

# Estimation of a Lower Heating Value of Vegetable Oil and Biodiesel Fuel

Pramod S. Mehta\* and K. Anand

Department of Mechanical Engineering, Indian Institute of Technology Madras, Chennai-600036, India

Received March 6, 2009. Revised Manuscript Received June 2, 2009

Due to concerns regarding energy security, fuel cost, and the environment, straight and processed vegetable oils are being considered as part or full replacement of diesel fuel in compression ignition engines. The lower heating value of a candidate fuel is an important characteristic used in energy release estimation. In this work, a convenient method of estimating the heating values of straight and processed vegetable oils based on the bond energies of their fatty acid/methyl ester constituents is proposed. The estimated lower heating values of 17 different straight vegetable oils are on the order of 37 MJ/kg and for 15 different processed fuels on the order of 38 MJ/kg. The accuracy of estimations when compared with the available experimental data is observed to be within 3%.

## 1. Introduction

The stringent emission norms and concerns on depleting fossil fuel resources are the major driving forces for the ongoing search for renewable and environment friendly fuels. The processed form of vegetable oil is emerging as a potential choice for replacing fossil diesel used in compression ignition engines. The scrutiny of several investigations<sup>1–12</sup> on different biodiesel-fueled compression ignition engines shows wide variations in specific fuel consumption, brake thermal efficiency, and nitric oxide emissions of these engines. Besides varying engine operating conditions, the other important cause of these variations could be the variability of fuel heating value due to compositional variations of the usable processed fuel (i.e., biodiesel) based on the type and origin of the fuel.<sup>13</sup> Since compositional variations can significantly change the fuel energy content, the estimation of the energy content of such fuels based on their composition can be very useful. There have been limited

efforts of evaluating the heating values of straight vegetable oils in terms of their easily measurable physical properties. Demirbas<sup>14</sup> presented a correlation for the higher heating value (HHV in MJ/kg) of straight vegetable oils in terms of density ( $\rho$  in g/cm<sup>3</sup>) and viscosity ( $\mu$  in mm<sup>2</sup>/s) as

$$\text{HHV} = 79.014 - 43.126 \rho \quad (1)$$

$$\text{HHV} = 37.945 + 0.049 \mu \quad (2)$$

More recently Sadrameli et al.<sup>15</sup> proposed a correlation for the higher heating value of saturated fatty acids in terms of their density as

$$\text{HHV} = 122.67 - 93.4 \rho \quad (3)$$

Since straight vegetable oils and their esters used as fuels in internal combustion engines combine saturated and unsaturated fatty acids in varying proportions, there have been attempts to estimate the higher heating values of various fatty acid, triglyceride, and fatty ester contents of the straight and processed vegetable oils in terms of their properties like molecular weight (MW), carbon number (CN), electron number (EN), saponification number (SN), and iodine number (IN) or their combinations. The proposed one-property or two-property correlations available in the literature (refer to Table 1) can be represented as follows.

$$\text{one-property correlation: } \text{HHV} = a + bP \quad (4)$$

$$\text{two-property correlation: } \text{HHV} = a + bP_1 + cP_2 \quad (5)$$

where  $P$ ,  $P_1$ , and  $P_2$  are the specific properties referred in a correlation and  $a$ ,  $b$ , and  $c$  are the empirical coefficients in respective cases.

(14) Demirbas, A. *Energy Convers. Manage.* **2000**, *41*, 1609–1614.

(15) Sadrameli, S. M.; Seames, W.; Mann, M. *Fuel* **2008**, *87*, 1776–1780.

(16) Freedman, B.; Bagby, M. O. *J. Am. Oil Chem. Soc.* **1989**, *66* (11), 1601–1605.

(17) Krisnangkura, K. *J. Am. Oil Chem. Soc.* **1991**, *68* (1), 56–58.

(18) Demirbas, A. *Fuel* **1998**, *77*, 1117–1120.

\* To whom correspondence should be addressed. Telephone: +91 44 22574670. Fax: +91 44 22574652. E-mail: psmehta@iitm.ac.in.

(1) Monyem, A.; Van Gerpen, J. H. *Biomass Bioenergy* **2001**, *20*, 317–325.

(2) Szybist, J. P.; Boehman, A. L.; Taylor, J. D.; McCormick, R. L. *Fuel Process. Technol.* **2005**, *86*, 1109–1126.

(3) Tat, M. E.; Van Gerpan, J.; Soyulu, S.; Canakci, M. *J. Am. Oil Chem. Soc.* **2000**, *77* (3), 285–289.

(4) Canakci, M.; Van Gerpan, J. ASAE Annual International Meeting, Sacramento, CA, July 30–Aug 1, 2001; Paper No. 016050.

(5) Pramanik, K. *Renewable Energy* **2003**, *28*, 239–248.

(6) Yusuf, A.; Hanna, M. A.; Leviticus, L. I. *Bioresour. Technol.* **1995**, *52*, 185–195.

(7) Krahl, J.; Munack, A.; Schroder, O.; Stein, H.; Bunger, J. SAE 2003-01-3199.

(8) Nabi, Md. N.; Akhter, Md. S.; Sahadat, M. Md. *Z. Bioresour. Technol.* **2006**, *97* (3), 372–378.

(9) Yoon, S. H.; Park, S. W.; Kim, D. S.; Kwon, S.; Lee, C. S. Proceedings of ICEF2005, ASME Internal Combustion Engine Division 2005 Fall technical conference, Ottawa, Canada, Sept 11–14, 2005.

(10) Carraretto, C.; Macor, A.; Mirandola, A.; Stoppato, A.; Tonon, S. *Energy* **2004**, *29*, 2195–2211.

(11) Raheman, H.; Phadatare, A. G. *Biomass Bioenergy* **2004**, *27*, 393–397.

(12) Kalligerous, S.; Zannikos, F.; Stournas, S.; Lois, E.; Anastopoulos, G.; Teas, Ch.; Sakellaropoulos, F. *Biomass Bioenergy* **2003**, *24*, 141–149.

(13) Graboski, M. S.; McCormick, R. L. *Prog. Energy Combust. Sci.* **1998**, *24*, 125–164.

Table 1. Summary of Existing Correlations for Estimating the Higher Heating Value<sup>a</sup>

S no.	author	fuel used	property related <i>P</i>	coefficients			maximum accuracy of prediction (%)	remarks
				<i>a</i>	<i>b</i>	<i>c</i>		
one-property correlation								
1	Freedman and Bagby <sup>16</sup>	methyl esters (saturated)	CN	320.95	647.56		2.64	
			EN	105.06	107.95			
			MW	-1803.64	46.15			
		methyl esters (unsaturated)	EN	114.47	108.87			
			EN	999.81	645.72			
		ethyl esters (saturated)	EN	138.87	107.61			
			MW	-1764.31	46.02			
triglycerides	EN	484.8	108.28					
two-property correlation								
2	Krishnangkura <sup>17</sup>	triglycerides	SN and IN	-6694	7932864	-2.51	1.16	SN appears as inverse function
		methyl ester	SN and IN	-1799	2585712	-0.3347		
3	Demirbas <sup>18</sup>	vegetable oils	SN and IN	49.43	-0.041	0.015	6.4	

<sup>a</sup> In the original estimations are correlated in kcal/mol. However, the coefficients provided in the table give estimations in MJ/kg.

Though the term higher heating value has wider acceptance in the fuel property literature, the engine calculations usually use lower heating values of the fuels whenever required in energy release estimates. For this reason, the methodology proposed in the paper concerns the estimation of lower heating value of straight and processed vegetable oils. However, the lower and higher heating values of the fuel can be conveniently related through the amount of water vapor content ( $m_{H_2O}$ ) in the products of complete combustion as

$$LHV = HHV - h_{fg}m_{H_2O} \quad (6)$$

where  $h_{fg}$  is the standard heat of vaporization of water.

These existing correlations relate the heating value with measured properties like density, viscosity, iodine value, and saponification number using regression analysis. These empirical correlations may lack generality and may remain limited to only those fuels considered in the study. Moreover, in the absence of measured data of correlated properties, the estimations of these properties will only be possible from compositions of oils. The method proposed here establishes a rather direct procedure for estimating the heating value from the knowledge of molecular composition and structure of vegetable oil/biodiesel fuels. Hence, the method is quite general and its predictive ability more precise. Since the straight and processed vegetable oils used in diesel engines are the complex chemical mixture of fatty acids and methyl esters, it is worthwhile to establish correlations for the lower heating value in terms of molecular structure and compositions of these fuels. This paper discusses a methodology of estimating the lower heating value of straight and processed vegetable oils based on bond energy values related to the chemical structure of different fatty acids and methyl esters present in these fuel molecules.

## 2. Methodology

In combustion calculations, the bond energies of chemical compounds have often been used in estimating their heat of formation.<sup>19</sup> The bond energy is defined as the contribution a particular bond makes to the energy required for dissociating the molecules into atoms. In this work, the bond energy method is employed for estimation of heating values of straight and processed vegetable oils by considering the structural and molecular formulas to account for the contribution of bond energies of reactants and products in the stoichiometric combustion equation of fatty acid or methyl ester contents of a straight or processed vegetable oil.

(19) Kuo, K. K. *Principles of combustion*; John Wiley & Sons: New York, 1986; pp 42–44, 62.

For this purpose, the lower heating value of a fatty acid/methyl ester will relate with the bond energies of its reactants (BR) and products (BP) as

$$(LHV)_i = BR - BP \quad (7)$$

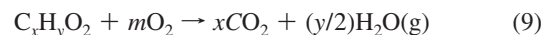
where the suffix *i* stands for a fatty acid/methyl ester under consideration.

Considering that straight and processed vegetable oils are mixtures of analogous compounds and behave as ideal solutions,<sup>20</sup> their heating values can be estimated by applying Kay's mixing rule<sup>21–23</sup> to the constituent fatty acids and their methyl ester as

$$LHV = \sum X_i(LHV)_i \quad (8)$$

where  $X_i$  is the molar fraction of the fatty acid/methyl ester content of the fuel.

It should however be noted that the estimates for vegetable oils are based only on their fatty acid composition with an assumption that an average property like the heating value has an insignificant influence of triglycerides contribution. To establish the methodology, it is necessary to consider a representative stoichiometric combustion equation for fatty acid/methyl ester constituents of the fuel. Thus, the complete chemical reaction occurring with any fatty acids/methyl ester can be written in a general form as



where  $x$  and  $y$  are the number of atoms of carbon and hydrogen, respectively, in a fatty acid or methyl ester molecule and  $m$  is the stoichiometric oxygen requirement given as

$$m = (x + y/4 - 1) \quad (10)$$

The fatty acid/methyl esters compositions of various vegetable oils<sup>18,24–26</sup> are shown in Table 2, and the corresponding values of the stoichiometric oxygen requirements for different fatty acids and their methyl esters of interest are included in Table 3.

(20) Goodrum, J. W.; Eitman, M. A. *Bioresour. Technol.* **1996**, *56*, 55–60.

(21) Kay, W. B. *Ind. Eng. Chem.* **1936**, *28*, 1014–1019.

(22) Clements, D. L. Proceedings of the third liquid fuels conference of the American society of agricultural engineers, Nashville, TN, Sept 15–17, 1996, pp 44–53.

(23) Van Gerpen, J.; Shanks, B.; Pruszko, R.; Clements, D.; Knothe, G. Biodiesel analytical methods, Subcontractor report, National Renewable Energy Laboratory, July 2004.

(24) Srivastava, A.; Prasad, R. *Renewable Sustainable Energy Rev.* **2000**, *4*, 111–133.

(25) Ma, F.; Hanna, M. A. *Bioresour. Technol.* **1999**, *70*, 1–15.

(26) Ikwuagwu, O. E.; Ononogbu, I. C.; Njoku, O. U. *Ind. Crops Prod.* **2000**, *12*, 57–62.

Table 2. Fatty Acid Compositions of Vegetable Oils

vegetable oil	C8:0	C10:0	C12:0	C14:0	C16:0	C16:1	C18:0	C18:1	C18:2	C18:3	C20:0	C22:0	C24:0	C22:1
corn					11.67		1.85	25.16	60.6	0.48				
cotton seed					28.0		1.0	13.0	58.0					
karanja					5.8		5.65	71.3	14.95				2.3	
linseed					5.0		2.0	20.0	18.0	55.0				
palm			0.1	1.0	42.8		4.5	40.5	10.1	0.2				
peanut					11.38		2.39	48.28	31.95	0.93	1.32	2.52	1.23	
rapeseed					3.49		0.85	64.4	22.3	8.23				
rubber seed					10.2		8.7	24.6	39.6	16.3				
soybean					11.75		3.15	23.26	55.53	6.31				
sunflower					6.0		3.0	17	74					
sesame					13.1		3.9	52.8	30.2					
castor					1.1		3.1	4.9, 89.6 <sup>a</sup>	1.3					
coconut	8.3	6.0	46.7	18.3	9.2		2.9	6.9	1.7					
hazelnut					4.9	0.2	2.6	83.6	8.5	0.2				
walnut					7.2	0.2	1.9	18.5	56.0	16.2				
crambe					2.0		1.0	19.0	9.0	7.0	2.0	1.0	1.0	58.0
safflower					7.3		1.9	13.6	77.2					

<sup>a</sup> C18:1 Ricinoleic acid.

Table 3. Stoichiometric Oxygen Requirement for Fatty Acids and Their Methyl Esters

S no.	name of the fatty acid/methyl ester	stoichiometric oxygen requirement for fatty acid/methyl ester			
		no. of hydrogen atoms		stoichiometric O <sub>2</sub>	
		fatty acid	methyl ester	fatty acid	methyl ester
1	caprylic (C8:0)	16	18	11.0	12.5
2	capric (C10:0)	20	22	14.0	15.5
3	lauric (C12:0)	24	26	17.0	18.5
4	myristic (C14:0)	28	30	20.0	21.5
5	palmitic (C16:0)	32	34	23.0	24.5
6	stearic (C18:0)	36	38	26.0	27.5
7	oleic (C18:1)	34	36	25.5	27.0
8	linoleic (C18:2)	32	34	25.0	26.5
9	linolenic (C18:3)	30	32	24.5	26.0
10	arachidic (C20:0)	40	42	29.0	30.5
11	behenic (C22:0)	44	46	32.0	33.5
12	erucic (C22:1)	42	44	31.5	33.0
13	lignoceric (C24:0)	48	50	35.0	36.5

Table 4. Bond Energies between Atoms<sup>19,27</sup>

S no.	bond	bond energy (kJ/mol)
1	C–C	347
2	C=C	611
3	C–H	414
4	C=O	741
5	C–O	339
6	O–H	460
7	O=O	497.4

Table 5. Resonance Energies of Compounds<sup>19</sup>

S no.	group	resonance energy (kJ/mol)
1	COOH	117.18
2	CO <sub>2</sub>	138.105

It may be noted that in the above reaction, the H<sub>2</sub>O molecule exists in the gaseous phase and hence the amount of energy released on combustion is referred as the lower heating value. The bond energies of the reactants and products in the above stoichiometric equation are estimated from the knowledge of various bonds that exist in fatty acids and their methyl esters. The standard values of the energy associated with various bonds are referred to in Table 4.

In addition to these bonds, there are functional groups like –COOH appearing in the structures of fatty acids and CO<sub>2</sub> and H<sub>2</sub>O arising during combustion. These groups would be contributing their resonance energies (refer Table 5) in the estimation of bond energies of the reactants and products, respectively. It may be noted that the resonance energy contribution of H<sub>2</sub>O vapor is zero. The

(27) Silcocks, C. G. *Physical Chemistry*, 2nd ed.; Macdonald & Evans Ltd.: London, 1972; p 42.

resonance energy mentioned here refers to the energy that must be added to the bond energy due to the functional groups existing in different structural forms.<sup>19</sup>

### 3. Results and Discussion

The proposed methodology of estimating the lower heating values of straight and processed vegetable oils using the bond energy method is evaluated by comparing the estimations with the experimental data of the lower heating value found in the literature.<sup>26,28–42</sup> As is evident from the methodology, determining the lower heating values of different fatty acids/methyl esters content of the fuel oils is a prerequisite. Hence, a comparison of estimated lower heating values of fatty acids/methyl esters with the corresponding experimental data<sup>43–45</sup> is shown in Figure 1. A good correlation is observed between the estimated and the measured values which fall within an absolute error of 2.2% for fatty acids and 3.8% for methyl esters. The estimated lower heating values of various fatty acids/methyl esters are presented in Table 6. An illustration for estimating the lower heating value of a typical fatty acid is provided in Appendix A.

In order to understand the role of the constituent fatty acid/methyl

(28) Beg, R. A.; Rahman, M. S.; Bose, P. K.; Ghosh, B. B. *SAE*, 2002–01–2692.

(29) Demirbas, A. *Energy Convers. Manage.* **2003**, *44*, 2093–2109.

(30) Fukuda, H.; Kondo, A.; Noda, H. *J. Biosci. Bioeng.* **2001**, *92* (5), 405–416.

(31) Machacon, H. T. C.; Shiga, S.; Karasawa, T.; Nakamura, H. *Biomass Bioenergy* **2001**, *20*, 63–69.

(32) Rao, P. S.; Gopalakrishnan, K. V. *Ind. J. of Tech.* **1991**, *29* (6), 292–297.

(33) Ramadhas, A. S.; Jayaraj, S.; Muraleedharan, C. *Renew. Energy* **2005**, *30*, 795–803.

(34) Raheman, H.; Phadatare, A. G. *Biomass Bioenergy* **2004**, *27*, 393–397.

(35) Altin, R.; Cetinkaya, S.; Yucsu, H. S. *Ener. Conv. and Manag.* **2001**, *42*, 529–538.

(36) Almeida, S. C. A.; Belchior, C. D.; Nascimento, M. V. G.; Vieira, L. S. R.; Fleury, G. *Fuel* **2002**, *81*, 2097–2102.

(37) Bhattacharyya, S.; Reddy, C. S. *J. Agric. Engng. Res.* **1994**, *57*, 157–166.

(38) Karaosmangalu, F.; Kurt, G.; Ozaktas, T. *Renewable Energy* **2000**, *19*, 219–221.

(39) Rakopoulos, C. D.; Antonopoulos, D. C.; Rakopoulos, D. C.; Hountalas, D. T.; Giakoumis, E. G. *Energy Convers. Manage.* **2006**, *47*, 3272–3287.

(40) Canakci, M. *Proc. IMechE* **2005**, *219*, 1–8.

(41) Srivastava, P. K.; Verma, M. *Fuel* **2008**, *87*, 1673–1677.

(42) Demirbas, A. *Fuel* **2008**, *87*, 1743–1748.

(43) Pattison, S. E. *Soap and Detergent Association*, 1968.

(44) Swern, D. *Bailey's industrial oil and fat products*, 4th ed.; John Wiley & Sons: New York, 1979; p 110.

(45) Klopfenstein, W. E.; Walker, H. S. *J. Am. Oil Chem. Soc.* **1983**, *60*, 1596–1598.

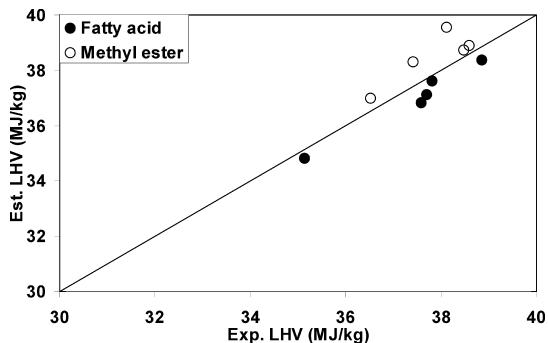


Figure 1. Comparison of estimated and experimental lower heating values of fatty acids and methyl esters.

Table 6. Estimated Lower Heating Values of Fatty Acids/ Methyl Esters

S no.	name of the fatty acid/ methyl ester	lower heating value (MJ/kg)	
		fatty acid	methyl ester
1	caprylic (C8:0)	31.619	33.816
2	capric (C10:0)	33.660	35.374
3	lauric (C12:0)	35.136	36.529
4	myristic (C14:0)	36.249	37.417
5	palmitic (C16:0)	37.119	38.120
6	stearic (C18:0)	37.819	38.692
7	oleic (C18:1)	37.705	38.591
8	linoleic (C18:2)	37.591	38.488
9	linolenic (C18:3)	37.476	38.385
10	arachidic (C20:0)	38.391	39.166
11	behenic (C22:0)	38.868	39.562
12	erucic (C22:1)	38.781	39.483
13	lignoceric (C24:0)	39.275	39.903

esters on the lower heating values of the straight and processed vegetable oils, the estimated lower heating values are plotted (see Figure 2) with the molecular weight of fatty acid/methyl esters. As the hydrogen atom in the functional group  $-COOH$  of fatty acids is replaced by another functional group  $-CH_3$  to form corresponding methyl esters, the increase in molecular weight for methyl esters compared to their fatty acids counterpart remains constant. It is observed that the lower heating values of fatty acids and methyl esters increase with an increase in molecular weight. The heating values of fatty acid/methyl ester constituents primarily depend on the number of carbon and hydrogen atoms present in their molecular structure and hence the molecular weight. However, the rate of change in the lower heating value is lowered as the molecular weight increases. The lower heating value of methyl esters is higher than their fatty acid counterparts due to an increase in their bond energies on account of the additional contribution from the  $CH_3$  functional group. The relative increase is observed

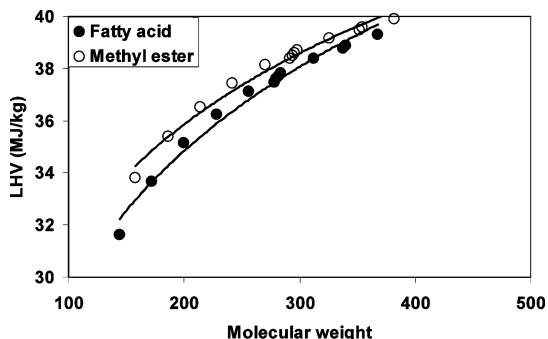


Figure 2. Variations in the lower heating value with molecular weight for fatty acids and methyl esters.

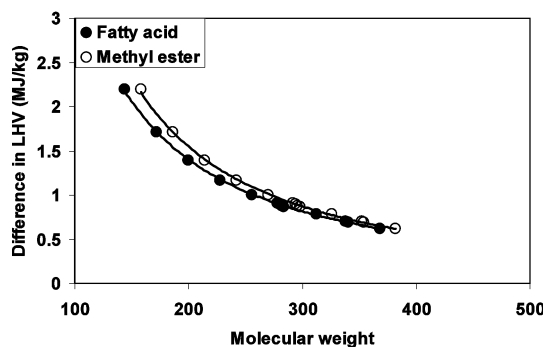


Figure 3. Variations in differences in the lower heating value between methyl esters and fatty acids with molecular weight.

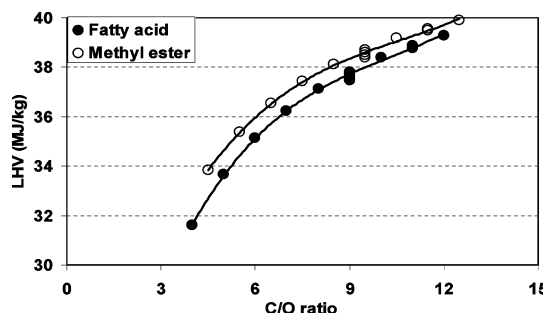


Figure 4. Variations in the lower heating value with the C/O ratio for fatty acids and methyl esters.

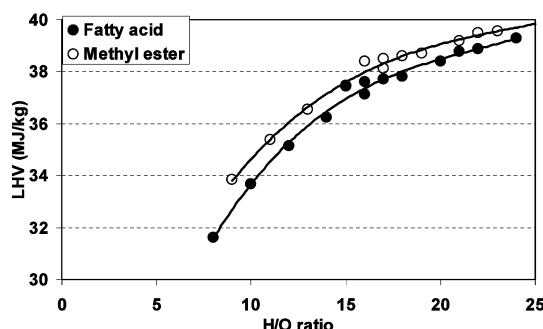


Figure 5. Variations in the lower heating value with the H/O ratio for fatty acids and methyl esters.

to be higher for lower molecular weight methyl esters and decreases with an increase in molecular weight as can be seen in Figure 3. This observation suggests that chemical modification of straight vegetable oils of a higher content of lower molecular weight fatty acid components fuel results in an increase in the heating value in its esterified form. While lower heating values increase with an increase in carbon chain length for saturated acids and esters, a slight decrease in lower heating values with an increase in the degree of unsaturation is observed. It is known that a decrease in the number of hydrogen atoms in the fuel molecule results in an increase in a degree of unsaturation and also a decrease in the molecular weight with its consequent effect on the heating value.

A comparison of estimated and measured lower heating values of the straight and processed vegetable oils are shown in Table 7 a and Table 7b, respectively. It is observed that the absolute maximum error between the estimated and the measured lower heating values of straight and processed vegetable oils is found to range between 2.5% and 3%, respectively. The lower heating values of a majority of the straight and processed vegetable oil samples presented here are found to be on the order of 37 and 38 MJ/kg, respectively. This relatively low variation is attributed

to the fact that a large content of fatty acid/methyl ester constituent includes C16–C18 compounds which tend to have identical lower heating values as evident from the calculations.

Further investigation into the effect of the molecular composition and structure of the fatty acid/methyl ester constituent of the straight and processed vegetable oils on the heating value provides a very interesting revelation. For this purpose, the lower heating value data are plotted with the carbon to oxygen (C/O) ratio, hydrogen to oxygen (H/O) ratio, and number of double bonds present in the fatty acid/methyl ester constituents in Figures 4, 5, and 6, respectively. The regression coefficients in each of these cases are observed to be over 0.99. Figure 6 also suggests that the effect of the number of double bonds on the lower heating value is rather linear. Thus, an effort is made to arrive at suitable correlations for predicting lower heating values of fatty acids/methyl esters in terms of C/O or H/O ratios with adequate corrections for the presence of the double bonds. The resultant correlations are as follows.

$$LHV = 0.0148(C/O)^3 - 0.4542(C/O)^2 + 5.1429(C/O) + 17.403 - 0.114N_{db} \quad (11)$$

For fatty acids

$$LHV = 0.0017(H/O)^3 - 0.1100(H/O)^2 + 2.6183(H/O) + 16.826 - 0.114N_{db} \quad (12)$$

For methyl esters:

$$LHV = 0.0109(C/O)^3 - 0.3516(C/O)^2 + 4.2000(C/O) + 21.066 - 0.100N_{db} \quad (13)$$

$$LHV = 0.0011(H/O)^3 - 0.0785(H/O)^2 + 2.0409(H/O) + 20.992 - 0.100N_{db} \quad (14)$$

where C is the number of carbon atoms, H is the number of hydrogen atoms, O is the number of oxygen atoms, and  $N_{db}$  is the number of double bonds.

#### 4. Conclusions

The estimations of the energy contents of the straight and processed vegetable oils (biodiesel) are important because of their becoming an acceptable alternative to fossil diesel fuel. The proposed method of estimating lower heating values of these alternative fuels in this paper reveals the following.

(1) The lower heating value of various straight and processed vegetable oils can be conveniently estimated from the bond energy values related to the molecular composition and the structure of the fatty acid/methyl ester contents of these fuels. Thus, a priori knowledge of the composition of various straight and processed vegetable oils is sufficient to estimate their lower heating values.

(2) The accuracy of estimating lower heating values is found to be well within 3% when compared with the available experimental data of various straight and processed vegetable oils.

(3) A database of lower heating values of 13 commonly

**Table 7. Comparison of Estimated and Experimental Lower Heating Values of Vegetable Oils and Biodiesel Fuels**

S no.	vegetable oil	lower heating value (MJ/kg)				
		estimation method			error (%)	
		present work	Demirbas <sup>14</sup>	experimental	present work	Demirbas <sup>14</sup>
(a) vegetable oil						
1	corn	37.56	37.41	37.59	-0.1	-0.5
2	cotton seed	37.47	37.16	37.06	1.1	0.3
3	karanja	37.70	37.28	38.42	0.5	3.0
4	linseed	37.53	36.89	37.25	0.8	-1.0
5	palm	37.36	36.94	36.54	2.2	1.1
6	peanut	37.67	37.66	36.96	1.9	1.9
7	rapeseed	37.64	37.30	37.61	0.1	-0.8
8	rubber seed	37.57	37.39	37.50	0.2	-0.3
9	soybean	37.56	37.23	37.30	0.7	0.2
10	sunflower	37.59	37.14	37.08	1.4	0.2
11	castor	35.49	35.35	35.08	1.2	0.8
12	coconut	35.16	35.16	35.00	0.5	6.0
13	crambe	37.56	37.54	37.83	-0.7	-0.8
14	hazelnut	37.68	NA	37.35	0.9	
15	safflower	37.58	37.22	37.16	1.1	0.2
16	sesame	37.6	37.20	36.99	1.6	0.6
17	walnut	37.57	NA	37.22	0.9	
lower heating value (MJ/kg)						
S no.	biodiesel	estimation method				
		estimation method			error (%)	
		present work	Krishnangkura <sup>17</sup>	experimental	present work	Krishnangkura <sup>17</sup>
(b) biodiesel fuels						
1	corn	38.47	37.46	38.73	-0.7	-3.3
2	cotton seed	38.39	37.35	38.13	0.7	-2.1
3	karanja	38.57	37.52	37.43	2.8	0.2
4	linseed	38.44	37.47	38.01	1.1	-1.4
5	palm	38.31	37.31	37.88	1.1	-1.5
6	peanut	38.54	37.50	38.05	1.2	1.4
7	rapeseed	38.53	37.55	37.70	2.2	-0.4
8	rubber seed	38.47	37.50	38.65	-0.9	3.0
9	soybean	38.46	37.44	37.68	2.1	-0.6
10	sunflower	38.49	37.48	38.44	0.1	-2.5
11	sesame	38.51	37.57	38.71	-0.5	-2.9
12	crambe	39.08	38.08	39.49	-1.0	-3.6
13	hazelnut	38.57	37.51	38.67	-0.3	-3.0
14	safflower	38.49	37.59	39.00	-1.3	-3.6
15	walnut	38.48	37.47	38.95	-1.2	-3.8

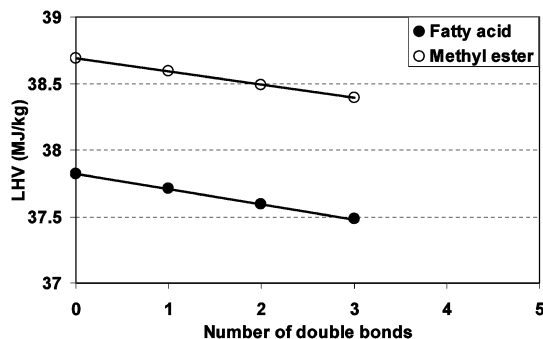


Figure 6. Variations in the lower heating value with the number of double bonds for C18. compounds.

occurring fatty acids and methyl esters in various straight and processed vegetable oils is given for use.

(4) There is a monotonic relationship of lower heating value of fatty acids/methyl esters with their molecular weights. However, the rate of change in the lower heating value is lowered as the molecular weight increases.

(5) The lower heating value of methyl esters is higher than their fatty acid counterparts. However, the relative increase is observed to be higher for lower molecular weight methyl esters and decreased with increasing molecular weight.

(6) The lower heating values increase with an increase in carbon chain length for saturated acids and esters. There is a slight decrease in the lower heating value with an increase in the degree of unsaturation.

(7) A high degree of correlation, showing a regression coefficient over 0.99, exists between lower heating values of fatty acids/methyl esters with the C/O ratio or H/O ratio and the number of double bonds and hence could be used for proposing appropriate correlations (eqs 11–14) for determining lower heating values of various fatty acids and methyl esters.

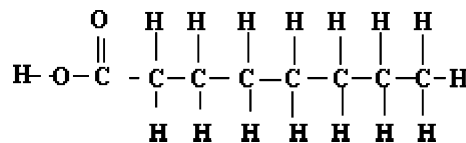
### Appendix A

An illustration for estimating the lower heating value of a typical fatty acid is briefly summarized below.

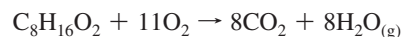
Table 8

S no.	no. of bonds	bond energy (kJ/mol)
1	C–C	$7 \times 347 = 2429$
2	C–H	$15 \times 414 = 6210$
3	C=O	$1 \times 741 = 741$
4	O–H	$1 \times 460 = 460$
5	C–O	$1 \times 339 = 339$
bond energy of caprylic acid		10179
add resonance energy for –COOH		117.18
total bond energy of caprylic acid		10 296.18
add bond energy of oxygen molecules		$11 \times 497.4 = 5471$
total bond energy of reactants, $B_R$		15 767.58

Step I: Molecular formula of caprylic acid:  $\text{CH}_3(\text{CH}_2)_6\text{COOH}$ . Molecular structure of caprylic acid:



Step II: Stoichiometric combustion equation for caprylic acid



Step III: Bond energies of reactants based on the number of bonds and their associated energies from Tables 4 and 5.

Bond energies of products of combustion

$$\begin{aligned}
 B_p &= 16(\text{C}=\text{O}) + 16(\text{O}-\text{H}) + 8\text{CO}_2(\text{resonance energy}) \\
 &= 16(741) + 16(460) + 8(138.105) = 20\,320.84 \text{ kJ/mol}
 \end{aligned}$$

Step IV: Lower heating value of caprylic acid

$$\begin{aligned}
 \text{LHV} &= B_R - B_p \\
 &= 15\,767.58 - 20\,320.84 \\
 &= -4553.26 \text{ kJ/mol} \\
 &= -4553.26 \times (1000/144) = 31.619 \text{ MJ/kg}
 \end{aligned}$$

EF900196R