World Academy of Science, Engineering and Technology
International Journal of Chemical and Molecular Engineering
Vol:8, No:5, 2014

Transesterification of Jojoba Oil-Wax Using Microwave Technique

Labiba I. Hussein, Maher Z. Elsabee, Eid A. Ismail, Hala F. Naguib, Hilda A. Aziz, Moataz A. Elsawy

Open Science Index, Chemical and Molecular Engineering Vol:8, No:5, 2014 publications.waset.org/9998200/pdf

***Abstract*—**Jojoba oil-wax is extracted from the seeds of the jojoba (*Simmondsia chinensis* Link Schneider), a perennial shrub that grows in semi desert areas in Egypt and in some parts of the world. The main uses of jojoba oil-wax are in the cosmetics and pharmaceutical industry, but new uses could arise related to the search of new energetic crops. This paper summarizes a process to convert the jojoba oil-wax to biodiesel by transesterification with ethanol and a series of aliphatic alcohols using a more economic and energy saving method in a domestic microwave. The effect of time and power of the microwave on the extent of the transesterification using ethanol and other aliphatic alcohols has been studied. The separation of the alkyl esters from the fatty alcohols rich fraction has been done in a single crystallization step at low temperature (−18°C) from low boiling point petroleum ether. Gas chromatography has been used to follow up the transesterification process. All products have been characterized by spectral analysis.

***Keywords*—**Jojoba oil, transesterification, microwave, gas chromatography jojoba esters, Jojoba alcohol.

I. Introduction

THE world is confronted with the crises of fossil fuel depletion and environmental pollution. The indiscriminate extraction and consumption of fossil fuels have led to a reduction in the limited petroleum reserves. Hence it is necessary to look for alternative fuels, which can be produced from available materials. Although vegetative oils can be fuel for diesel engines, however, their high viscosities, low volatilities and poor cold flow properties have led to the investigation of their various derivatives. Among the different possible sources, fatty acid methyl esters, known as biodiesel fuel derived from triglycerides (vegetable oil and animal fates) by transesterification with methanol, present the promising alternative substitute to diesel fuels and have received the most attention now a day.

The main advantages of using biodiesel are its renewability, better quality exhaust gas emission, its biodegradability and the organic carbon present in it. It is photosynthetic in origin, non-toxic and essentially free of sulfur and aromatics. It does not contribute to a rise in the level of carbon dioxide in the atmosphere and consequently to the greenhouse effect [1]. Biodiesel fuel has the potential to reduce the level of pollutants and the level of potential or probable carcinogens [2].

Biodiesel is defined as "a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats" [3]-[5]. Transesterification (also called alcoholysis) of triglycerides for biodiesel manufacture has been extensively studied in the past few years [6]. The most commonly used oils for the production of biodiesel are soybean [7], [8], sunflower [9], [10], palm [11], rapeseed [12], canola [13], cotton seed [14], jatropha [15] and jojoba oil-wax [16]. As much as possible, the biodiesel source should fulfill two requirements: low production costs and large production scale.

Often the vegetable oils investigated for their suitability as biodiesel are those which occur abundantly in the country of testing. Therefore, soybean oil is of primary interest as biodiesel source in the United States while many European countries are concerned with rapeseed oil, and countries with tropical climate prefer to utilize coconut oil, hazelnut or palm oil [17], [18] In the search for a viable vegetable oil as fuel for Egypt, jojoba ranks high as the vast area of the Egyptian deserts can be used for production the seeds are used to produce the jojoba fuel [19], [20].

Unlike vegetable oils and animal fats, jojoba oil is not a triglyceride but a mixture of long chain esters (97–98 wt %) of fatty acids and fatty alcohols therefore is more properly referred to as a wax. Many studies have been working on jojoba as a promising vegetable oil fuel for diesel engines for many years [19], [20]. These studies showed that the viscosity of jojoba raw oil is high and that lead to blockage of fuel lines, filters, high nozzle valve opening pressures and poor atomization [21], thus warrants treatment of oil before it becomes a viable engine fuel to solve the problems associated with the high viscosity of jojoba raw oil.

Jojoba oil-wax contains minor amounts of free fatty acids and alcohols, phytosterols, tocopherols, phospholipids and trace amounts of a triacylglycerol which have been carefully analyzed [22]. The jojoba oil-wax has a low chemical reactivity and a very high normal boiling point (398^{o}C) that gives this product very important physico-chemical properties and uses.

Transesterification of jojoba oil-wax has been investigated [23]-[25] using sodium methoxide as a catalyst and the transesterification reaction was carried in an autoclave at 60^{o}C for 4hrs. The present work is focused on using a more economic and energy saving method for the transesterification which is carried using microwave heating. The time of almost

L. I. Hussein is with Egyptian Petroleum Research Institute, Nasser City 11727, Cairo, Egypt (e-mail: Labiba51@yahoo.com).

M. Z. Elsabee and H. F. Naguibare with Cairo University, Faculty of Science, Department of Chemistry, Cairo, Egypt 12613 (e-mail: mzelsabee@yahoo.com, halanaguib2007@yahoo.com).

E. A. Ismail and H. A. Aziz are with Egyptian Petroleum Research Institute, Nasser City 11727, Cairo, Egypt.

M. A. Elsawy is with Egyptian Petroleum Research Institute, Nasser City 11727, Cairo, Egypt (phone: 00201013636013; e-mail: mo3taz_elsawy@yahoo.com).

Open Science Index, Chemical and Molecular Engineering Vol:8, No:5, 2014 publications.waset.org/9998200/pdf

complete transesterification (>90%) using the alkaline catalyst ranged from 3 to 10 minutes only. Another target is to investigate the synthesis of different jojoba esters using four different alcohols for the preparation of different jojoba esters which could be of commercial use later on.

II. Materials and Methods

A. Materials

The Jojoba oil-wax, a commercial grade, was purchased from Egyptian Natural Oil Company NATOIL (Cairo, Egypt). Table I presents several physical and chemical characteristics of the Jojoba oil used in our experiments along with corresponding Jojoba values reported in literature for comparison purposes [26]. Ethanol, isopropanol, pentanol, octanol, and petroleum ether (b.p. 40–60°C), sodium metal, hydrochloric acid, all were commercial grade and used without drying or purification.

TABLE I
Physical and Chemical Characteristics of Jojoba Oil Compared with Literature Values

Characteristic	Value for this study	Corresponding value from literature
Specific gravity at 25 °C	0.860	0.863
Flash point (°C)	295	295
Fire point (°C)	338	338
Freezing point (ºC)	10.6 – 7.0	9.0
Boiling point (°C)	398	398
Ash (%wt)	0.10	0.10
Moisture content (%water)	Less than 0.05	**
Iodine value (g/100 g)	81-82	82
Saponification value	92-95	92
Average molecular weight	606	**
pH	6.7-7.0	7.0–7.3
Refractive index at 25 °C	1.460	1.465

B. Instrumentation

The evidence of the transesterification reaction of jojoba oil to its corresponding derivatives was monitored using FTIR and 1H-NMR spectroscopy. Infrared analysis was carried out using a Perkin–Elmer 398 FTIR spectrophotometer between 400- 4000cm^{-1}. ^{1}H-NMR analysis of samples was carried out on a Bruker AC-400 at 20°C in $CDCl_3$ solution. Pour point measurements were carried out using SEAT cloud and pour point cryostat (UK) according to ASTM method D 5853-97. Viscosity of different samples was measured using Cannon Fenske routine viscometer (ASTM D 446-93). High calorific value (kJ g^{-1}) was determined using Parr Calorimeter according to the (ASTM D 240). GC analyses were determined in GC-Agilent 7890A system, column, HP5, 30 meter, injector temperature 275°C Start at 80°C by ramp 8/min to 300°C (15min), Detector-325 FID.

C. Transesterification of Jojoba Oil-wax to Ethyl Jojoboate

Commercial kitchen microwave oven was used to carry out the transesterification reactions. 0.07g of freshly cut sodium metal was added to 2.5ml ethyl alcohol over 30min period, the solution obtained was poured over 10ml of jojoba oil and 5ml of ethyl alcohol, all in quick fit bottomed round flask [23]. The flask was inserted in the microwave oven adjusted for time and power. The reaction was investigated for powers (90, 360, 600 and 800 watt), duration time (3, 6, 8 and 10 minutes), and alcohols (ethanol, isopropanol, pentanol and octanol). At the end of the reaction the mixture was neutralized by adding 0.3ml concentrated HCl with vigorous stirring at room temperature. The crude product was dissolved in petroleum ether and cooled to temperature range of (-18 to -25°C) overnight. The obtained white crystals of jojobyl alcohol were filtered off on cold Bűchner funnel using water pump. The separated solid part (jojobyl alcohol) was left to melt in room temperature and the liquid part (the ester) was concentrated in a rotary evaporator.

D. Determination of the Conversion Rate

The gas chromatography analyses (GC) were used to follow the conversion rate of the transesterification reaction. The processes were followed by determination the area under the peaks of jojoba oil and comparing it with the corresponding peak after the reaction to determine the conversion rate using the following equation.

$$CR = (1 - \frac{A}{A^{\circ}}) \times 100$$

where A is area under the peak of Jojoba oil before transesterification, A° is area under the peak of Jojoba oil after transesterification

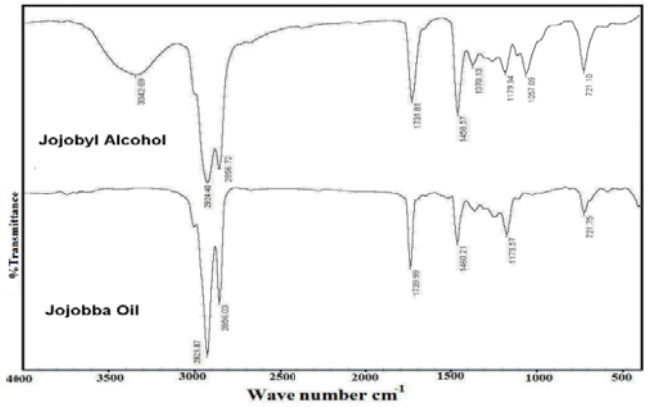
III. Results and Discussion

A. Characterization of Jojoba Oil and its Derivatives

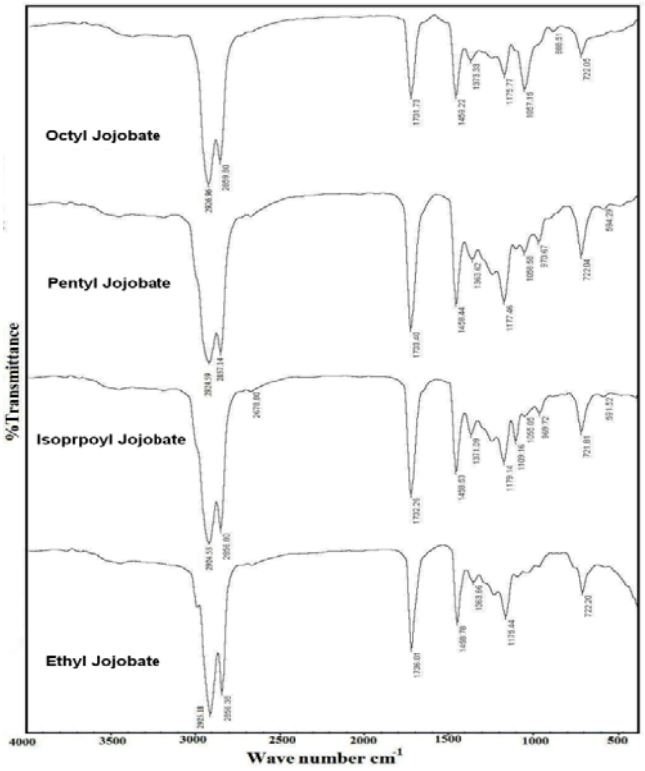
1. FTIR Spectroscopy

The FTIR spectra of the jojoba oil and jojoba esters Fig. 1 (a) clearly show almost absence of the broad band at 3342cm^{-1} characteristic for the OH stretching vibration. However, in Fig. 1 (b) the jojoba alcohol shows a clear band at 1731cm^{-1} characteristic for the C=O stretching indicating that the alcohol is still contaminated with either ester or unchanged jojoba meanwhile, the esters seem to be in a purer state due to absence of this wide broad band at 3342cm^{-1}. All the spectra have the characteristic C=O band at around 1731-1739cm^{-1} and the band at 1458-1460cm^{-1} due to the double bond. All compounds have one or two double bonds. This finding has been augmented with NMR measurements.

Open Science Index, Chemical and Molecular Engineering Vol:8, No:5, 2014 publications.waset.org/9998200/pdf



(a)

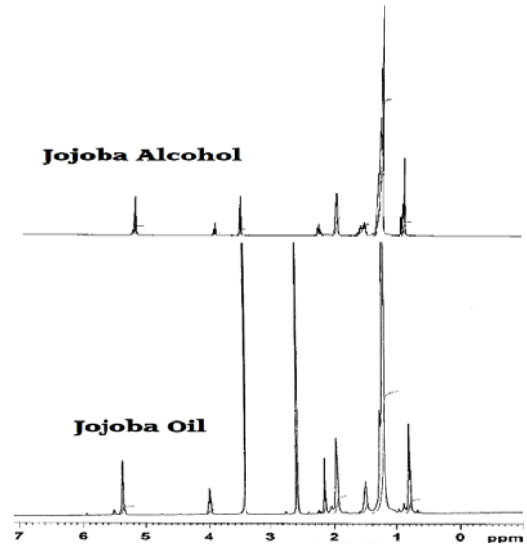


(b)

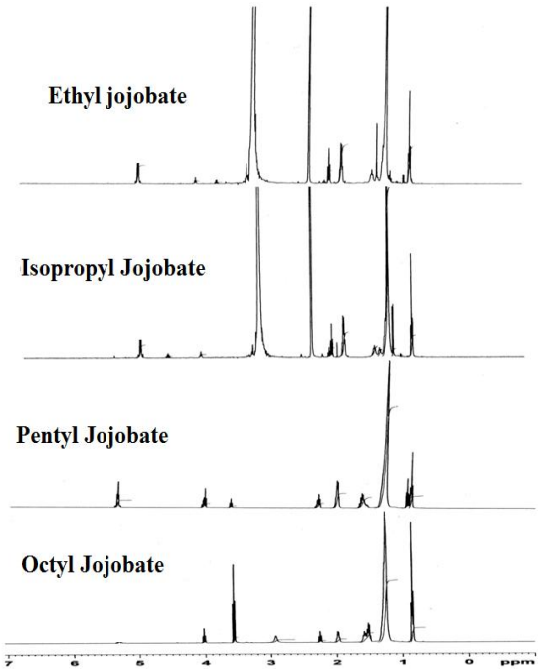
Fig. 1 FTIR spectra of (a) jojoba oil and alcohol (b) jojoba esters

2. ^{1}H-NMR Spectroscopy

Fig. 2 shows bands for jojoba oil (DMSO) and jojoba alcohol ($CDCl_3$) ^{1}HNMR δ 0.761-0.791 (m 6 H, CH_3), 1.17 (–$(CH_2)_n$-), 1.46 (4 H, (CH_2), 1.89 (-CH_2-C=C), 2.07 (–CH_2-C=O), 3.8-3.9 (O-CH_2) and 5.19 (–CH=CH-) [23]. All the NMR spectra of ethyl, isopropyl, pentyl and octyl jojobate show similar characteristic bands. However, it was difficult to evaluate the exact numbers of protons from the intensities of the individual spectra. The reason could be the slight contamination of separated components alcohol and esters). The ethylenic protons of the double bond at 5.19ppm are evident in all spectra. The rest of band assignments are similar to jojoba and its alcohol. The spectrum of jojoba oil has small band at 8.32ppm possibly due to some aromatic impurities.



(a)



(b)

Fig. 2 ^{1}HNMR spectra of (a) jojoba oil and alcohol (b) ^{1}HNMR spectra for ethyl, isopropyl in (DMSO) pentyl and octyl in (CDCl3)

3. Gas Chromatography

Jojoba wax was heated in a microwave oven with different alcohols in order to perform alcoholysis. After separation of the products they were analyzed by GC. Fig. 3 is a representation of the GC curves for the products obtained after alcoholysis for different time intervals. It is obvious that the peak due to the original jojoba oil is decreasing in intensity sharply after just 3min. Four new bands arise due mainly to the ester, alcohol and probably to an array of esters and

Open Science Index, Chemical and Molecular Engineering Vol:8, No:5, 2014 publications.waset.org/9998200/pdf

alcohols with different chain length as jojoba oil is actually a mixture of several chains with different lengths. A small band appears after 10min of heating in the microwave which could possibly be due to slight oligomerization reaction.

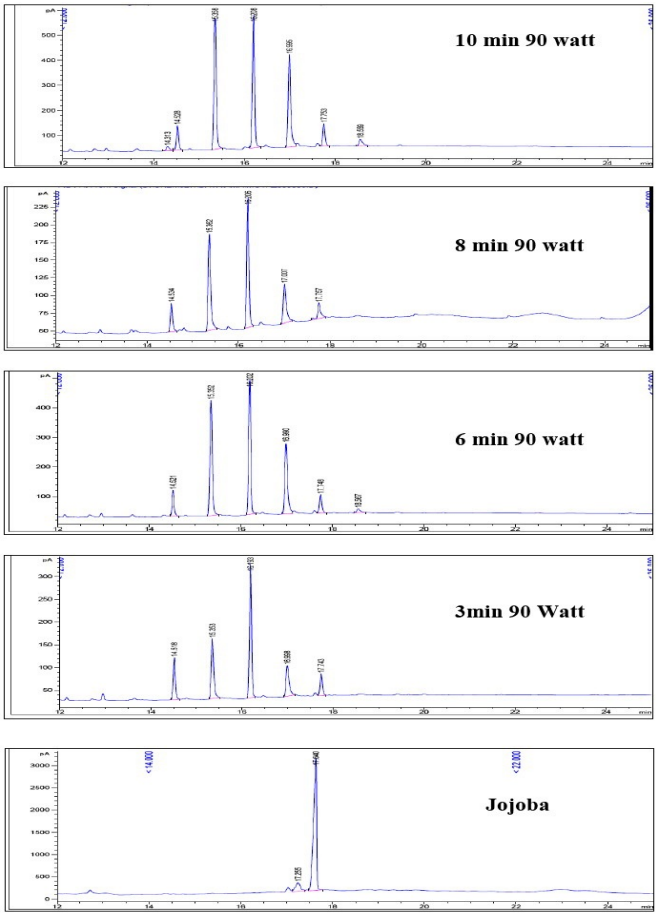
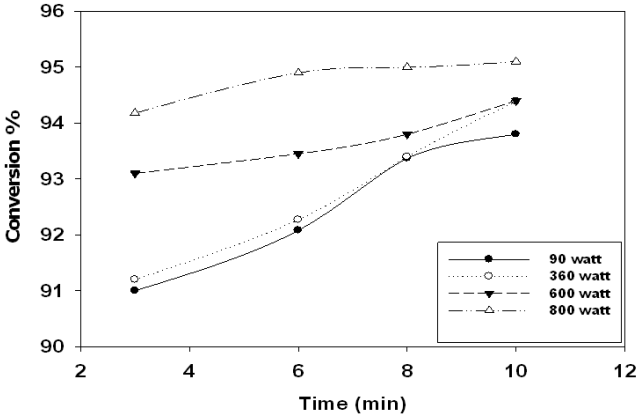


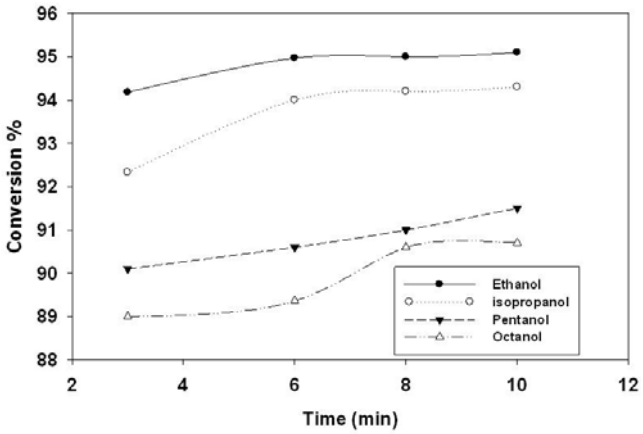
Fig. 3 G. C. curves of jojoba oil and after heating in microwave at 90 watt for 3 min, 6 min, 8 min and 10 min

B. Influence of Reaction Conditions on the Conversion Rate

The effect of the time and microwave power on the extent of the transesterification reaction can be seen in Fig. 4. It took only 3min microwave heating to reach an extent of transesterification around 90% even at 90 Watt, the lowest microwave power. The extent of reaction also increases with increasing both time and power of the microwave which is a reasonable conclusion since higher power or time may lead to degradation of the products. At constant microwave condition (power and time), the transesterification process of jojoba oil was studied with a series of alcohols. The conversion rate of the transesterification of jojoba oil with deferent alcohol can be seen in the Fig. 4 (b). It is obvious that the conversion rate has a relation with the alcohol chain length which decreased with decreasing the alcohol chain length. This can attributed to the steric effect of long chain alcohol in the reaction.



(a)



(b)

Fig. 4 Effect of (a) time, (b) type of alcohol on the extent of transesterification of jojoba oil–wax

C. Characterization of Jojoba Ester Derivative as a Biofuel

The obtained esters have been characterized by some physical measurements: Density, Kinematic viscosity; and calorific value and were compared with the original Jojoba wax. The physical data are depicted in Table II. Ethyl and isopropyl jojobate have lower density and much smaller viscosity than the original jojoba wax this finding could be important for further applications of these esters as biofuel.

TABLE II
PHYSICAL CHARACTERISTICS OF JOJOBA OIL AND SOME DERIVATIVES

Sample	Density at 20°C (kg $^{m-3}$) ASTM D 4052	Kinematic viscosity at 40°C (mm^2s^{-1}) ASTM D 445	High calorific value (kJ g^{-1}) ASTM D 2382
Jojoba oil – Wax	862.6	26.31	41.647
Ethyl Jojoboate	857.7	13.39	40.278
Isopropyl Jojoboate	858.7	13.45	40.155
Pentyl Jojoboate	861.1	15.85	40.044
Octyl Jojoboate	868.9	16.02	40.011

D. Pour Point Depressant

The obtained esters have another important characteristic for their ability to be used as pour point depressant for crude waxy oils to prevent the wax deposition on pipelines. The wax

deposition on the surface of transportation lowers the transportation efficiency of oil and increase manufacture cost. A pour point depressant (PPD) is an additive used to lower the wax deposition temperature (wax appearance temperature (WAT) and usually composed of long chain hydrocarbons which could interfere with the crystallization of the wax molecules and hinder their deposition. [27]- [29]

Accordingly the obtained jojoba esters were tested in the cloud and pour point cryostat to find out their effect as pour point depressants and the results are depicted in Table III. The pour point value of the untreated crude oil is 3°C. From the table it seems that the isopropyl derivatives can act well as PPD; it lowered the PP by 15°C, all other esters as well as the original jojoba wax slightly decrease the PP.

TABLE III
POUR POINT DEPRESSING VALUES OF JOJOBA OIL AND ITS DERIVATIVES

Sample	Pour point (OC)			
Conc.	100 ppm	500 ppm	1000 ppm	5000 ppm
Jojoba oil – Wax	0	0	-3	-6
Ethyl Jojoboate	0	-3	-6	-6
Isopropyl Jojoboate	-3	-6	-9	-12
PentylJojoboate	0	-3	-3	-6
Octyl Jojoboate	0	-6	-9	-9

IV. CONCLUSION

Jojoba oil as a renewable resource has a big potential for the production of biofuel with a low price. Biofuel production requires the hydrolysis of the oil into alcohol and ester both components could have potential applications in the petroleum and cosmetic industries. The hydrolysis of jojoba has been successfully achieved by heating in the microwave oven. GC was used to monitor the reaction conversion rate; almost complete conversion of the oil into its two components was carried out in 3-10min. Ethyl, isopropyl, pentyl and octyl alcohol were used in the transesterification reaction. All esters and alcohol were characterized by FTIR and NMR techniques to elucidate their structures. The physical characteristics; viscosity, density and calorific values of jojoba and its derivatives have been measured. The pour point depression capacity of all investigated compounds was measured and the isopropyl ester of jojoba shows the highest potential for further applications.

REFERENCES

[1] Singh SP, Singh D. Biodiesel production through the use of different sources and characterization of oils and their esters as the substitute of diesel: A review. Renewable and Sustainable Energy Reviews 2010; 14: 200–216
[2] Ma F, Clement LD, Hanna MA. The effect of mixing on transesterification of beef tallow. BioresourTechnol 1999;69: 289–93.
[3] Ratledge, Boulton CA. Fats and oils. In: Moo Young M., Blanch HN, Dream S, Wang DIC, editors, Comparative Biotechnology in industry, agriculture and medicine, vol. 3. New York: Pergamon Press; 1985, p. 983–1003.
[4] Lee I, Johnson LA, Hammond EG. Use of branched-chain esters to reduce the crystallization temperature of Biodiesel. J Am Oil ChemSoc 1995; 72: 1155–60.
[5] European Committee for Standarisation (DIN). Automotive fuels. Fatty acid methyl esters (FAME) for diesel engines. Requirements and test methods. European Standard EN 14214; 2003.
[6] Alcantara R, Amores J, Canoira L, Fidalgo E, Franco MJ, Navarro A. Catalytic production of biodiesel from soy-bean oil, used frying oil and tallow. Biomass and Bioenergy 2000; 18: 515–27.
[7] Freedman B, Butterfield RO, Pryde EH. Transesterification kinetics of soybean oil. J Am Oil ChemSoc 1986; 63(10):1375–80.
[8] Noureddini H, Zhu D. Kinetics of transesterification of soybean oil. J Am Oil ChemSoc 1997; 74: 1457–63.
[9] Antolın G, Tinaut FV, Briceno Y, Castano V, Perez C, Ramırez AI. Optimization of Biodiesel production by sunflower oil transesterification. BioresourTechnol 2002; 83(2): 111–4.
[10] Mohamed M, Soumanoua B, Uwe T, Bornscheuer A. Improvement in lipasecatalyzed synthesis of fatty acid methyl esters from sunflower oil. Enzyme MicrobTechnol 2003; 33: 97–103.
[11] Darnoko D, Cheryan M. Kinetics of palm oil transesterification in a batch reactor. J Am Oil ChemSoc 2000; 77(12): 1263–7.
[12] Kusdiana D, Saka S. Kinetics of transestrification in rapseed oil to biodiesel fuel as tested in supercritical methanol. Fuel 2001; 80: 693–5.
[13] Zou L, Atkinson S. Characterizing vehicle emissions from the burning of biodiesel made from vegetable oil. Environ Technol 2003; 24: 1253.
[14] Kose O, Tuter M, Aksoy HA. Immobilized candida antarctica lipase-catalyzed alcoholysis of cotton seed oil in a solvent-free medium. BioresourTechnol 2002; 83:125–9.
[15] Foidl N, Foidl G, Sanchez M, Mittelbach M, Hackel S. Jatropha curcas L. as a source for the production of biofuel in Nicaragua. BioresourTechnol 1996; 58: 77–82.
[16] LaureanoCanoira_, Ramo´ n Alca´ ntara, M% a Jesu´ s Garcı´a-Martı´nez, Jesu´ s Carrasco. Biodiesel from Jojoba oil-wax: Transesterification with methanol and properties as a fuel. Biomass and Bioenergy 2006; 30: 76–81.
[17] He Y, Bao YD. Study on cottonseed oil as a partial substitute for diesel oil in fuel for single-cylinder diesel engine. Renew Energ 2005;30:805–13.
[18] Mustafa C, Ahmet E, Erol A. Performance and exhaust emissions of a biodiesel engine. ApplEnerg 2006;83:594–605.
[19] Radwan MS, Ismail MA, Elfeky SMS, Abu-Elyazeed OSM. Jojoba methyl ester as a diesel fuel substitute: preparation and characterization. ApplThermEng 2007;27:314–22.
[20] Selim MYE, Radwan MS, Saleh HE. Performance of dual fuel engine running on jojoba oil as pilot fuel and CNG or LPG. In: Summer heat transfer conference. Canada: ASME-JSME Thermal Engineering; 2007.
[21] Ejim CE, Fleck BA, Amirfazli A. Analytical study for atomization of biodiesels and their blends in a typical injector: surface tension and viscosity effects. Fuel 2007;86:1534–44
[22] Busson-Breysse J, Farines M, Soulier J. Jojoba wax: its esters and some of its minor components. J Am Oil ChemSoc 1994; 71(9): 999–1001.
[23] Canoira L, Alca′ntara R, García-Martínez MJ, Carrasco J. Biodiesel from jojoba oil-wax: transesterification with methanol and properties as a fuel. Biomass and Bioenergy 2006; 30: 76–81.
[24] Hamilton R J, Raie M Y. Structure of the Alcohols Derived From Wax Esters in Jojoba Oil. Chemistry and Physics of Lipids 1975; 14: 92-96
[25] Shani A, Lurie P. Synthesis of jojobamide and homojojobamide. J Am Oil ChemSoc 1980; 112–4.
[26] Al-Widyan, A. Mu'taz, Al-Muhtaseb, Energy Conversion and Management 51, 1702 (2010).
[27] Silverstein R. M. Clayton Bassler G. Morrill T. C.Spectrometric Identification of Organic Compounds, John Wiley, Fifth Ed. (1991).
[28] D. Groffe, P. Groffe, S. Takhar, Petroleum Science And Technology 19(2001) 205
[29] Al-Sabagh A. M. NoorEl-Din M. R. Morsi R. E. Elsabee M Z. Oil Soluble Styrene- Maleic Anhydride Copolymer Derivatives and Their Flow Improver Properties of Waxy Crude Oil. J Petroleum Science and Engineering 65 (200).

Open Science Index, Chemical and Molecular Engineering Vol:8, No:5, 2014 publications.waset.org/9998200/pdf