

# Heats of Combustion of Fatty Esters and Triglycerides<sup>1</sup>

B. Freedman\* and M.O. Bagby

Northern Regional Research Center, Agricultural Research Service, U.S. Department of Agriculture, 1815 North University Street, Peoria, Illinois 61604

Gross heats of combustion (HG) have been measured for three classes of fatty esters and two classes of triglycerides (TGs). The esters included saturated methyl esters, Me 6:0–22:0; saturated ethyl esters, Et 8:0–22:0; and unsaturated methyl esters, Me 12:1–22:1, Me 18:2 and Me 18:3. The TGs included the saturated TGs, C 8:0–22:0, and unsaturated TGs, C 11:1, C 16:1, C 18:1, C 18:2, C 18:3, C 20:1 and C 22:1. HG were measured in a Parr adiabatic calorimeter according to a modification of ASTM D240 and D2015. Linear regression analysis (LINREG) yielded equations that related HG to carbon number (CN) or chain length, electron number (EN) or number of valence electrons and molecular weight (MW). Calculated HG values from CN, EN, or MW were nearly identical. Thus, any one of these three variables can be used to predict HG satisfactorily. R squared values for all equations were 0.99. Equations for correlating HG of saturated or unsaturated TGs with molecular characteristics of these molecules have not been reported. With LINREG, we developed equations that permitted predictions of HG from structures of the saturated and unsaturated TGs. Equations for predicting HG of methyl and ethyl esters were compared to those in the literature and were found to be more accurate and precise.

During the early 1980s, vegetable oils (VO) and fatty esters derived from VO were investigated intensively as alternative fuels for farm tractors (1–6). One of the more important properties of these compounds related to their use as potential fuels is gross heat of combustion (HG). Thus, several investigators have measured the HG of various VO (7,8). The determined heat contents were ca 88 percent of No. 2 diesel oil (7,9). Fatty esters can also be obtained from VO by transesterification and have the potential to solve some of the problems associated with VO as fuels (10,11). For this reason, the HG of various mixed VO esters was also reported (12,13).

One of our primary objectives was to gain a better understanding of the relationship between HG and molecular properties of VO and their esters so as to be able to predict HG based on these molecular characteristics. Another objective was to compare our equations for calculating the HG of methyl and ethyl esters to those in the literature (14,15). Despite the recent interest in the HG of VO and their mixed esters, no one has systematically measured the HG of pure triglycerides (TGs), both saturated and unsaturated, that compose these VO. Likewise, the HG of fatty methyl and ethyl esters that can be derived from these TGs has not been systematically determined. To accomplish our objectives, it was first necessary to measure the HG of these compounds.

## EXPERIMENTAL

*Materials.* Benzoic acid, a primary standard for bomb calorimetry, was obtained from Parr Instrument Co., Moline, IL. Saturated TGs, C 8–22, and unsaturated TGs C, 18:1 and 18:2, were purchased from Sigma Chemical Co., St. Louis, MO — purity 99%. All other methyl and ethyl esters and unsaturated TGs were obtained from Nu-Chek Prep, Inc., Elysian, MN — purity >99%.

*Instrumentation.* Heats of combustion were determined in a Parr Adiabatic Oxygen Bomb Calorimeter, Model 1241. Auxiliary equipment included a bucket-filling system, water heater, water cooler and dedicated computer. The bucket-filling system, Model 1561, consisted of a temperature-controlled reservoir and automatic pipet for dispensing repeatably ca. 2000 ml of distilled water at a pre-set temperature into a stainless-steel bucket. The water heater, Model 1541, maintained and delivered hot water at a controlled temperature to allow adjustment of the calorimeter jacket temperature. The water cooler, Model 1551, provided a uniform supply of properly cooled water for adjusting jacket temperature.

An oxygen bomb, Model 1108, was pressurized to 450 psig with a Parr Auto Charger, Model 1841. To increase the number of runs per day, two oxygen bombs were employed. While one was being processed after a run, the second was started for a new run. Solids were converted to pellets with a Parr 2811 Pellet Press. This was essential to obtain consistent results with solid samples. The calorimeter was equipped with a dedicated computer, Master Control, Model 1680, which received the experimental data and then calculated and produced a printout of HG. HG output was in cal/g which we converted to kg-cal/mole, the standard unit for HG.

*Use of ASTM methods.* ASTM method D240-76 (1980) was used for liquid fuels, and D2015-77 (1978) for solid fuels. Both methods were modified by using the RAPID mode of the Master Control rather than the REFERENCE mode as called for by the ASTM methods. This RAPID mode was used to expedite the analyses.

Other changes from the ASTM procedures were as follows. Temperatures for both the water jacket and bucket were accurately measured by both a thermometer and a thermistor. The bomb was fired automatically after the jacket and bucket temperatures equilibrated to within 0.001°C of each other as determined by the Master Control. After the bomb reached a maximum constant temperature, the Master Control calculated and printed out a preliminary HG. Data for corrections for the heat of formation of nitric acid (formed by the oxidation of N<sub>2</sub> in air) and for the heat of combustion for the fuse wire were entered into the Master Control that then calculated a final HG. To standardize the calorimeter, a total of 6 calibration runs was made for each bomb. For these runs the mean ( $\bar{X}$ ) value of W was 2409, its standard deviation (SD) was 1.25 and its relative standard deviation (RSD) was 0.05%.

*Statistical procedures.* For each compound at least 3 replicates were run. The difference in HG between these

\*To whom correspondence should be addressed.

<sup>1</sup>Presented in part at the AOCS meeting in New Orleans, LA, in May 1987.

3 replicates did not exceed 31 cal/g, as called for by the ASTM procedures. For those 3 replicates that satisfied this requirement, we determined the  $\bar{X}$ , SD and RSD. Linear regression analysis (LINREG) was used to determine a mathematical relationship between HG and CN, EN or MW. It reported a regression equation that related calculated HG to carbon number or acid chain length (CN), the number of valence electrons present in the molecule (EN) and molecular weight (MW). For TGs, the acid chain length of a single chain only was considered. EN was calculated by first subtracting from the formula

all CO<sub>2</sub> present in the molecule and then determining the sum of (the carbon atoms times 4) plus (the hydrogen atoms times 1). Methyl acetate thus has an EN of 14. R squared was also reported for each regression equation. "Error" and "% Error" showed the difference between calculated and measured HG values.

## RESULTS AND DISCUSSION

*HG of fatty compounds.* Table 1 summarizes the HG values determined for six classes of fatty compounds. A

TABLE 1  
Heats of Combustion of Fatty Compounds<sup>a</sup>

Class name	HG, kg-cal/mole									RSD <sup>b</sup> range %
	Chain length									
<b>I. Saturated compounds</b>										
	<b>6</b>	<b>8</b>	<b>10</b>	<b>12</b>	<b>14</b>	<b>16</b>	<b>18</b>	<b>20</b>	<b>22</b>	
Alcohols	—	—	1582	1899	2202	2512	2826	3138	3453	0.04–0.14
Me esters	1000	1313	1625	1940	2254	2550	2859	3170	3481	0.02–0.10
Et esters	—	1465	1780	2098	2406	2717	3012	3321	3632	0.03–0.30
Triglycer.	—	3647	4747	5672	6607	7554	8558	9433	10327	0.04–0.44
<b>II. Unsaturated compounds</b>										
	11:1	12:1	14:1	16:1	18:1	18:2	18:3	20:1	22:1	
Me esters	—	1899	2208	2521	2828	2794	2750	3153	3454	0.05–0.37
Triglycer.	5115	—	—	7452	8389	8259	8152	9326	10230	0.06–0.31

<sup>a</sup> Based on a minimum of 3 replications.

<sup>b</sup> RSD is relative standard deviation.

TABLE 2  
Linear Regression Analysis of HG vs Cn<sup>a</sup>, EN or MW for Saturated Triglycerides

Chain length	Input				Output		
	Measured HG, kg-cal/mole	CN	EN	MW	Calc. HG, kg-cal/mole	Error	% Error
8	3647	8	146	470.77	3743	-96	-2.64
10	4747	10	182	554.95	4693	54	1.13
12	5672	12	218	639.13	5643	29	0.51
14	6607	14	254	723.31	6593	14	0.21
16	7554	16	290	807.49	7543	11	0.14
18	8558	18	326	891.67	8493	65	0.76
20	9433	20	362	975.85	9443	-10	-0.11
22	10327	22	398	1060.03	10393	-66	-0.64
		<b>Equations</b>			<b>R squared</b>		
		HG = - 56.43 + 474.97 CN			0.99		
		HG = - 109.20 + 26.39 EN			0.99		
		HG = -1569.1 + 11.29 MW			0.99		

<sup>a</sup> CN, EN and MW are chain length, electron number and molecular weight.

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preliminary report of these findings has been published (9). Previously reported HG values for fatty alcohols (16) are shown here for comparison with the esters and TGs. For a given chain length, HG values of saturated compounds increased in going from the alcohol to the methyl and ethyl esters because of increased carbon-hydrogen to oxygen ratios. Within a given class, HG values increased with increasing chain length as expected. Also as expected, HG values of TGs were ca three times that of their single chain counterparts. Increasing unsaturation for a given chain length for both esters and TGs resulted in a decrease in HG due to loss of hydrogen. RSD for all classes studied was very low showing the excellent reproducibility of the apparatus. The range of 0.04–0.44 for the saturated TGs was relatively large, reflecting the difficulty of completely combusting these compounds.

*Equations for calculating HG for saturated TGs.* In 1925 Kharasch and Sher developed equations for predicting HG of many classes of organic compounds based on the number of valence electrons present in the molecule (14). A comparison has been made between their equation and one developed from LINREG for predicting HG of fatty alcohols (16). A similar comparison for fatty esters is presented later in this paper.

Later, Kharasch reported HG values for only two saturated and two unsaturated fatty TGs: C 12:0, 5706.3; C 14:0, 6650.3; C 22:1 (*cis*), 10264.7 and C 22:1 (*trans*), 10235.8 kg-cal/mole (15). However, no equations for predicting the HG of saturated or unsaturated TGs were reported. For this reason LINREG was applied.

Input and output values associated with the LINREG program that determined the calculated HG for saturated TGs are shown in Table 2. As expected, CN, EN and MW all gave identical values for calculated HG, Error and % Error. Thus, any of these three could be used to predict HG by employing the appropriate regression equation

shown at the bottom of Table 2. The R squared values of 0.99 show a very high correlation between the X and Y variables. The % Error between calculated and measured HG values was 1% or less for most of the TGs. Thus, the equations developed provide a satisfactory means for predicting HG of saturated TGs.

*Equations for calculating HG for saturated esters.* Kharasch did not report HG values for saturated or unsaturated fatty esters, although equations for predicting HG of methyl and ethyl esters were given (15). Klopfenstein and Walker have reported HG for four fatty esters—Me 12:0, Me 14:0, Me 16:0 and Me 18:0 (17). Their data were comparable to that reported in Table 3. A comparison of measured and calculated HG for all the saturated esters (Table 3) shows excellent agreement as indicated by the low % Error. The high R squared values attest to the validity of the regression equations. Again, as expected, all three equations for methyl esters gave the same calculated HG, Error and % Error, thus any of the three may be used. The same applies to the equations for ethyl esters.

*Equations for HG for unsaturated esters and TGs.* HG values for these two classes of unsaturated compounds have not been reported except for the two unsaturated TGs noted earlier. Thus, equations that predict HG for these two classes should be particularly useful. Chain length could not be employed in the usual manner for the unsaturated compounds as there was no way to accommodate 18:2- and 18:3-compounds among the monounsaturated compounds. However, when only monounsaturated compounds were analyzed by LINREG, correlations were excellent for both monoene esters and TGs. Both classes could be analyzed with all unsaturated compounds included with either EN or MW. Although both EN and MW produced correlations with R squared values of 0.99%, % Error values were somewhat lower with EN than with MW for both unsaturated classes.

TABLE 3

Comparison of Measured and Calculated HG for Saturated Esters

Saturated methyl esters				Saturated ethyl esters			
Chain	Meas. HG, kg-cal/mole	Calc. HG, kg-cal/mole	% Error	Chain	Meas. HG, kg-cal/mole	Calc. HG, kg-cal/mole	% Error
6:0	1000	1005	-0.50	8:0	1465	1474	-0.61
8:0	1313	1315	-0.15	10:0	1780	1782	-0.11
10:0	1625	1624	0.06	12:0	2098	2091	0.33
12:0	1940	1934	0.31	14:0	2406	2400	0.25
14:0	2254	2244	0.44	16:0	2717	2708	0.33
16:0	2550	2553	-0.12	18:0	3012	3017	-0.17
18:0	2859	2863	-0.14	20:0	3321	3326	-0.15
20:0	3170	3172	-0.06	22:0	3632	3634	-0.06
22:0	3481	3482	-0.03	—	—	—	—
<b>Methyl Ester Equations</b>				<b>Ethyl Ester Equations</b>			
			<b>R squared</b>				<b>R squared</b>
HG =	76.71 +	154.77 CN	0.99	HG =	238.96 +	154.33 CN	0.99
HG =	25.11 +	25.80 EN	0.99	HG =	33.19 +	25.72 EN	0.99
HG =	-431.08 +	11.03 MW	0.99	HG =	-421.68 +	11.00 MW	0.99

Equations developed using only EN to predict calculated HG values are shown in Table 4. For esters, % Error ranged from 0.10 to 0.62%. For TGs, the range was -0.04 to 0.79%. These ranges are comparable to those of the saturated esters. The regression equations at the bottom of Table 4 can be used to calculate HG from the number of valence electrons present in the unsaturated compound.

*Comparison of our equations with Kharasch's equations for methyl and ethyl esters.* Kharasch proposed the equation —  $HG = 16.5 + 26.05 EN$  — to predict HG of

both methyl and ethyl esters of monobasic acids of known structure (15). Note the similarity of this equation to that shown in Table 3 for saturated methyl esters —  $HG = 25.11 + 25.80 EN$ . His data showed good agreement between measured and calculated HG for a number of esters; however, fatty esters were not included among those he examined. Therefore, we applied his equation to fatty esters, and compared the results obtained with our equation as summarized in Table 5. The measured HG values were determined by us. Statistical analysis of the data led to the following conclusions. Both equations

TABLE 4

Comparison of Measured and Calculated HG for Unsaturated Esters and Unsaturated Triglycerides

Unsaturated methyl esters				Unsaturated triglycerides			
Chain	Meas. HG, kg-cal/mole	Calc. HG, kg-cal/mole	% Error	Chain	Meas. HG, kg-cal/mole	Calc. HG, kg-cal/mole	% Error
12:1	1899	1901	-0.11	11:1	5115	5137	-0.43
14:1	2208	2213	-0.23	16:1	7452	7466	-0.19
16:1	2521	2525	-0.16	18:1	8389	8398	-0.11
18:1	2828	2838	-0.35	18:2	8259	8243	0.19
18:2	2794	2785	0.32	18:3	8152	8088	0.79
18:3	2750	2733	0.62	20:1	9326	9330	-0.04
20:1	3153	3150	0.10	22:1	10230	10262	-0.31
22:1	3454	3462	-0.23	—	—	—	—
Methyl Ester Equation			R squared	Triglyceride Equation			R squared
$HG = 27.36 + 26.02 EN$			0.99	$HG = 115.87 + 25.88 EN$			0.99

TABLE 5

Comparison of Equations for Calculating HG of Saturated Methyl Esters

Ester chain length	Measured HG, kg-cal/mole	Literature <sup>a</sup>		This work <sup>b</sup>	
		Calculated HG	% Differ. <sup>c</sup>	Calculated HG	% Differ. <sup>c</sup>
6	1000	1006	-0.60	1005	-0.50
8	1313	1319	-0.46	1315	-0.15
10	1625	1632	-0.43	1624	0.06
12	1940	1944	-0.21	1934	0.31
14	2254	2257	-0.13	2244	0.44
16	2550	2569	-0.75	2553	-0.12
18	2859	2882	-0.80	2863	-0.14
20	3170	3195	-0.79	3172	-0.06
22	3481	3507	-0.75	3482	-0.03
Average % difference		-0.55		-0.021	

<sup>a</sup> Kharasch, M.S., (15);  $HG = 16.5 + 26.05 EN$

<sup>b</sup>  $HG = 25.11 + 25.80 EN$

<sup>c</sup> Percent difference between measured and calculated HG.

TABLE 6

Comparison of Equations for Calculating HG of Saturated Ethyl Esters

Ester chain length	Measured HG, kg-cal/mole	Literature <sup>a</sup>		This work <sup>b</sup>	
		Calculated HG	% Differ. <sup>c</sup>	Calculated HG	% Differ. <sup>c</sup>
8	1465	1475	-0.68	1474	-0.61
10	1780	1788	-0.45	1782	-0.11
12	2098	2101	-0.14	2091	0.33
14	2406	2413	-0.29	2400	0.25
16	2717	2726	-0.33	2708	0.33
18	3012	3038	-0.86	3017	-0.17
20	3321	3351	-0.9	3326	-0.15
22	3632	3664	-0.88	3634	-0.06
Average % Difference		-0.57		-0.024	

<sup>a</sup> Kharasch, M.S., (15);  $HG = 16.5 + 26.05 EN$

<sup>b</sup>  $HG = 33.19 + 25.72 EN$

<sup>c</sup> Percent difference between measured and calculated HG.

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predicted HG values within 1% of the measured values. Within this series, however, Kharasch's calculated HG values were biased toward an overprediction in every case examined, while the values from the LINREG-derived equations were randomly scattered about the measured values. Also, the average % difference between measured and calculated HG values was larger ( $P < 0.01$ ) for Kharasch's equation.

A similar comparison was made for the fatty ethyl esters (Table 6). Average percent differences for the ethyl esters were very similar to those for the methyl esters. Statistical analysis led to the same conclusions noted for the methyl esters: Kharasch's equation overestimated the predicted values in every case, and the average percent difference was larger ( $P < 0.01$ ). Thus, although both equations gave estimates that were within 1% of measured values, within that 1%, the LINREG-derived equations gave estimates that were more accurate and precise.

**ACKNOWLEDGMENTS**

We thank Haifa Khoury for laboratory assistance and Terry C. Nelsen for statistical assistance.

**REFERENCES**

1. Fazzolare, R.A. and C.B. Smith (ed.) *Beyond the Energy Crisis — Opportunity and Challenge*, Vol. III, Third International Conference on Energy Use Management, West Berlin, October 26–30, 1981, Pergamon Press, Oxford.
2. *Vegetable Oil as Diesel Fuel*, Seminar II, Northern Regional Research Center, Peoria, Illinois, October 21–22, 1981.
3. *Ibid.*, Seminar III, ARM-NC-28, Northern Regional Research Center, Peoria, Illinois, October 19–20, 1983.
4. *Vegetable Oil Fuels*, Proceedings of the International Conference on Plant and Vegetable Oils as Fuels, American Society of Agricultural Engineers, St. Joseph, MI, 1982.
5. Pryde, E.H., *J. Am. Oil Chem. Soc.* 60:5234 (1983).
6. *Ibid.* 61:1609 (1984).
7. Goering, C.E., A.W. Schwab, M.J. Daugherty, E.H. Pryde and A.J. Heakin, *Trans. Am. Soc. Agric. Eng.* 25:1472 (1982).
8. Ryan, T.W. III, L.G. Dodge and T.J. Callahan, *J. Am. Oil Chem. Soc.* 61:1610 (1984).
9. Bagby, M.O., B. Freedman and A.W. Schwab, *Am. Soc. Agric. Eng.*, Paper No. 87-1583 (1987).
10. Freedman, B., E.H. Pryde and T.L. Mounts, *J. Am. Oil Chem. Soc.* 61:1638 (1984).
11. Freedman, B., in *Oleochemicals: Fatty Acids, Fatty Alcohols, Fatty Amines — A Short Course*, AOCS Short Course, Kings Island, OH, September 1987.
12. Clark, S.J., L. Wagner, M.D. Schrock and P.G. Piennaar, *J. Am. Oil Chem. Soc.* 61:1632 (1984).
13. Pischinger, G.H., A.M. Falcon, R.W. Siekman and F.R. Fernandes, in *Vegetable Oil Fuels*, Proceedings of the International Conference on Plant and Vegetable Oils as Fuels, American Society of Agricultural Engineers, St. Joseph, MI, 1982, p. 198.
14. Kharasch, M.S. and B. Sher, *J. Phys. Chem.* 29:625 (1925).
15. Kharasch, M.S., *J. Res. Natl. Bur. Stand. (U.S.)* 2:359 (1929).
16. Freedman, B., M.O. Bagby and H. Khoury, *J. Am. Oil Chem. Soc.* 66:595 (1989).
17. Klopfenstein, W.E. and H.S. Walker, *Ibid.* 60:1596 (1983).

[Received 2/24/89]