Correlation of Heats of Combustion with Empirical Formulas for Fatty Alcohols[1]

B. Freedman*, **M.O. Bagby** and **H. Khoury**
Northern Regional Research Center, Agricultural Research Service, U.S. Department of Agriculture, Peoria, IL 61604

Gross heats of combustion (Hg) for the homologous series of saturated fatty alcohols C_{10}-C_{22} were measured in a Parr adiabatic calorimeter according to ASTM D240 and D2015. The measured values for these alcohols ranged from 1582 to 3453 kg-cal/mole. We developed equations that related carbon number (CN) or chain length, electron number (EN) or number of valence electrons and molecular weight (MW) to calculated Hg by linear regression analysis (LINREG). These equations are: $Hg = 26.00 + 155.60\ CN$; $Hg = 26.00 + 25.94\ EN$; and $Hg = -172.2 + 11.00\ MW$. R squared values for all three equations were 0.99. The results obtained with LINREG were compared to a literature method. Comparisons were made for both the fatty alcohols above and C_1-C_5, C_7, C_8 and C_{16} alcohols of the literature method. For the former alcohols there was no difference in accuracy or precision between the two methods. For the latter alcohols LINREG was both more accurate and precise. Measured Hg vs. chain length for C_1-C_{22} alcohols showed a perfect linear relationship. Thus, knowing chain length, Hg can be predicted accurately for alcohols in this range.

During the past decade, vegetable oils have been reexamined as fuels for diesel engines. To formulate vegetable oil-rich fuels with desirable viscosity characteristics, we have studied various hybrid fuels including aqueous alcohol-in-oil microemulsions (1). Shorter chain-length alcohols (C_4-C_{14}) have proven valuable as dispersing agents in these formulations; however, heat contents of the fuels are somewhat low (2-4). Fatty alcohols with chain lengths of C_{10}-C_{18} are effective as dispersers and also provide fuels with higher heat contents. To assist us in formulating fuels, it is desirable to know the gross heats of combustion (Hg) of various potential fuel components. No systematic study of Hg has been reported for saturated fatty alcohols. However, in 1925, Kharasch and Sher developed a mathematical formula that permitted calculation of Hg for alcohols from the electron number (defined by Kharasch as number of valence electrons present in the alcohol) (5). In 1929, Kharasch reported both calculated and measured Hg for C_1-C_5, C_7, C_8 and C_{16} alcohols (6). We measured Hg for six additional fatty alcohols, and then used linear regression analysis (LINREG) to correlate Hg with carbon number (CN) or chain length, electron number (EN) and molecular weight (MW). Both Kharasch's alcohol data and our data were used for comparing Kharasch's equation with that obtained by LINREG for predicting Hg.

EXPERIMENTAL

The fatty alcohols were purchased from Nu Chek Prep, Elysian, MN. These alcohols had a minimum purity of 99%. Hg were determined in a Parr Adiabatic Oxygen Bomb Calorimeter, Model 1241. We used ASTM method D240-76 (1980) for liquid fuels, and D2015-77 (1978) for solid fuels. The calorimeter was standardized with benzoic acid using 6 calibration runs for each of 2 bombs. The mean ($\overline{X}$) was 2415, standard deviation (SD) 1.6 and relative standard deviation (RSD) 0.07%. For each alcohol, at least 3 replicates were run whereby the difference in Hg between these 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 ($\overline{X}$), (SD) and (RSD). 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 one of these three variables.

RESULTS AND DISCUSSION

Table 1 shows Hg and statistical data for the even-numbered n-alcohols from C_{10}-C_{22} based on three or more replicates for each compound. As expected, there is a regular increase in Hg with increasing chain length. The RSD for all seven alcohols averaged 0.09%. Although the Parr apparatus reported Hg in cal/g, we converted these units to kg-cal/mole, the standard unit for Hg (7), to be able to compare our results directly with those from Kharasch's studies.

LINREG was used to determine linear relationships between Hg and CN, EN or MW. The resulting equations were: $Hg = 26.0 + 155.60\ CN$; $Hg = 26.0 + 25.94\ EN$; and $Hg = -172.2 + 11.00\ MW$. R squared values for all three equations were 0.99. The very high R-squared values show a very high correlation between X and Y variables. These equations can be used to accurately predict Hg from the empirical formula of a straight-chain fatty alcohol, as CN, EN or MW can be readily determined.

Kharasch described an equation for calculating Hg based on the empirical formula of a compound (5, 6). To predict Hg of alcohols, he used the equation $Hg = 26.05 \times N + 13$, where N is the electron number (EN) of the compound. The calculated Hg reported for methanol was $Hg = 26.05 \times 6 + 13 = 169.3$ kg-cal/mole. Experimentally, Kharasch determined 170.9 kg-cal/mole. He reported comparably close agreement between calculated and measured Hg for all alcohols (C_1-C_5, C_7, C_8 and C_{16}) studied (6), thus showing the validity of his equation. Note that our equation, $Hg = 25.94\ EN + 26$, is quite similar to his equation, $Hg = 26.05\ N + 13$, but specifically fits the C_{10}-C_{22} alcohols.

We were interested in knowing whether Kharasch's equation or LINREG would produce a better predication of Hg for the alcohols he reported. Although the average percentage differences between calculated and

TABLE 1

Hg of Fatty Alcohols[a]

Alcohol name	Chain length	Hg (cal/g)			Hg (kg-cal/mole)
		X̄	SD	RSD %	
Decyl	10	9920	10.1	0.10	1582
Lauryl	12	10110	14.5	0.14	1899
Myristyl	14	10190	7.8	0.08	2202
Palmityl	16	10280	8.1	0.08	2512
Stearyl	18	10360	4.5	0.04	2826
Arachidyl	20	10420	10.2	0.10	3138
Behenyl	22	10480	8.7	0.08	3453

[a]Based on a minimum of 3 replications.

measured Hg by both methods were not significantly different (P > 0.40), Kharasch's percentage difference had a larger variance (P = 0.06) and a systematic bias in that percentage difference was related to chain length (correlation = −0.74). A similar comparison was made between the two equations for the C_{10}-C_{22} alcohols. Analyses of these data showed that average percentage differences were not significantly different (P = 0.29), variances were not different (P = 0.13) and biases were not found. Thus, for Kharasch's alcohols, LINREG was both more accurate and precise, but for the C_{10}-C_{22} alcohols both equations gave comparable results. Use of LINREG for measured Hg values vs. chain length for combined data sets from Kharasch and the fatty alcohols reported here, C_1-C_{22}, gave the equation:

$$Hg = 14.42 + 156.27 \text{ CN (R squared 0.99)}.$$

This equation may be used to calculate Hg from any straight chain alcohol C_1-C_{22} if chain length is known.

ACKNOWLEDGMENTS

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