

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Empirical Approach for Improving Calorific Value and Pour Point of Biodiesel.

Ashraf Amin, AG Gadallah*, NN El-Ibiari, and GI El-Diwani.

Chemical Engineering and Pilot Plant Department, National Research Centre, El Buhouth St., Dokki, Cairo 12311, Egypt.

ABSTRACT

The aim of the work is to study the influence of the feedstock composition on biodiesel quality. Four types of vegetable seeds were extracted and converted to biodiesel (fatty methyl esters - FAME). Density, kinematic viscosity, flash point, calorific value and pour point were tested according to the standard ASTM (D6751). Statistically significant relationships were elucidated between calorific value and flash point, calorific value and density, calorific value and kinematic viscosity. The final equation relating the calorific value with density, kinematic viscosity and flash point was also predicted. Influences of blending ratios between biodiesel samples according to their fatty acid methyl acid composition were studied.

Keywords: Biodiesel blending- Vegetable oil- Calorific value - Transesterification

**Corresponding author*

INTRODUCTION

The depleting reserves of fossil fuel, increasing demands for diesels and uncertainty in their availability is considered to be the important trigger for many initiatives to search for the alternative source of energy, which can supplement or replace fossil fuels. Various alternative fuels are considered and efforts were made to analyze the suitability of the fuel and its demonstration. Renewable fuels have received more attention as it reduces the environmental pollution (by completing carbon cycle). Hence, researchers and scientific community worldwide have focused on the development of biodiesel and the optimization of the processes to meet the standards and specifications needed for the fuel to be used commercially. The most commonly used oils for the production of biodiesel are soybean [1, 2], sunflower [3, 4], palm [5], rapeseed [6], canola [7], cotton seed [8] and *Jatropha* [9]. Since the prices of edible vegetable oils are higher than that of diesel fuel, therefore waste vegetable oils and non-edible crude vegetable oils are preferred as potential low priced biodiesel sources.

From a chemical point of view, oils from different sources have different fatty acid compositions. The fatty acids vary in their carbon chain length and in the number of unsaturated bonds they contain. Fats and oils are primarily water-insoluble, hydrophobic substances in the plant and animal kingdom that are made up of one mole of glycerol and three moles of fatty acids and are commonly referred to as triglycerides [10].

Table 1: Standard specifications for biodiesel fuel (B100) [13-15]

Property	Units	Biodiesel		Petro diesel	
		EN14214	ASTM D6751	EN 590	ASTM D975
Density @15° C	g/cm ³	0.86-0.90	0.88	0.82-0.845	0.850
Kinematic viscosity (40° C)	cSt (mm ² /s)	3.50-5.00	1.9-6.0	2.0-4.5	2.60
Flash point	°C	120 Min	100-170 Min	≥55	60-80
Cetane number	-	51 Min	47 Min	Min 51	40-55
Cloud point	°C	-	-3 to -12	-20 to -5	-20
Pour point	°C	-	-15 to 10	-	-35
Water content	%(v/v) or (mg/kg)	500(mg/kg) Max	.05(v/v) Max	Max 200	0.05%
Acid number	mg KOH/g	0.50 max	0.80 max	-	0.062
Lower heating value	MJ/kg	35	-	-	42-46
Total glycerine	% mass	0.25 max	0.24 max	-	-
Sulfated ash content	% mass	0.02 max	0.02 max	10(mg/kg)	.05%(v/v)
Ester content	%mass	96.5 min	-	Max 0.5% (m/m)	-

Triglycerides are esters of three fatty acids and one glycerol. These contain substantial amount of oxygen in their structures. When three fatty acids are identical, the product is simple triglycerides, when they are dissimilar the product is mixed triglycerides. Fatty acids which are fully saturated with hydrogen have no double bonds. Those with one missing hydrogen molecule have one double bond between carbon atoms and are called mono saturated. And those with more than one missing hydrogen molecule have more than one double bond and are called polyunsaturated. Fully saturated triglycerides lead to excessive carbon deposits in engines. The fatty acids are different in relation to the chain length, degree of unsaturation or presence of other chemical functions. Chemically, biodiesel is referred to as the mono-alkylesters of long-chain-fatty acids derived from renewable lipid sources [11]. The important properties of vegetable oils are classified into three groups [12]:

- Physical properties - viscosity, cloud point, pour point, flash point etc.
- Chemical properties - chemical structure, acid value, saponification value, sulphur content, copper corrosion, oxidation resistance and thermal degradation etc.
- Thermal properties - distillation temperature, thermal conductivity, carbon residue and calorific value etc.

The first objective of this study was to estimate mathematical relationships between calorific value CV, viscosity, density and flash point measurement of various biodiesel fuels from various vegetable oils by transesterification method. The second one is the influence of blending ratio between biodiesel samples according to their fatty acid composition in order to improve their properties. The fuel properties of biodiesel must meet the standard specification of biodiesel fuel either the European Committee EN-14214 or the American society of testing materials (ASTM) D-6751. Table (1) shows the standard specifications for biodiesel fuel.

EXPERIMENTAL

Materials

Rape seeds, castor seeds were supplied by Cultivation and Production of Medicinal and Aromatic Plant Dept. at National Research Centre of Egypt. Jatropha seeds were obtained from Ministry of Agriculture and palm oil was obtained from a local store. Analytical reagents grade of methanol (99.8% purity) was procured from Merck and commercial hexane obtained from Alexandria Petroleum Company of Egypt. The potassium hydroxide was used as catalyst has a purity of 85%, obtained from Modern Lab Company. Glacial acetic acid analytical grade (Merck) was used to stop the reaction:

Procedure

Extraction

The seeds of castor and Jatropha were decorticated to separate kernel and husk. The oil was extracted from the grinded seeds of rape, castor and Jatropha in Soxhlet apparatus by using hexane as solvent. The solvent was recovered using rotary evaporator and the residual oil was cooled and weighed. The oil was then transesterified to fatty acid methyl esters.

Transesterification

The reactor was initially charged with the oil and preheated to the desired temperature. The catalyst (potassium hydroxide) was dissolved in the methanol and the resulted solution was added to the agitated reactor. The reaction was timed as soon as the catalyst and methanol solution was added. After the prefixed time, the reaction was immediately quenched with the stoichiometric amount of acetic acid to neutralize the catalyst. Then methanol was separated from biodiesel portion via rotary evaporation. The residual was transferred to a separating funnel, and allowed to separate gravitationally. The upper biodiesel layer was dried at 80°C.

Analytical methods

The composition and quantity of methyl ester in biodiesel was determined using a HP 6890 series 2 gas chromatograph with a flame ionization detector. The capillary column was a DB-WAX column of 30 m length, and 530 μm inner diameters packed with Apiezon. Detector temperature was 280°C, injection temperature was 300°C and the column temperature was programmed from 100 to 240°C at 15°C/min.

RESULTS AND DISCUSSION

Table 2 illustrates the analysis results of the biodiesel fatty acid methyl esters composition percentage and the calculated ratios of saturated, monounsaturated and polyunsaturated fatty acids. The degree of unsaturation (DU) and cetane number (CN) were estimated from the following empirical equations found in literature [16]:

$$\text{DU} = (\text{monounsaturated Cn: 1, wt. \%}) + 2 \cdot (\text{Poly-unsaturated Cn: 2, 3, wt \%})$$

$$\text{CN} = \sum X_{\text{ME}} (\text{wt \%}) \text{CN}_{\text{ME}}$$

Where **CN** is the Cetane number of biodiesel, X_{ME} is the weight percentage of each methyl ester and CN_{ME} is the Cetane number of individual methyl ester.

A total of 8 fatty acids were found in the bio-oils. Castor and palm oils have six fatty acids in each, while rape seed oil has seven fatty acids. Jatropha has only four fatty acids. Castor oil is mostly composed of ricinoleic fatty acid. Palm oil and jatropha oil are composed of three main fatty acids: palmitic, oleic, and linoleic. Rape seed oil contains three main fatty acids: oleic, linoleic, and linolenic.

Palm oil has the highest degree of saturation followed by Jatropha, rape seed then castor, so the cetane number of palm is the highest one and that of castor is the lowest one, as shown in Figure 1. This agrees with literature [17, 18], the more saturated the molecules, the higher the cetane number.

As shown from Figure 1 and Table 2, Castor oil has the highest concentration of monounsaturated fatty acids (87.38%) and low concentration of both saturated and polyunsaturated, which are considered preferred properties for cold flow and oxidative stability of biodiesel [16, 19]. Palm oil satisfies the limit of cetane number, flash point and density which is distinguished by low poly unsaturated fatty acids and high content of saturated fatty acids (14.5 and 59.57% respectively). Rape seed oil satisfies the limit of carbon residue and density parameters which is characterized by a low content of fatty acids (7.33%). Jatropha oil does not satisfy any parameters of the European Standard UNE-EN 14214 which is characterized by a high content of poly unsaturated fatty acids (48.18%).

Table 2: Composition of Investigated Vegetable Oils in the study (%)

Fatty acid	Castor	Palm	Rape seed	Jatropha
Palmitic (16:0)	1.45	54.24	4.39	18.22
Stearic (18:0)	1.7	4.87	1.67	5.14
Oleic (18:1)	8.24	25.93	60.95	28.46
Linoleic (18:2)	8.5	13.2	19.04	48.18
Linolenic (18:3)	0.97	1.3	11.76	0
Ricinoleic (18:1) OH	79.14	0	0	0
Ecosanoic (20:0)	0	0.46	1.27	0
Erucate (22:1)	0	0	0.9	0
Saturated	3.15	59.57	7.33	23.36
Monounsaturated	87.38	25.93	61.85	28.46
Polyunsaturated (2,3)	9.47	14.5	30.8	48.18
DU	106.32	54.93	123.45	124.82
Cetane number	40.47927	65.22783	50.90268	54.02552

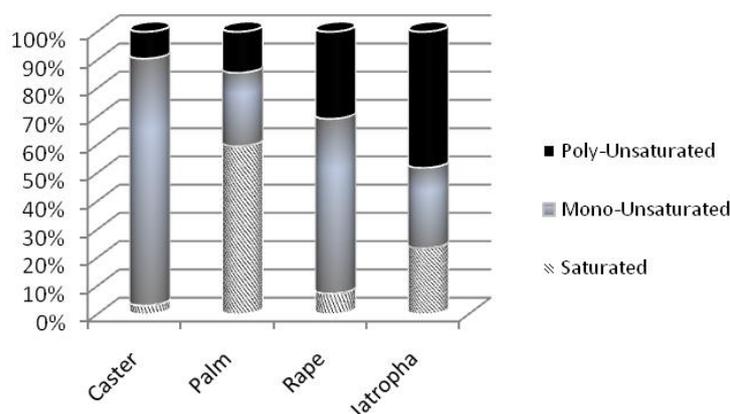


Figure 1: The saturated/unsaturated composition of the vegetable oils

From Table 3, castor oil is distinguished by the highest density, kinematic viscosity, carbon residue, and flash point; and by the lowest pour point, cloud point, and calorific value. On the other side, Jatropha oil is

distinguished by the highest calorific value and cloud point; and by the lowest density, carbon residue and flash point. However, the low calorific value of castor oil has to be addressed either by using castor oil with a higher calorific value or by mixing castor with other oils to improve its calorific value. To address this issue, we will proceed mathematically by developing a set of equations. The proposed equations will be set to provide a relationship between the parameters of biodiesel with each other and with the fatty acid constituents of the oil.

Table 3: Physical properties of biodiesel

Property	Castor	Palm	Rape seed	Jatropha
Density, g/l, @15.6°C	0.9307	0.8839	0.8815	0.87
Kinematic viscosity, cSt, @40°C	15.25	4.44	4.8	5.7
Pour point, °C	-30	-6	0	-9
Cloud point, °C	-18	-3	6	6
Carbon residue, wt. %	0.35	0.258	Nil	Nil
Flash point, °C	194	163	176	160
Calorific value, kJ/kg	36782	40079	39553	40590

Figures 2, 3 and 4 show the calorific value as a function of flash point, kinematic viscosity, and density respectively. Calorific value is inversely proportional to flash point, kinematic viscosity, and density. Mathematical equations were developed to model the individual relationships between calorific value with flash point, kinematic viscosity, and density.

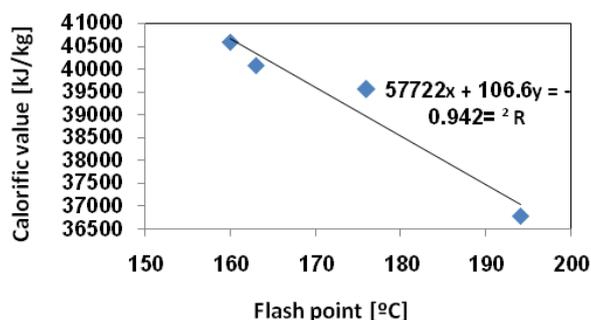


Figure 2: Correlation between flash point and calorific value

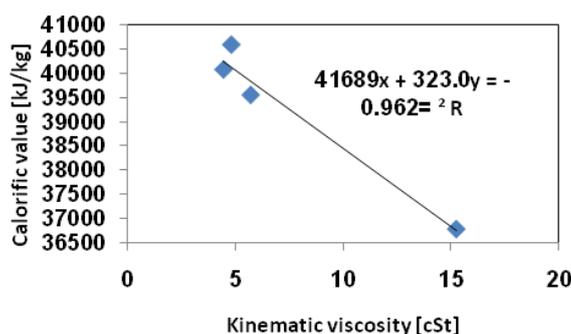


Figure 3: Correlation between kinematic viscosity and calorific value

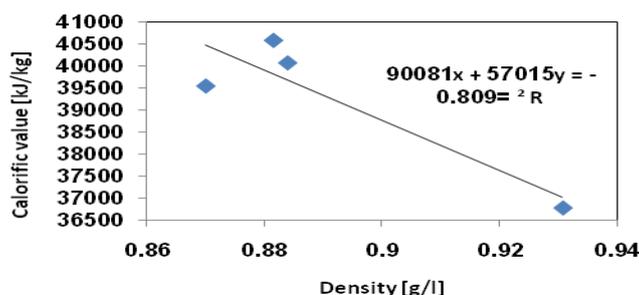


Figure 4: Correlation between density and calorific value

Based on the fitting equations presented in Figures 2-4, the calorific value CV (kJ/kg) as a function of kinematic viscosity η (cSt), density ρ (g/ml), and flash point FP (°C) can be calculated using the following equation, which was fitted using least square method:

$$CV = 93401 - 103.76 \times FP + 172.7 \times \eta - 42037 \times \rho$$

In accordance with the fitting equations (Figures 2-4), density and flash point show an inverse proportionality in Equation 1 while the kinematic viscosity shows a direct proportionality with the calorific value in Equation 1 which does not agree with the equation shown in Figure 2. But the observations from Equation 1 agree with the results reported in literature [20]. Table 4 illustrates the comparison between calculated and measured values of the calorific values of different bio-oils as reported in literature and predicted using Equations 1.

Table 4: Comparison between calculated and measured values

Oil	CV from literature[20], kJ/kg	CV from Equation 1, kJ/kg	%Error
Soybean	41,280	40,310	2.35
Corn	41,140	41,350	-0.51
Hazelnut	41,120	41,470	-0.85
Sesame	40,900	41,880	2.396

Blending of Castor Oil with other oil types

Castor oil has a low calorific value and low pour point. To enhance its properties, we suggest mixing castor oil with other oils to increase its calorific value and its pour point. Based on the data in Table 2 and 3, the individual relationships between the mass percentage of fatty acids for each oil type with the calorific value and pour point of vegetable oils are represented (Figure 5) to predict the suitable blends ratios. It could be concluded that the dependency of either the calorific value or the pour point on the mass percentage of each fatty acid is not valid to be related (as cleared in values of R^2), and the effect of fatty acid types are interacted. To overcome this problem, two equations were developed for calculating the pour point and calorific value by fitting data in Tables 2 and 3 using least square method. The equations relate the mass percentage of each fatty acid with the pour point and calorific value of the vegetable oil. As shown in Equations 2 and 3, the calorific value and pour point of the vegetable oil can be calculated by multiplying the mass percentage of each fatty acid by a certain parameter, which is unified for all vegetable oils under study. Table 5 shows the abbreviations used for the mass percentage of each type of fatty acid. A good agreement has been achieved between the experimental data and the model prediction.

The equation will take the form, as an example for calorific value:

$CV = 402.8 \times A + 401.2 \times B + 387.8 \times C + 418.1 \times D + 394.8 \times E + 358.6 \times F + 399.4 \times G + 399.6 \times H$	(2)
$Pour\ Point = 3.02 \times A - 35.2 \times B + 1.9 \times C + 1.3 \times D - 0.15 \times E + 0.01 \times F - 140.1 \times G + 94.3 \times H$	(3)

Equations 2 and 3 were fitted assuming that all the fatty acids are contributing to the pour point and the calorific value of the vegetable oil. By multiplying each fatty acid mass percentage with a factor to account for its effect on the vegetable oil pour point and calorific value, an arbitrary value was chosen as the initial guess for each fatty acid factor. By minimizing the sum of squared error between the model and the experimental values, the best fit was reached when the sum of squared error is minimum by changing the values of the multiplying factors. The multiplying factors gave the best fitting are shown below in Equations 2 and 3. Equation 2 shows that all fatty acids have almost similar effect on the calorific value of the vegetable oil. Equation 3 shows that the effect of Stearic, Ecosanoic, and Erucate are more dominant on the pour point of the vegetable oil than the other fatty acids. By comparing Equations 2 and 3 prediction with literature, we have found good agreement between the calculated values and the experimental results from Moser [21] as shown in Table 6. By employing Equations 2 and 3 to increase the calorific value and pour point of castor oil, we suggest mixing it with rape seed oil. As shown in Figure 6, by increasing the rape seed mass fraction by 0.1 gradually, increases the calorific value of blend compared to castor alone, while the pour point of the mixture became in the range required when we added 0.5% of rape seed to castor.

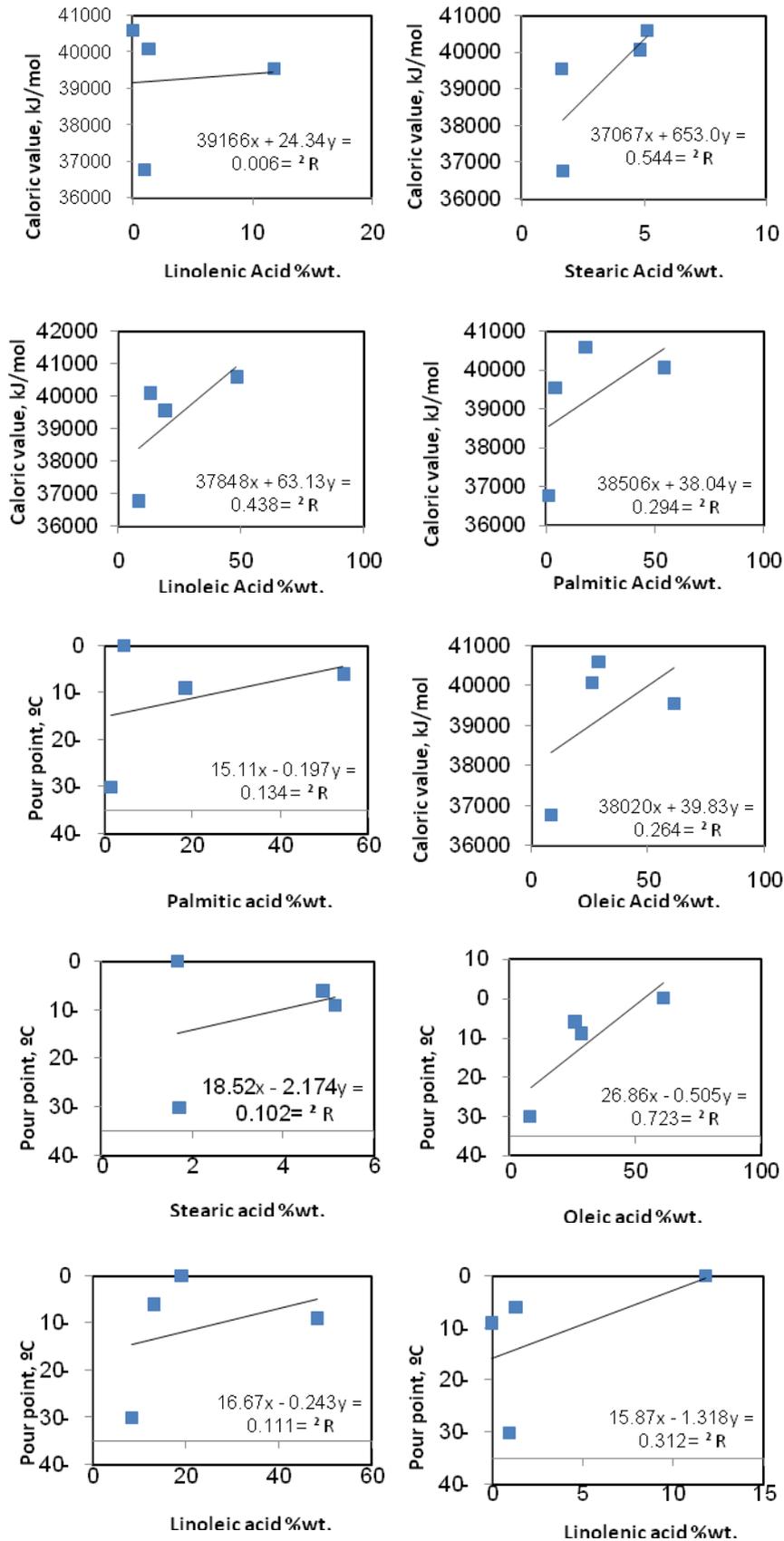


Figure 5: Individual relationships between the mass percentage of fatty acids with the calorific value in kJ/kg and pour point in °C

Table 5: Correlation of Calorific value (kJ/kg) and pour point (°C) as a function of oil composition in mass percentage

Fatty acid	Mass (%) symbol
Palmitic (16:0)	A
Stearic (18:0)	B
Oleic (18:1)	C
Linoleic (18:2)	D
Linolenic (18:3)	E
Ricinoleic (18:1) OH	F
Ecosanoic (20:0)	G
Erucate (22:1)	H

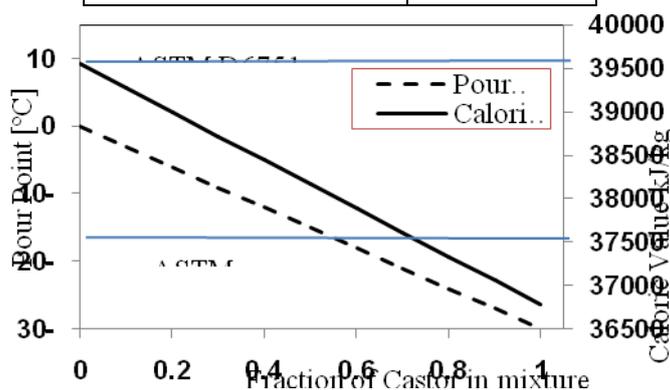


Figure 6: Variation of calorific value and pour point as a result of blending Castor and Rape seed

Table 6: The predicted and measured values of calorific value and pour point

	Calorific Value kJ/kg			Pour Point °C		
	Predicted	Measured [21]	Error	Predicted	Measured [21]	Error
Canola	39484	37300-39870	2.3	-9	-11	18.1
Soybean	40678	39720-40080	2	1	2	50
Sunflower	39168	38100-38472	2.35	-2	-4	50

CONCLUSION

The difference in fatty acid composition apparently affected various fuel properties of the esters such as density, viscosity, pour point, flash point and calorific value. Four types of vegetable seeds were extracted and transesterified to biodiesel. The quality of biodiesel synthesized wastested according tothe standard ASTM (D6751). Cetane number of these four types were calculated and it was found that palm oil has the higher cetane number and castor oil has the lowest one (the more saturated the molecules, the higher the cetane number).Mathematical equations were developed to model the individual relationships between the calorific value with flash point, kinematic viscosity, and density. Then a final equation relating the calorific value with density, kinematic viscosity and flash point was also predicted.Influences of blending ratios between biodiesel samples according to their fatty acid methyl acid composition were studied according to calorific value and pour point. Biodiesels made of different vegetable oils have compatible properties as conventional diesels thus can be used as neat or blended fuels in diesel engine.

ACKNOWLEDGEMENT

The authors gratefully appreciate the support of the Science and Technology Development Fund (STDF) in Egypt.



REFERENCES

- [1] B Freedman, R Butterfield, E Pryde. *J Am Oil Chem Soc* 1986;63:1375-1380.
- [2] H Nouredini, D Zhu. *J Amer Oil Chem Soc* 1997;74:1457-1463.
- [3] G Antolín, FV Tinaut, Y Briceño, V Castaño, C. Pérez, Al Ramírez. *Biores Technol* 2002;83:111-114.
- [4] MM Soumanou, UT Bornscheuer. *Enz Microb Technol* 2003;33:97-103.
- [5] D Darnoko, M Cheryan. *J Amer Oil Chem Soc* 2000;77:1263-1267.
- [6] D Kusdiana, S Saka. *Fuel* 2001;80:693-698.
- [7] L Zou, S Atkinson. *Environ Technol* 2003;24:1253-1260.
- [8] Ö Köse, M Tüter, HA Aksoy. *Biores Technol* 2002;83:125-129.
- [9] N Foidl, G Foidl, M Sanchez, M Mittelbach, S Hackel. *Biores Technol* 1996;58:77-82.
- [10] N Sonntag. Structure and composition of fats and oils, in: A.E. Bailey, D. Swern (Eds.) *Bailey's Industrial oil and fat products*, John Wiley and Sons, New York, 1979.
- [11] J Singh, S Gu. *Renewable and Sustainable Energy Reviews* 2010;14:2596-2610.
- [12] GL Narayana Rao, AS Ramadhas, N Nallusamy, P Sakthivel. *International Journal Of Energy And Environment* 2010;1:919-926.
- [13] E Alptekin, M Canakci. *Renewable Energy* 2008;33:2623-2630.
- [14] AK Agarwal. *Prog Energy Combust Sci* 2007;33:233-271.
- [15] AE Atabani, AS Silitonga, IA Badruddin, TMI Mahlia, HH Masjuki, S Mekhilef. *Renewable and Sustainable Energy Reviews* 2012;16:2070-2093.
- [16] MJ Ramos, CM Fernández, A Casas, L Rodríguez, Á Pérez. *Biores Technol* 2009;100:261-268.
- [17] D Bajpai, V Tyagi. *Journal of Oleo Science* 2006;55:487-502.
- [18] A Demirbas. *Prog Energy Combust Sci* 2005;31:466-487.
- [19] SK Hoekman, A Broch, C Robbins, E Cenicerros, M Natarajan. *Renewable and Sustainable Energy Reviews* 2012;16:143-169.
- [20] K Sivaramakrishnan, P Ravikumar. *International Journal of Engineering Science and Technology* 2011;3:7981-7987.
- [21] BR Moser. *Energy Fuels* 2008;22:4301-4306.