Estimation of Heat of Combustion of Triglycerides and Fatty Acid Methyl Esters

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Equations were developed for the estimation of gross heat of combustion (HG) of triglycerides (TGs) and fatty acid methyl esters (FAMEs) from their saponification number (SN) and iodine value (IV). HG of TG = 1,896,000/SN − 0.6 IV − 1600 and HG of FAME = 618,000/SN − 0.08 IV − 430. When these equations were tested on cottonseed oil, soybean oil, partially hydrogenated soybean oil, peanut oil, sunflower oil, sunflower oil methyl esters, soybean oil methyl esters and cottonseed oil methyl esters, predicted HG values agreed well with those reported in the literature.

KEY WORDS: Heat of combustion, iodine number, saponification number, vegetable oil, vegetable oil methyl ester.

Vegetable oils and their methyl esters have long been considered as potential alternative fuels for diesel engines (1-3). In addition to ignition quality, the gross heat of combustion (HG) of an oil is one of more important properties in determining its suitability for use in diesel engines. The HG of several vegetable oils and their methyl esters have been measured by other investigators (4-8), and they are slightly lower than that of No. 2 diesel oil (7,8).

Although the HG of organic compounds is not difficult to determine, these measurements require proper equipment and are time-consuming. However, the HG of vegetable oil can be calculated from its saponification number (SN) and iodine value (IV) by Bertram's equation (9) or from its electron number by Kharasch's equation (10). Recently, Freedman and Bagby (11) developed several equations for calculating the HG of pure triglycerides (TG) and fatty acid methyl esters (FAME) from their carbon numbers, electron numbers or molecular weights. The calculated HG values are very accurate, but they are limited to pure TG or FAME. All natural vegetable oils and their methyl esters contain several different fatty acids with various degrees of unsaturation so Freedman and Bagby's equations (11) cannot be used directly for vegetable oils or mixed methyl esters. This paper proposes two alternative equations for the estimation of HG of TGs and FAMEs from their saponification numbers (SN) and iodine values (IV).

EXPERIMENTAL

Equation 1 was developed by Freedman and Bagby (11) for estimation of the HG of two saturated FAMEs from its molecular weight (MW).

$$HG = 11.03\ MW - 431.08 \qquad [1]$$

MW is converted into SN by multiplication with 56000/SN and equation 1 becomes

$$HG = 617800/SN - 431.08 \qquad [2]$$

or approximately

$$HG = 618000/SN - 430. \qquad [3]$$

Equation 3 is limited to saturated FAMEs only but it is extended to unsaturated FAMEs by introducing an unsaturation term, iodine value (IV), and equation 3 becomes

$$HG = 618000/SN - 430 + cIV \qquad [4]$$

where c is a constant. Values of c are solved for by substituting HG, SN and IV of each unsaturated FAME (Table 1) into equation 4 and are summarized in the last column of Table 1. The average value of c (−0.08) is substituted back into equation 4 to give equation 5

$$HG = 618000/SN - 0.08\ IV - 430 \qquad [5]$$

Equation 6 was similarly derived by starting from Freedman and Bagby's (11) equation for saturated TGs (HG = 11.29 MW − 1569).

$$HG = 1{,}896{,}000/SN - 0.6\ IV - 1600. \qquad [6]$$

The unit of HG in both equations 5 and 6 is kg-cal/mol. They can be converted into kg-cal/kg by multiplication with SN/56 and SN/56 × 3, respectively.

RESULTS AND DISCUSSION

The estimated HGs of saturated and unsaturated FAMEs by equation 5 are listed in Table 2 and those of TGs by equation 6 are listed in Table 3. The SN and IV values were calculated from their molecular weights and degrees of unsaturation. The HG of FAMEs and TGs measured by Freedman and Bagby (11) are also included in both tables for comparison. The differences between the calculated HG and the measured values are less than 1% for FAMEs and less than 2% for TGs.

When these equations are used to estimate the HG of FAMEs and TGs of mixed fatty acids, the calculated HGs agree well with those reported in the literature as shown in Table 4. Differences are approximately the same as those of pure FAMEs and TGs.

Bertram (9) also used SN and IV for the calculation of HG of vegetable oils. Bertram's equation gives acceptable HG values for vegetable oils and pure TGs with fatty acid carbon chains longer than 10 (results not shown), but the HG of glyceryl trioctanoate is 4.8% too low.

Results in Tables 2, 3 and 4 show that the HG/mol of TGs are about 3 times those of FAMEs, but HGs of FAMEs per unit weight are slightly higher than TGs with the same fatty acid composition. Thus conversion of vegetable oils to methyl esters for use as diesel fuels is advantageous because FAMEs have

TABLE 1

Values of HG, SN, IV and c of Unsaturated FAME

Chain length	HG[a] (kg-cal/mol)	SN[b]	IV[b]	c
12:1	1899	264.2	119.8	− 0.085
14:1	2208	233.3	105.8	− 0.103
16:1	2521	209	94.8	− 0.063
18:1	2828	189.2	85.8	− 0.098
18:2	2794	109.5	172.8	− 0.116
18:3	2750	191.8	260.9	− 0.161
20:1	3153	172.8	78.4	+ 0.084
22:1	3454	159.1	72.2	− 0.060
Average				− 0.08

[a] HG obtained from Freedman and Bagby (11).
[b] Calculated from molecular weights and degrees of unsaturation.

TABLE 2

Comparison of Calculated HG of FAMEs with Values Determined by Freedman and Bagby (11)

Chain length	SN[a]	IV[a]	HG (kg-cal/mol) Freedman & Bagby (11)	HG (kg-cal/mol) Equation 5	% Difference
Saturated FAMEs					
6	430.7	—	1000	1004.9	− 0.49
8	354.4	—	1313	1313.8	− 0.06
10	301.1	—	1625	1622.5	0.16
12	261.7	—	1940	1931.5	0.44
14	231.7	—	2253	2237.2	0.74
16	207.4	—	2550	2549.7	0.01
18	187.9	—	2859	2859.0	0.00
20	171.8	—	3170	3167.2	0.09
22	158.2	—	3481	3476.4	0.13
Unsaturated FAMEs					
12:1	264.2	119.8	1899	1899.5	− 0.03
14:1	233.3	105.8	2208	2209.5	− 0.07
16:1	209.0	94.8	2521	2526.9	− 0.23
18:1	189.2	85.8	2828	2829.1	− 0.04
18:2	190.5	172.8	2794	2800.3	− 0.22
18:3	191.8	260.9	2750	2771.2	− 0.76
20:1	172.8	78.4	3150	3140.1	0.31
22:1	159.1	72.2	3454	3448.5	0.16

[a] Calculated form molecular weights and degrees of unsaturation.

TABLE 3

Comparison of Calculated HG of TGs with Values Determined by Freedman and Bagby (11)

Chain length of fatty acid	SN[a]	IV[a]	HG (kg-cal/mol) Freedman & Bagby (11)	HG (kg-cal/mol) Equation 6	% Difference
Saturated TGs					
8	356.8	—	3647	3714.0	− 1.84
10	302.7	—	4747	4663.6	1.76
12	262.8	—	5672	5614.6	1.01
14	232.3	—	6607	6561.8	0.68
16	208.0	—	7554	7515.4	0.51
18	188.4	—	8558	8463.7	1.10
20	172.2	—	9433	9410.4	0.24
22	158.5	—	10327	10362.1	− 0.34
Unsaturated TGs					
16:1	209.6	94.8	7452	7388.9	0.85
18:1	189.7	85.8	8389	8343.2	0.55
18:2	191.0	172.8	8259	8223.0	0.44
18:3	192.3	260.9	8152	8103.1	0.27
20:1	173.2	78.4	9326	9300.0	0.28
22:1	159.4	72.2	10230	10251.3	0.21

[a] Calculated from molecular weights and degrees of unsaturation.

TABLE 4

Comparison of Calculated HG Values of Vegetable Oils and Methyl Esters with Literature Values

Oil	SN	IV	HG (literature) (MJ/kg)	HG (calculated) MJ/kg	HG (calculated) kg-cal/mol	% Difference
Cottonseed	194[a]	109.5[a]	38.85[b]	39.20	8108	− 0.90
Cottonseed methyl ester	194[a]	109.5[a]	40.15[c]	39.84	2747	0.77
Sunflower	188.3[d]	134.3[d]	39.65[e]	39.63	8445	0.05
Sunflower methyl ester	188.3	134.3	40.0[e]	40.00	2846	0.0
Soybean (degummed)	190[d]	129.2[d]	39.39[d]	39.30	8300	0.23
Soybean (Hydrotreated)	190.5[d]	102.3[d]	39.82[d]	39.36	8291	1.16
Soybean methyl ester	190.8[f]	135.1[f]	39.8[f]	39.92	2728	− 0.30
Peanut (crude)	189.4[g]	92.36[g]	39.61[g]	39.43	8354	0.45

[a] Saponification number and iodine value calculated from Sonntag (12).
[b] HG obtained from Broder *et al.* (7).
[c] HG obtained from Fort and Blumberg (13).
[d] Saponification number and iodine value calculated from Ryan *et al.* (6).
[e] HG obtained from Tahir *et al.* (8).
[f] Values obtained from Clark *et al.* (4).
[g] Values obtained from Ryan *et al.* (5).

higher HGs per unit weight and higher cetane numbers (14).

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