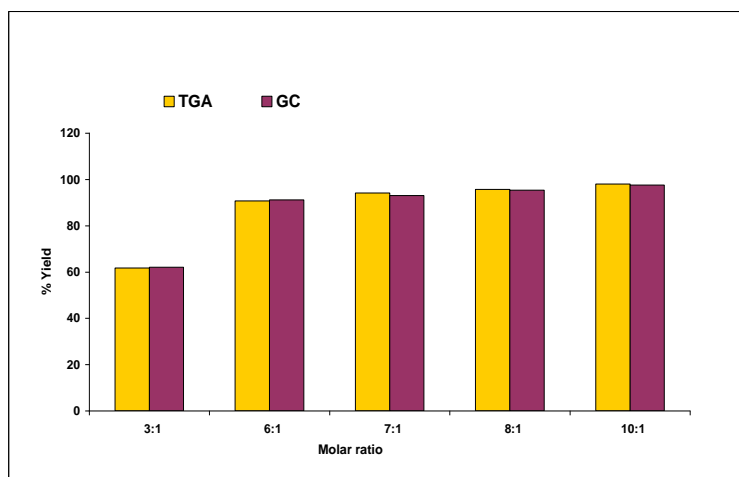


Fig. 4. Effect of molar ratio of alcohol to oil

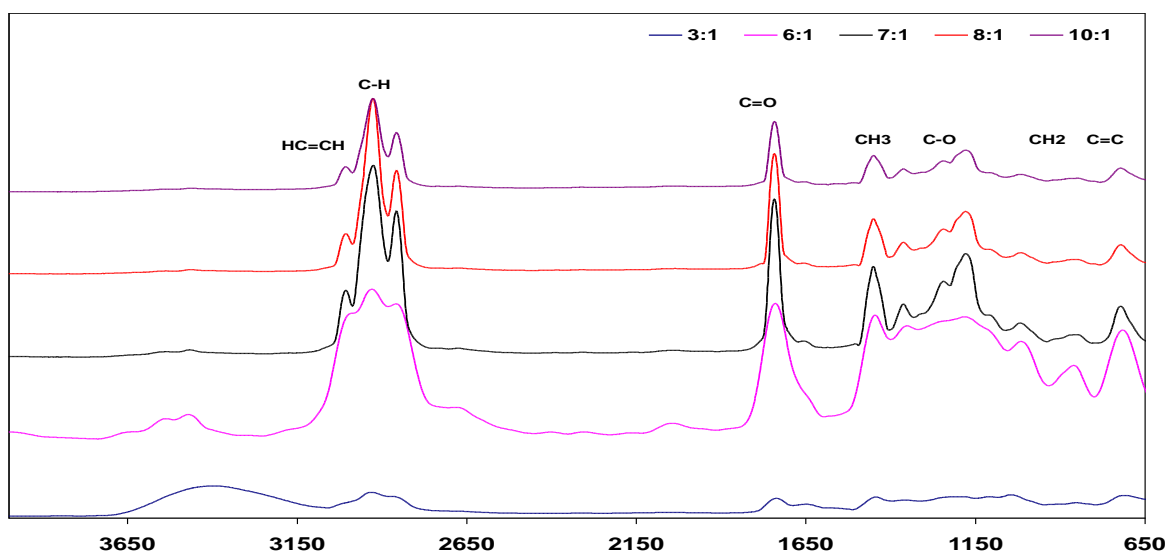


Fig. 5. Comparison between the different molar ratios FTIR curves

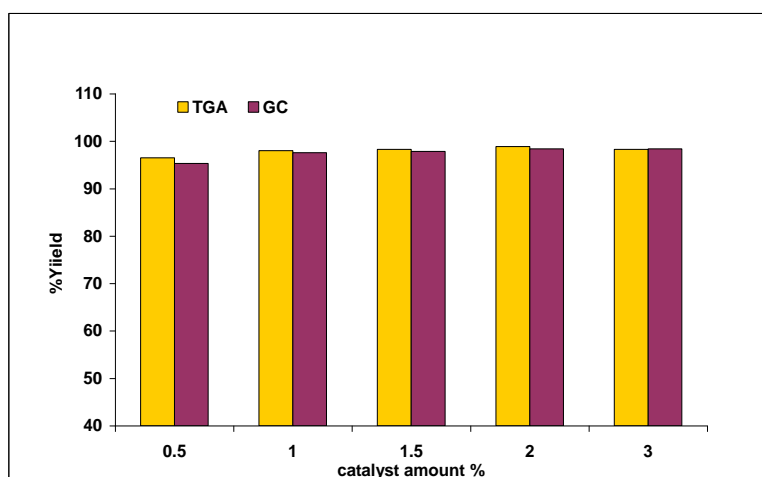


Fig. 6. Effect of catalyst amount

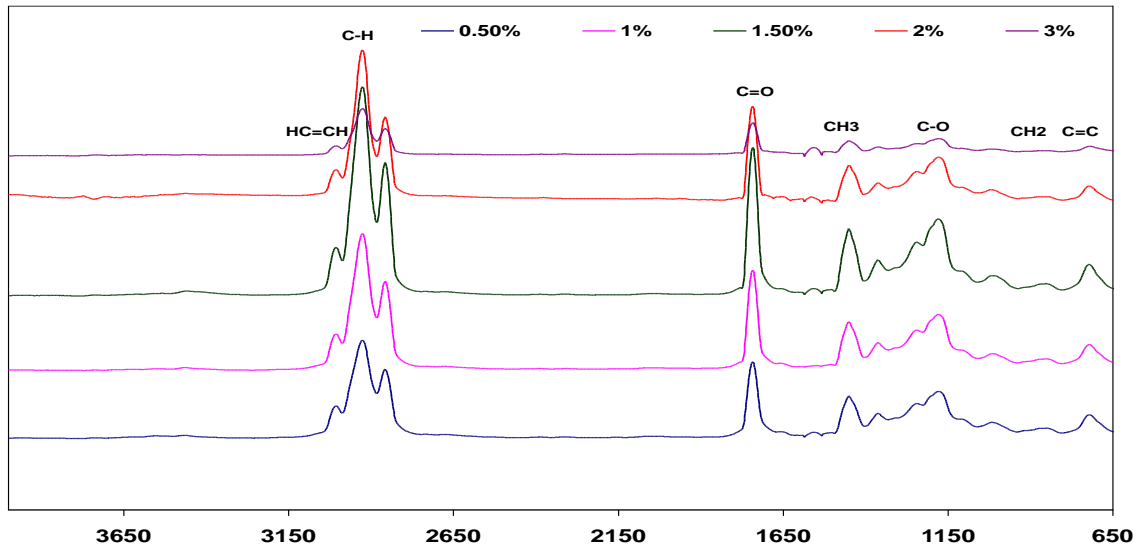


Fig. 7. Comparison between the different catalyst amount FTIR curves

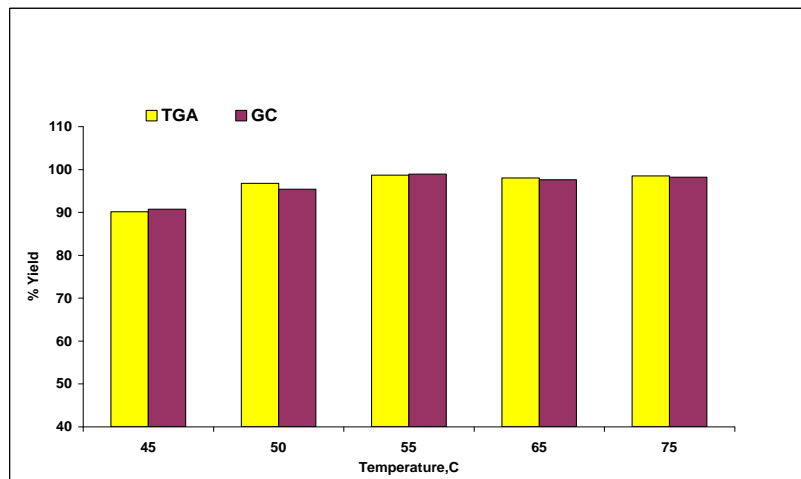


Fig. 8. Effect of reaction temperature

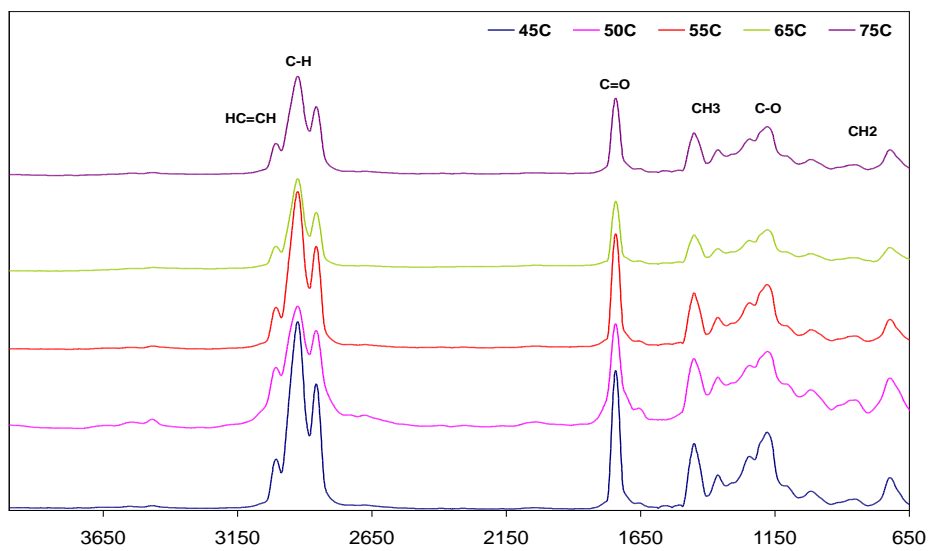


Fig. 9. Comparison between the different temperature FTIR curves

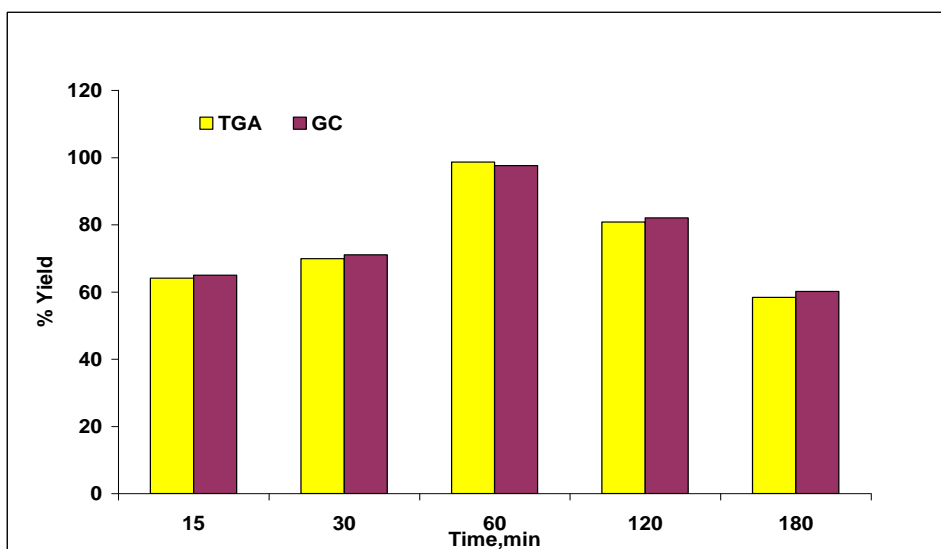


Fig. 10. Effect of reaction time

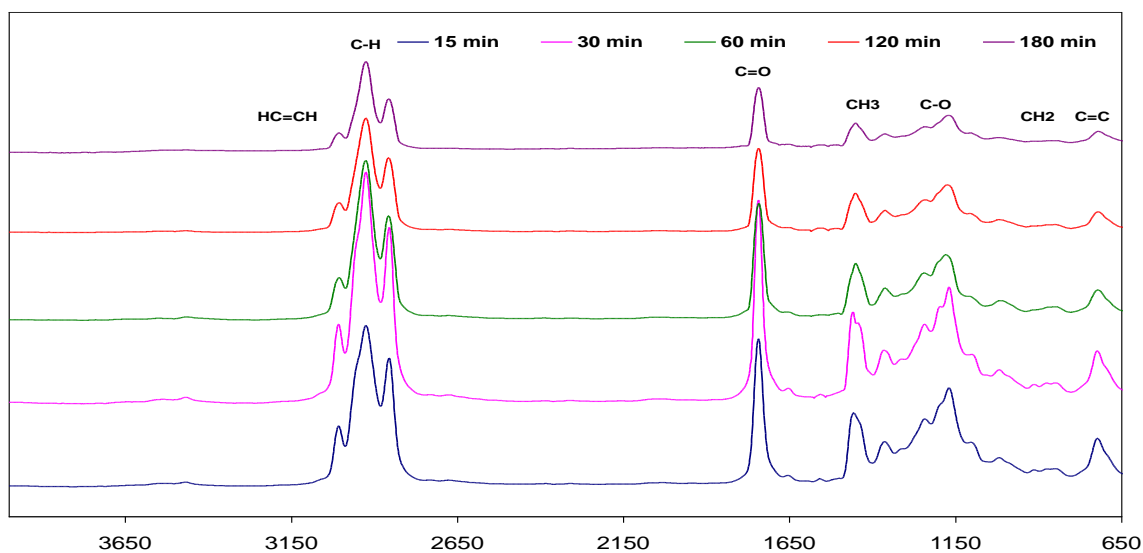


Fig. 11. Comparison between the different time of reaction FTIR curves

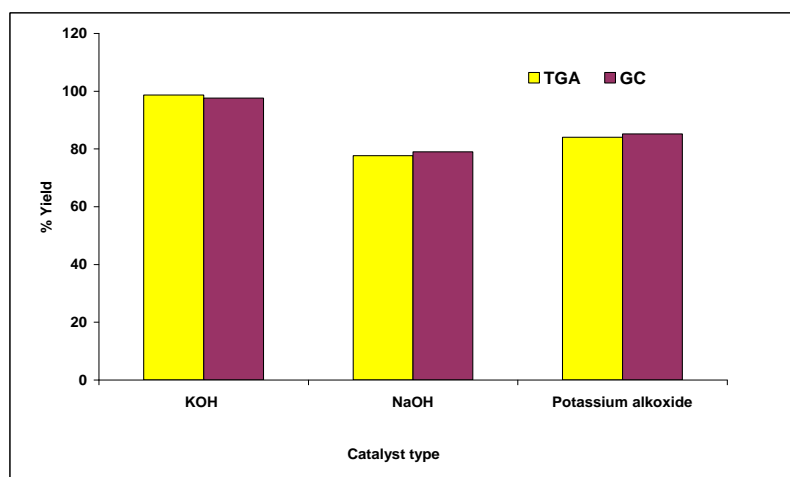


Fig. 12. Effect of catalyst type

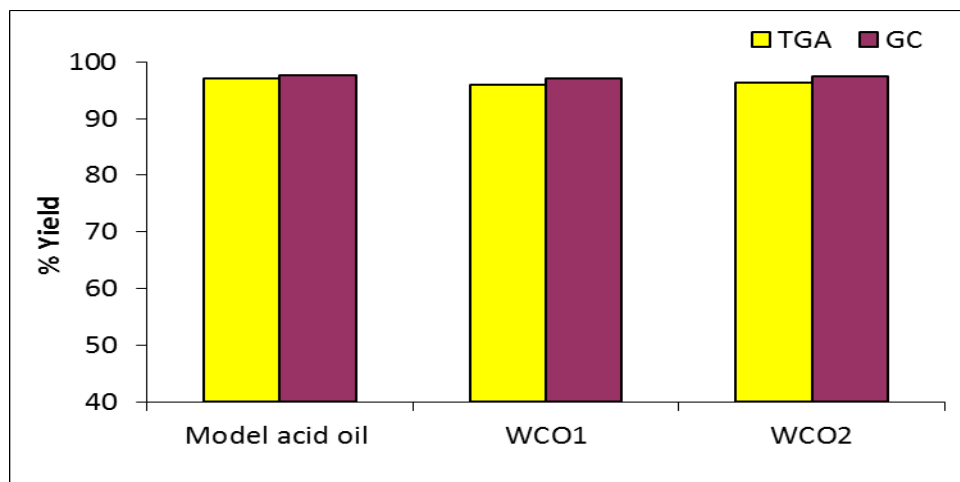


Fig. 13. Comparison between different types of oil

The percentage of biodiesel and refined mixed oil in a sample could be calculated from the TGA plot of the sample. The biodiesel conversion as measured by TGA analysis, also analyzed using GC to determine the biodiesel conversion as shown in figure (2) and table (1). The linear regression analysis suggests that TGA accurately quantifies the amount of biodiesel present. It is clear that there is good correlation between the two characterization methods.

3.2. Calibration curve for using TGA in mixture identification

Different samples of highest conversion prepared biodiesel and model acid oil mixtures (20, 50,75 and 95%) was analyzed using TGA. Figure (3) and table (2) shows that relative conversion for each sample was very similar to their actual values based on weight percent in those mixtures. The linear fit between the two data series results in an R^2 value of 0.996, which confirms this conclusion.

3.3. Effect of alcohol to oil ratio

The reaction was carried out at a constant temperature of 65 °C and with stirring at 300 rpm & 1wt% of KOH as catalyst for 1 hour. The molar ratio of methanol to oil was varied between 3:1 to 10:1, figure (4) shows the percentage conversion plot. Figure (4) showed the variations of the relative conversion as a function of the molar ratio of alcohol /oil. As the molar ratio was increased from 3:1 to 6:1 the conversion of produced biodiesel increased. It rose from 61.6 % for the ratio 3:1 to 90.6% for the ratio 6:1. Approximately 50% increased based on lower value of 61.6 %. A further increase of methanol to oil molar ratio from 6:1 to 10:1 gave an increase in the conversion of about 7 % (90.6 to 98%). The variation in biodiesel conversion with different molar ratios was observed from FT-IR spectra (as shown in figure 5) as the specific function groups intensities changed according to molar ratio used, as cleared in comparing between specific biodiesel peaks for molar ratio 3:1 and for 10:1. The excess of methanol than this ratio could interfere with the separation of ester product and by-product by increasing solubility of glycerol. Consequently, part of the diluted glycerol remained in the ester phase,

leading to foam formation and therefore apparent loss of ester product and difficulties in separation. So the optimum ratio in this study was 10:1. The figure also shows conversion s calculated using TGA technique and GC measurement to determine FAME conversion comparing the produced values. It showed that they almost have the same trend and there was a very small difference between the two values. This indicates that TGA can be used instead of GC as TGA more easily, save time and money so this reduces the biodiesel analysis cost.

3.4. Effect of the catalyst amount

Effect of varying the amount of catalyst was studied at the reaction conditions of 10:1, T=65 °C, agitation speed of 300 rpm and the catalyst amount varied from 0.5 to 3 % based on weight of oil) of KOH. Transmethylation occurs approximately 4000 times faster in presence of an alkaline catalyst than in the presence the same amount of acidic catalyst. [35] As they are less corrosive to industrial equipments, alkaline catalysts are preferred in industrial processes, potassium hydroxide (KOH) was chosen to study the effect of concentration of catalyst on biodiesel conversion. Figure (6) shows that increasing KOH concentration from 0.5 wt% to 1 wt% increased the percentage conversion of biodiesel from 96% to 98% for 0.5 wt% and 0.75 wt% respectively. But increasing concentration of catalyst more than 1%, showed very slight increase in the percentage conversion, this also shown from FTIR finger print (figure 7) for catalyst amount comparison . Beyond this limit the conversion slightly decreased with increase of the catalyst amount. This can be attributed to the formation of some saponified products with increase in catalyst amount or due to the formation of an emulsion [36], which increases the viscosity and leads to the formation of gels. These hinder the glycerol separation and hence, reduce the apparent ester conversion.

3.5. Effect of reaction temperature

For this case the reaction temperature was varied in the range $T = 45$ to 75 °C, the molar ratio of alcohol to oil was 10:1, the amount of catalyst used was 1% (based on weight of oil) KOH and the stirring speed was set at 300 rpm. The results obtained are shown in figure (8). In this figure, it can be seen that as the temperature increase from 45 °C to 55 °C, the conversion increased from about 90% to 98.7%. However when the temperature was increased up to 75 °C, there was a very slight decrease in the conversion. This is because high temperature tends to accelerate the transesterification and saponification of the glycerides by the alkaline catalyst before completion of the alcoholysis, which is an undesirable result. Beyond FTIR spectra (figure 9) cleared the small difference in conversion value. So the optimum temperature used in this study was 55 °C.

3.6. Effect of reaction time

The reaction time effect was studied at molar ratio of alcohol to oil of 10:1, the amount of catalyst used was 1% (weight of oil) KOH and the stirring speed was set at 300 rpm at 55 °C by varying values from 15 to 180 min. Figure (10), observed that the conversion of biodiesel was low initially (64 to 69.8 wt%) at lower reaction time due to high content of triglyceride and also due to the mixing and dispersion of methanol into the oil as from 15 min to 30 min. With increasing the reaction time to about 60 min conversion increased to reach 98.7 wt%. FTIR also proved that as shown in (figure 11) by comparing different intensities. By increasing reaction time more than 60 min the behavior was reversed and conversion started decrease again. This can be due to that increasing time gave the reaction the chance to be reversed and the di- and monoglycerides increased at the beginning and then decreased.

3.7. Effect of catalyst type

The performance of different alkaline catalysts were outstanding, as shown in figure (12) at the reaction conditions of 10:1, $T = 55$ °C, agitation speed of 300 rpm and catalyst amount 1% (based on weight of oil). Figure (12) showed that KOH gave the highest conversion. Also, as it can be observed, the hydroxides gave rise to higher conversion than the corresponding methoxides.

3.8. Effect of types of oil

Three different types of oil were used, model acid oil, home domestic waste cooking oil and restaurant domestic waste cooking oil. The operational temperature was 55 °C, the alcohol/oil molar ratio was kept constant at 10:1, the reaction was performed at 300 rpm with KOH as alkaline catalyst with approximately 1wt% (based on weight of oil). Figure (13) shows the conversion comparison using TGA and GC. The figure obvious that there is small difference between the two calculated conversion as in table (3), that conclude TGA can be used as method to detect the biodiesel conversion.

4. Conclusions

Biodiesel is a clean-burning diesel fuel with a chemical structure of fatty acid alkyl esters. Of the various methods available for producing biodiesel, the alkali-catalyzed transesterification of vegetable oils and animal

fats is currently the most commonly adopted method. The transesterification reaction requires an alcohol as a reactant and a catalyst. The conversion rate of fatty acid esters increases with reaction time but the conversion of the biodiesel product reaches a maximum at 60 min reaction time. Higher reaction temperatures can decrease the viscosity of oils, enhancing the reaction rate. The optimal temperature was found 55 °C. The optimal condition of catalyst concentration is about 1 wt. % for KOH which is the most commonly used catalyst. The molar ratio of alcohol to oil 10:1 was found to be the optimal ratio to obtain the optimum conversion. Thermogravimetric analysis showed to be a helpful technique in characterization of thermal stability and determining conversions of the biodiesel products.

References

- [1] F. Ma and MA. Hanna. (1999). Biodiesel production: a review. *Bioresource Technology*. 70 (1): 1–15.
- [2] A. Srivastava and R. Prasad. (2000). Triglycerides-based diesel fuels. *Renew Sust Energy Rev*. 4: 111–33.
- [3] G. Xu and G.Y. Wu. (2003). The investigation of blending properties of biodiesel and No. 0 diesel fuel. *Journal of Jiangsu Polytechnic University*. 15:16–18.
- [4] R. Alcantara, J. Amores, L. Canoira, E. Fidalgo, M. J. Franco and A. Navarro. (2000). *Biomass and Bioenergy*. 18: 515–527.
- [5] M.M. Gui, K.T. Lee and S. Bhatia. (2008). Feasibility of edible oil vs. non-edible oil vs. waste edible oil as biodiesel feedstock. *Energy*. 33: 1646–1653.
- [6] J. Kansedo, K.T. Lee and S. Bhatia. (2009). *Cerbera odollam* (sea mango) oil as a promising non-edible feedstock for biodiesel production. *Fuel*. 88: 1148–1150.
- [7] A. K. Tiwari, A. Kumar and H. Raheman. (2007). Biodiesel production from jatropha oil (*Jatropha curcas*) with high free fatty acids: an optimized process. *Biomass Bioenergy*. 31: 569–75.
- [8] P.K. Sahoo and L.M. Das. (2009). Process optimization for biodiesel production from *Jatropha*, *Karanja* and *Polanga* oils. *Fuel*. 88: 1588–1594.
- [9] P.D. Patil and S. Deng. (2009). Optimization of biodiesel production from edible and nonedible vegetable oils. *Fuel*. 88: 1302–1306.
- [10] M J. Haas. (2005). Improving the economics of biodiesel production through the use of low value lipids as feedstocks: vegetable oil soap stock. *Fuel Process Technology*. 86: 1087–96.

- [11] M. Canakci and J.V. Gerpen. (2003). Transactions of the ASAE . 46 (4): 945–954.
- [12] R. Alcantara, J. Amores, L. Canoira, E. Fidalgo, M.J. Franco and A. Navarro. (2000). Biomass and Bioenergy. 18: 515–527.
- [13] J. Cvengroš and Z. Cvengrošová. (2004). Biomass and Bioenergy. 27: 173–181.
- [14] M.P. Dorado, E. Ballesteros, J.A. Almeida, C. Schellert, H.P. Löhrllein and R. Krause (2002). Transactions of the ASAE. 45 (3): 525–529.
- [15] A.V. Tomasevic and S.S. Siler-Marinkovic. (2003). Fuel Processing Technology. 81: 1–6.
- [16] C. Adams, J. Peters, M. Rand, B. Schroer and M. Ziemke. (1983). Investigation of soybean oil as a diesel fuel extender: endurance tests. Journal of the American Oil Chemists' Society. 60: 1574–1579.
- [17] Anon. (1982). Filtered used frying fat powers diesel fleet. Journal of American Oil Chemist Society. 59:780A–1A.
- [18] C. Engler, L. Johnson, W. Lepori and C. Yarbrough. (1983). Effects of processing and chemical characteristics of plant oils on performance of an indirect-injection diesel engine. Journal of the American Oil Chemists' Society. 60: 1592–1596.
- [19] C. Peterson, D. Auld and R. Korus. (1983). Winter rape oil fuel for diesel engines: recovery and utilization. Journal of the American Oil Chemists' Society. 60: 1579–1587.
- [20] R .Strayer, J. Blake and W. Crai. (1983). Canola and high erucic rapeseed oil as substitutes for diesel fuel: preliminary tests. Journal of the American Oil Chemists' Society. 60: 1587–92.
- [21] A.W. Schwab, M.O. Bagby and B. Freedman. (1987). Preparation and properties of diesel fuels from vegetable oils. Fuel. 66: 1372–8.
- [22] C. Chang and S. Wan. (1947). China's motor fuels from tung oil. Industrial and Engineering Chemistry. 39: 1543–1548.
- [23] A. Crossley, T.D. Heyes and B. Hudson. (1962).The effect of heat on pure triglycerides. Journal of the American Oil Chemists' Society. 39: 9–14.
- [24] R.A. Niehaus, C.E. Goering, Jr L.D. Savage and S.C. Sorenson. (1986). Cracked soybean oil as fuel for a diesel engine. Transactions of the American Society of Agriculture Engineers. 29: 683–689.
- [25] D. Pioch, P. Lozano, M.C. Rasoanantoandro, J. Graille, P. Geneste and A. Guida. (1993). Biofuels from catalytic cracking of tropical vegetable oils. Oleagineux. 48: 289–291.
- [26] A. Sonntag. (1979). Reactions of fats and fatty acids. In: Swern D. editor. Bailey's industrial oil and fat products. New York: John Wiley & Sons.
- [27] P.B. Weisz, W.O. Haag and P.G. Rodeweld. (1979). Catalytic production of high-grade fuel (gasoline) from biomass compounds by shape-selective catalysis. Science. 206:57–58.
- [28] H.A. Farag, A. El-Maghraby and N.A. Taha . (2011). Optimization of factors affecting esterification of mixed oil with high percentage of free fatty acid. Fuel Processing Technology. 92: 507–510.
- [29] Standard Test Method for Compositional Analysis by thermogravimetry, E-1131-08, ETS (2010).
- [30] D. E. López , J. G. Jr. Goodwin, D. A. Bruce and E. Lotero. (2005). Transesterification of triacetin with methanol on solid acid and base catalysts. APPI.Catal. 295: 97-105.
- [31] S. Zullaikah, C. C. Lai, S. R. Vali and Y. H. Ju. (2005). A two-step acid catalyzed process for the production of biodiesel from rice bran oil. Journal of Biotechnology. 196: 1889-1896.
- [32] W. Yong , O. Shiyi, L. Pengzhan, X. Feng and T. Shuze. (2006). Comparison of two different processes to synthesize biodiesel by waste cooking oil. Journal of Molecular catalysis A: Chemical. 252: 107-112.
- [33] J.W. Robinson. (2005).Undergraduate Instrumental analysis.6 th Ed, Marcel Dekker, New York.
- [34] [http://: www.andesonmaterials.com/tga.html](http://www.andesonmaterials.com/tga.html).
- [35] M.W. Formo. (1954). Ester reactions of fatty materials. Journal of the American Oil Chemists' Society. 31(11). 548-59.
- [36] J. M. Encinar, J. F. González and R. A. Rodriguez. (2007). Ethanolysis of used frying oil: Biodiesel preparation and characterization. Fuel processing Technology. 88: 513-522.