

Heats of Combustion of Fatty Acids and Fatty Acid Esters

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Abstract The military uses JP-8, a kerosene type hydrocarbon, to fuel most of its vehicles and is seeking a renewable alternative fuel that meets strict JP-8 specifications. Biodiesel is typically a mixture of different alkyl esters produced from the transesterification of triglycerides readily available in plant oils and used cooking oil. To date, no traditional biodiesel meets the requirements for heat of combustion, freezing point, viscosity and oxidative stability to be a stand-alone replacement for JP-8. This work is a fundamental survey of the heat of combustion of single fatty acid esters and a predictive model for estimating the heat of combustion given a known molecular structure. The gross heat of combustion of various C6–C18 fatty acids and the methyl, propyl and isopropyl esters of these fatty acids was measured. This study sought to relate the effect of chain length, degree of unsaturation and branching to the critical fuel property of the gross heat of combustion (H_c). It was found that H_c (kJ/g) increased with chain length. A nearly linear relationship was found between wt% carbon and hydrogen, and H_c . Group contribution models previously published for hydrocarbons and polymers were modified to more accurately predict the heat of combustion of the fatty acids and esters.

Modification of the molar heat values of carboxylic acid, methyl, and methylene groups improved correlation of the model with the experimental results.

Keywords JP-8 · Biodiesel · Heat of combustion · Fatty acids · FAME · Group contribution method · Modeling

Abbreviations

ARL	Army Research Laboratory
FA/FAME	Fatty acid/fatty acid methyl ester
H_c	Gross heat of combustion measured experimentally
GCM	Group contribution method used to predict gross heat of combustion based on atomic structure
Q_c	Gross heat of combustion calculated from the group contribution method
i	Molecular sub-group assigned a heat value in the GCM
N_i	Number of molecular sub-group i in the structure
M_i	Mass of molecular sub-group i
H_i	Heat value assigned to molecular sub-group i

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Introduction

JP-8 is the predominant fuel for Army vehicle platforms. Its properties are specified under MIL-PRF-83133E. The net heat of combustion requirement is a minimum of 42.8 MJ/kg. The Army has developed policies and guidelines based on recent Federal legislation that require greater usage of

renewable energy sources [1–4]. According to the Energy Policy Act of 2005, ‘the term ‘biodiesel’ means a diesel fuel substitute produced from nonpetroleum renewable resources that meets the registration requirements for fuels and fuel additives established by the Environmental Protection Agency under section 211 of the Clean Air Act (42 U.S.C. 7545) and that meets the American Society for Testing and Materials D6751–02a Standard Specification for Biodiesel Fuel (B100) Blend Stock for Distillate Fuels’ [5]. Due to greenhouse gas emissions, increasing cost, and decreasing availability, the military has been interested in finding more economical and renewable alternative fuels that meet stringent JP-8 specifications.

There is a significant difference in the chemical structure of JP-8 and biodiesel. JP-8 is primarily a kerosene type fuel comprised of hydrocarbons ranging in size from 6–18 carbon atoms [6]. This hydrocarbon mixture is 58 vol % saturated alkanes, 20 vol % cycloalkanes, 20 vol % aromatics and 2 vol % olefins [7] with additives to suppress freezing, static sparking and antioxidants to improve storage stability according to MIL-PRF-83133E. Typical biodiesel is the product of methanol transesterification of plant oil triglycerides (fatty acid esters of glycerol) and as such contains a mixture typically ranging in number from 4 to 12 different fatty acid methyl esters (FAME) [8, 9]. Many simple esters are made by reacting fatty (carboxylic) acids and low molecular weight alcohols (e.g., methanol and ethanol). Methanol is widely used because of the significantly lower cost relative to other alcohols.

To date, no traditional biodiesel meets the requirements for heat of combustion, freezing point, viscosity and oxidative stability to be a stand-alone replacement for JP-8. This work is a fundamental survey of the gross heat of combustion of single fatty acid alkyl esters and a predictive model for estimating the heat of combustion given a known molecular structure. Alkyl esters of single fatty acids were studied to more easily relate the effects of structural differences to the gross heat of combustion. Gross heat of combustion, also referred to as higher heat value (HHV) for fuels, is the total energy output from the oxidation of the fuel to produce CO₂ (g) and H₂O (l). This value differs from the net heat of combustion, also referred to as lower heat value (LHV), by the heat of vaporization of water produced. In open combustion systems, water vapor is expelled with exhaust gasses, and the heat to vaporize this water reduces the energy yielded.

We synthetically prepared methyl, propyl and isopropyl esters from fatty acids of various chain lengths, degrees of unsaturation, branching, cyclic and aromatic structures. Furthermore, the authors have modified a group contribution model to accurately predict the bond energies and the heat of combustion of a fatty acid or ester based on chemical structure.

Experimental Method

Materials

The fatty acids used to synthesize esters for this study ranged from C6 to C18 straight chain saturated acids (hexanoic acid, octanoic acid, decanoic acid, dodecanoic acid, palmitic acid and stearic acid), unsaturated fatty acids with one or two carbon–carbon double bonds (cis-5-dodecenoic acid, oleic acid and linoleic acid), benzoic acid, furoic acid, cyclohexanoic acid, branched acids (2-propylpentanoic acid, 2-butyloctanoic acid, 2-hexyldecanoic acid, 16-methylheptadecanoic acid and 2-methyloctadecanoic acid) and diacids (suberic acid, sebacic acid and dodecanedioic acid). A few aromatic and aliphatic hydrocarbons (benzene, toluene, xylene, decane and hexadecane) were also included in the study.

Ester Preparation

The materials of interest in this study were methyl, propyl and isopropyl esters made from carboxylic acids purchased from Sigma Aldrich. Acid catalyzed Fischer esterification was used to prepare the esters from fatty acid and alcohol reactants. The carboxylic acid (limiting reagent) was mixed with an alcohol (ten times molar excess) in the presence of sulfuric acid (10 mol% based on fatty acid) and the reactants were heated to boiling. Reaction progress was monitored by titration of a small sample of the reaction mixture with a standardized base solution to calculate acid number. As the reaction proceeded and carboxylic acid was consumed to produce ester, the acid number decreased. When the acid number remained relatively constant with time, the reaction was complete.

After the ester reaction had reached equilibrium, excess alcohol in the reaction mixture was removed using a rotary evaporator under vacuum. The reaction mixture concentrate was then dissolved in diethyl ether, transferred to a separatory funnel and washed several times with saturated aqueous sodium bicarbonate solution until the aqueous layer was no longer acidic. The organic layer was dried over magnesium sulfate to remove any water traces left from the extraction process. The magnesium sulfate was removed by vacuum filtration using a Büchner funnel. Then diethyl ether was removed using a rotary evaporator. Lastly, a few PTFE boiling chips were added to the purified ester and the open flask was placed in a vacuum oven at ambient temperature and 30'' Hg vacuum overnight to remove any remaining trace solvent.

Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance (NMR) spectroscopy was run on synthesized compounds to ensure the proper products

were prepared and the samples were pure. Solutions for NMR analysis were prepared by dissolving 18–20 mg of the analyte in 1 ml of deuterated chloroform (CDCl₃). Proton NMR was performed on a Bruker AC 250 600 MHz spectrometer running 16 scans with a 4 s delay time.

Differential Scanning Calorimetry

A TA Instruments Q1000 DSC was used to determine whether any trace solvent or water remained in the sample. A sample between 5 and 10 mg was crimped in an aluminum hermetic pan. The sample was cooled to –90 °C at 10 °C/min, held at temperature for 10 min and then heated to 150 °C at 5 °C/min. The thermal profiles were examined for distinct endotherms at 35 or 100 °C indicating the vaporization of diethyl ether or water, respectively. Depending on the alcohol used to synthesize the ester, peaks might be observed for methanol, isopropanol, or *n*-propanol at 65, 82 or 97 °C, respectively.

Bomb Calorimetry

A Parr 6400 oxygen bomb calorimeter was used to determine the gross heat of combustion (H_c) of the materials. Daily verification of the instrument's accuracy was performed by testing a pellet of benzoic acid with a known heat of combustion (26.453 kJ/g). Samples of 0.5000–1.000 g were placed in the oxygen bomb. All samples were run in triplicate.

Group Contribution Methodology for Predicting Heat of Combustion

In the design and synthesis of fuels and fuel substitutes, it is important to be able to accurately predict a material's heat of combustion from its molecular structure. In a Federal Aviation Administration technical note, Walters [10] published a method for predicting the heat of combustion of numerous polymeric materials. To illustrate the method, the theoretical heat of combustion for methyl hexanoate (Fig. 1) is calculated here.

The molecule is divided into its most basic structural groups listed in the Walters model. The groups of interest for this example can be seen in Table 1. N_i denotes the number of each structural group in the molecule and each structural group has a mass, M_i (g/mol). The group

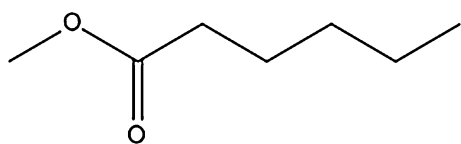


Fig. 1 Molecular structure of methyl hexanoate

Table 1 Walters group contribution method heat of combustion values for methyl hexanoate

Structural group, i	N_i	M_i (g/mol)	Group H_i (kJ/mol)	$N_i M_i$ (g)	$N_i H_i$ (kJ)
–CH ₃	2	15.0345	775	30.0690	1,550
–CH ₂ –	4	14.0266	670	56.1063	2,680
–COO– (ester)	1	44.0095	112	44.0095	112
Total =				130.1848	4,342

contribution method (GCM) has assigned a heat of combustion value, H_i (kJ/mol) for each component, i , derived from extensive experimental data [10]. In this case, methyl hexanoate has three different structural groups; two methyl groups (–CH₃), four methylene groups (–CH₂–), and one ester group (–COO–).

The bomb calorimeter measures the gross heat of combustion. The GCM was used to calculate gross heat, Q_c (kJ/g), by Eq. 1:

$$Q_c = \sum N_i H_i / \sum N_i M_i. \quad (1)$$

In the example of methyl hexanoate, $Q_c = 4,342$ kJ/130.1848 g = 33.35 kJ/g. The average experimental value for heat of combustion of methyl hexanoate was 32.17 kJ/g. The percent error in the predicted value from the experimental value for methyl hexanoate was 3.7 %.

Further discussion of the GCM and the modifications made to the heat values (H_i) assigned to the structural groups is presented with the results.

Results and Discussion

Sample Purity

A cross section of samples was titrated with standardized KOH solution after ester purification to determine the presence of unreacted carboxylic acid. All samples analyzed showed no detectible acid content. Additionally, proton NMR was chosen to examine sample purity because of method sensitivity and the distinct signature peaks of diethyl ether, low MW alcohols and water are easily identified and separated from the peaks of the ester structure. While gas chromatography is more commonly used for sample characterization, NMR poses no possibility for thermal degradation of the sample. Lastly, DSC was used to determine the onset of freezing (not discussed in this work) and check for the presence of solvents or water.

NMR and DSC results indicated that the proper products were formed as close to 100 % purity as can be measured. Example NMR spectra before and after vacuum drying are shown in Fig. 2 for isopropyl benzoate. Before vacuum

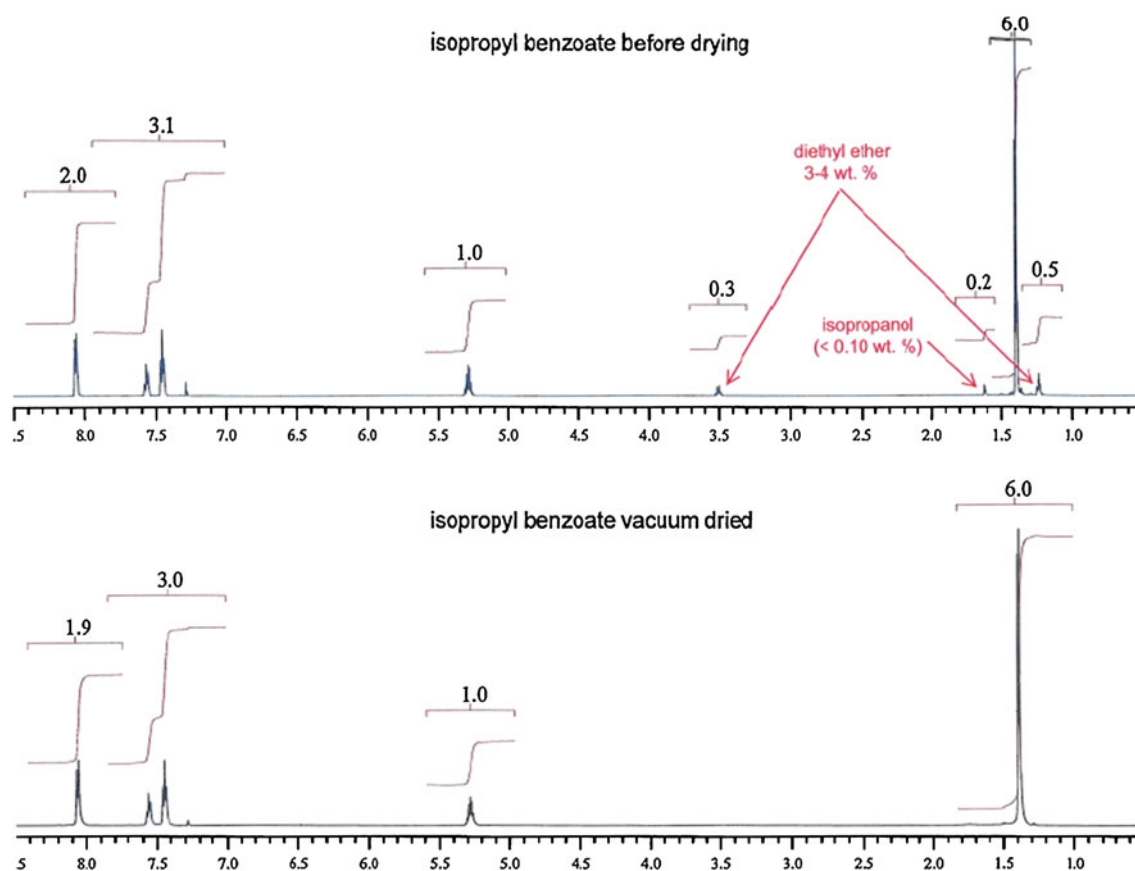


Fig. 2 Proton NMR spectra for isopropyl benzoate in CDCl_3 before (*top*) and after (*bottom*) vacuum drying

drying, proton NMR was able to detect traces of isopropanol (1.6 ppm) at less than 0.10 wt% and diethyl ether (3.5 and 1.2 ppm) at 3–4 wt%. The spectrum after drying showed no presence of diethyl ether, isopropanol or water (4.3 ppm). In addition, the ratio of methyl protons to aromatic protons was as expected for this molecule. DSC results showed no peaks due to boiling of diethyl ether ($\sim 35^\circ\text{C}$), isopropanol ($\sim 82^\circ\text{C}$) or water ($\sim 100^\circ\text{C}$) during the heating ramp. A sharp endothermic peak at -27.49°C is due to melting of isopropyl benzoate (Fig. 3). The dramatic exotherm found approximately -75°C was caused by the crystallization upon cooling of isopropyl benzoate. In our research we found certain samples would become super-cooled well below the melting point before crystallizing. This phenomenon is partly due to the dynamic temperature ramp of DSC experiments and the complexity of crystal nucleation and propagation to complete sample freezing.

Experimental Results for Heat of Combustion

JP-8 properties are specified under MIL-PRF-83133E. The minimum net heat of combustion (42.8 MJ/kg) for a

material meeting the JP-8 specification is depicted as a red dotted line in Fig. 4. This number falls within the range of 41.9–43.3 MJ/kg determined by Al-Ghouti et al. [11] for the net heat of combustion for conventional diesel fuel. Net heat is the gross heat of combustion minus the heat of vaporization of water formed during combustion. In a bomb calorimeter that is sealed, under pressure and near ambient conditions, the water vapor formed as a combustion product condenses in the bomb and transfers the heat of condensation to the calorimeter. In an internal combustion engine, water vapor formed during the combustion of fuel is lost with the exhaust gasses [12]. Therefore, the heat of water vaporization is lost when the fuel is burned in an open system as would be the case in most industrial and transportation applications. The corresponding higher heating value (equivalent to gross heat of combustion) for conventional diesel is listed as 45.8 MJ/kg [13], which matches well with the average experimental gross heat of combustion of 45.9 MJ/kg for JP-8. The average measured gross heat of combustion for JP-8 is shown by the green dotted line in Fig. 4.

Figure 4 shows that for fatty acids and fatty acid esters, the heat of combustion (kJ/g) is a function of the

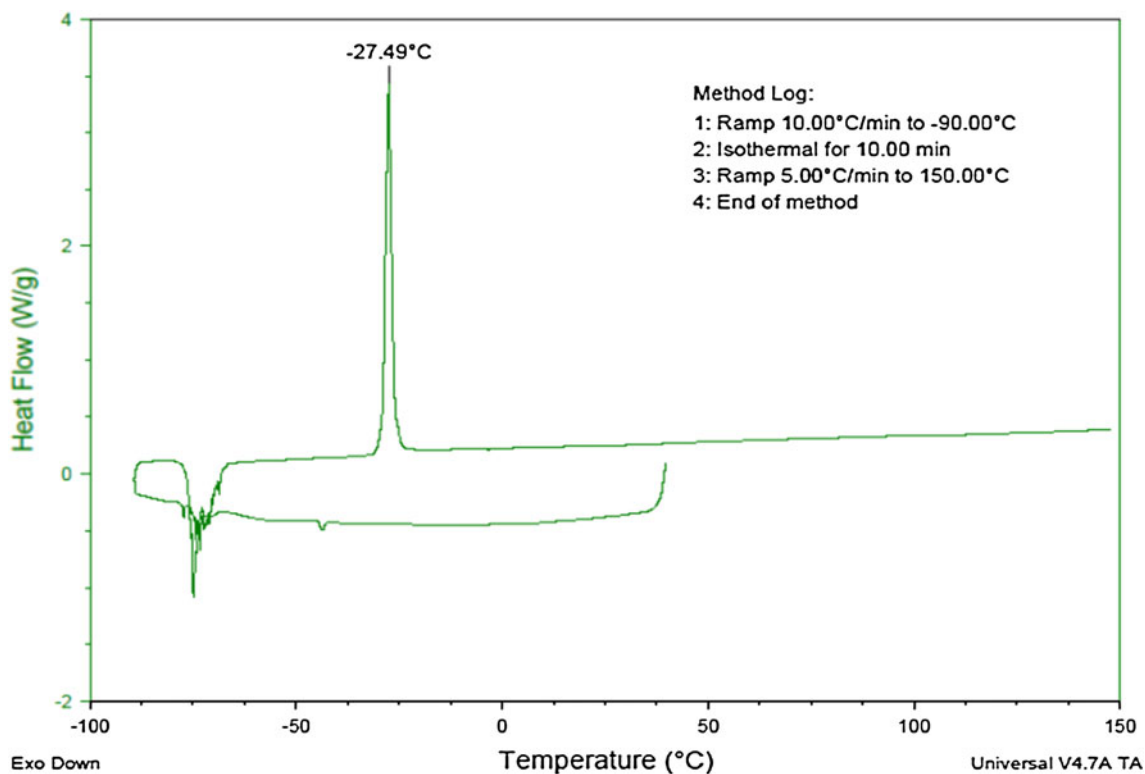


Fig. 3 DSC graph of vacuum dried isopropyl benzoate showing no solvent peaks from 35 to 100 °C

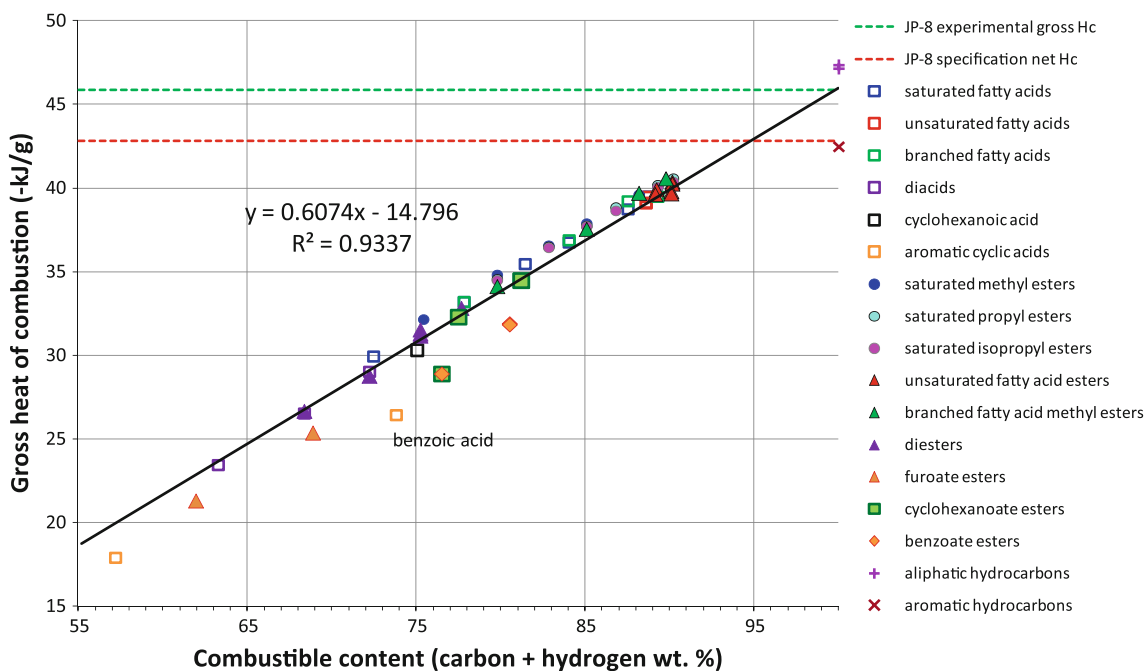


Fig. 4 Experimental gross heat of combustion (H_c) as a function of combustible content for various fatty acids, synthesized esters and hydrocarbons. The solid black line is the best fit through the experimental data (equation and R^2 also shown)

combustible content, which is the sum of the carbon and hydrogen content (wt%). As the combustible content increased, the gross heat of combustion also increased in a fairly linear relationship described by Eq. 2:

$$H_c(\text{kJ/g}) = 0.61(\text{wt\% combustible content}) - 14.80 \quad (2)$$

The negative y -intercept of the best fit line through the data in Fig. 4 is an artifact of the x -axis being the sum of the carbon and hydrogen content of the compound. Only materials containing some amount of carbon and hydrogen were included in this study and as such, an x value of zero (i.e., the y -axis) is not part of the experimental space explored in this paper. Extrapolation of these data to the y -axis is not valid.

As can be seen in Fig. 4, none of the fatty acids or synthesized esters in this study met the JP-8 specification. The best fit line through all experimental data crosses the JP-8 specification value at 95 wt% combustible content. This is a result of the oxygen content in the fatty acids/esters that reduces the heat of combustion. A saturated fatty acid, methyl ester or propyl ester would have to reach a length of over 40 carbon atoms to achieve 95 wt% combustible content, in contrast to JP-8, which is 100 % combustible. Fatty acids or esters of this length are not commonly produced in nature and would have extremely high melting points thus making them unusable as liquid fuels. For reference, Sigma-Aldrich reports the melting point of stearic acid (18 carbons, saturated) to be 69–71 °C and linoleic acid (18 carbons, 2 C=C double bonds) to be –5 °C.

Army Research Laboratory (ARL) experimental results for gross heat of combustion of several methyl esters were compared in Table 2 to heats of combustion determined by Freedman and Bagby [14] and Klopfenstein and Walker [15]. Values in the last column were calculated from the enthalpies of formation and published in the CRC Handbook of Chemistry and Physics (92nd ed.) ARL results were within experimental error of those published by Freedman and Bagby for five of eight compounds listed. The ARL results

for methyl octanoate, methyl decanoate and methyl palmitate vary <0.5 % from Freedman and Bagby. There was less agreement between ARL data and Klopfenstein and Walker's results. Only the values for methyl palmitate were within experimental error for ARL and Klopfenstein and Walker. Other experimental results reported by ARL differ from Klopfenstein and Walker by as much as 2.6 %. Lastly, for four of five methyl esters, ARL results were within 0.4 % of the values calculated from enthalpies of formation. The ARL value for methyl hexanoate was within 0.6 % of the calculated value from the CRC.

Saturated fatty acids and saturated fatty acid methyl esters had nearly identical heats of combustion for the same combustible content. However, there was a small increase in the heat of combustion (~0.4 kJ/g) of saturated methyl esters compared to saturated fatty acids for the materials in this study. This increase in energy yield for methyl esters is likely due to the lower bond energy of the C–O bond in the ester group that replaced the more energetic O–H bond in fatty acids. Inputting less energy to break the C–O bonds led to more heat evolution upon combustion.

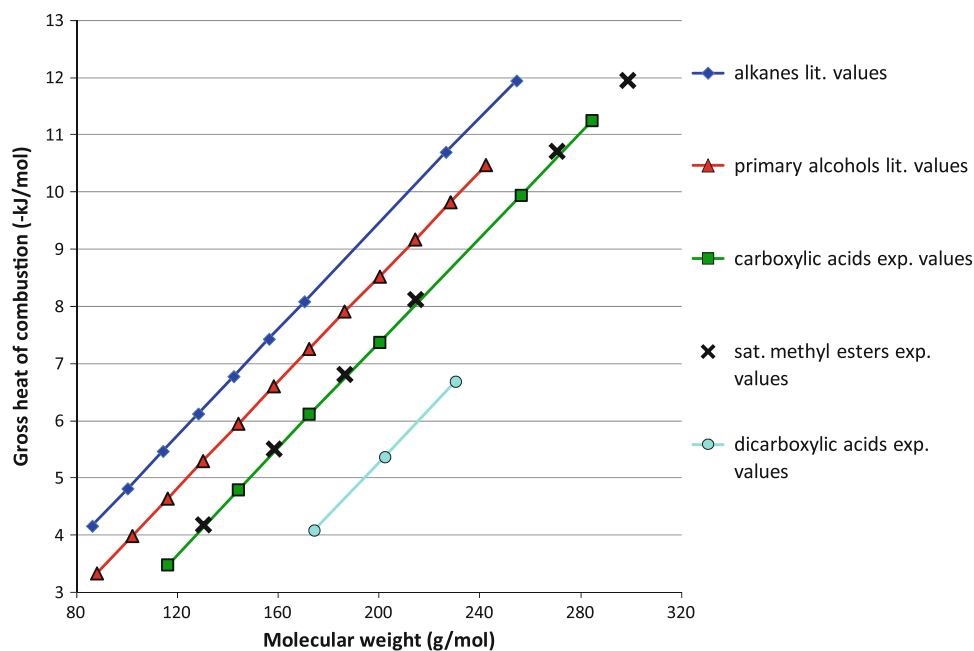
It was found that changing the ester group from a methyl to a propyl or an isopropyl group increased the heat of combustion exactly proportional to the increase in combustible content. Branching in the fatty acid chain had no effect on gross heat of combustion as a function of combustible content. This is not unexpected since branching is merely an isomeric rearrangement of the molecule and results in no real chemical differences in total bond energy or combustion products formed. Difunctional acids and esters had lower energy content per gram due to the lower combustible content and higher oxygen content of these molecules. Unsaturation within the alkyl chain lowered the heat of combustion per gram for each additional carbon–carbon double bond. Furthermore, esters synthesized from unsaturated cyclic compounds (furoic and benzoic acids) tended to have below average heat of combustion for the combustible content of these fuels. It is known that there is

Table 2 Comparison of ARL experimental H_c results (kJ/g) to other published experimental results for several methyl esters

	ARL (kJ/g)	Freedman and Bagby (kJ/g) [14]	Klopfenstein and Walker (kJ/g) [15]	Calculated from enthalpy of formation (kJ/g) [13]
Methyl hexanoate	32.17 ± 0.07	32.14 ± 0.03		32.38
Methyl octanoate	34.84 ± 0.04	34.72 ± 0.03		34.91
Methyl decanoate	36.59 ± 0.03	36.50 ± 0.04		36.67
Methyl laurate	37.91 ± 0.01	37.87 ± 0.04	36.995 ± 0.167	37.97
Methyl palmitate	39.63 ± 0.04	39.45 ± 0.04	39.543 ± 0.008	
Methyl stearate	40.06 ± 0.03	40.07 ± 0.04	40.229 ± 0.013	
Methyl oleate	39.93 ± 0.11	39.91 ± 0.15	38.890 ± 0.001	40.09
Methyl linoleate	39.65 ± 0.02	39.70 ± 0.15	38.719 ± 0.377	

Values listed in the last column are calculated from the enthalpy of formation and published in the CRC Handbook of Chemistry and Physics

Fig. 5 Gross heat of combustion of various classes of organic materials with increasing molar oxygen content



an inherent energetic stabilization associated with conjugated double bonds found in furoic acid and benzoic acid [16]. This stabilization required additional energy input to achieve combustion and, therefore, lowered energy evolution. This effect was not seen for aliphatic cyclic structures of cyclohexanoic acid and cyclohexanoate esters. This energetic effect is mirrored by the lower gross heat given off by aromatic hydrocarbons relative to aliphatic hydrocarbons, both comprised entirely of carbon and hydrogen.

To explore the effect of oxygen content on combustion energy, literature values for the gross heat of combustion (kJ/mol) of simple alkanes and primary alcohols were plotted with the experimental results for straight chain saturated fatty acids, methyl esters of straight chain saturated fatty acids and dicarboxylic acids as a function of molecular weight. As shown in Fig. 5, heat of combustion (kJ/mol) decreased as the molar content of oxygen increased. Alkanes have the highest energy density and contain no oxygen [13]. The heat of combustion of the oxygenated compounds decreased in order of increasing oxygen content: alkanes (0 mol of oxygen per mole), primary alcohols (1 mol of oxygen per mole), fatty acids and esters (2 mol of oxygen per mole) and diacids (4 mol of oxygen per mole).

Group Contribution Method for Predicting Heat of Combustion

For organic compounds containing only hydrogen, carbon and oxygen, the heat of combustion is the energy released when the compound is completely converted into CO_2 and H_2O . The heat generated from this reaction is the difference in the total enthalpy of the reactants and the products.

Stated another way, the heat of combustion is the sum of the energies of the bonds broken (an endothermic process absorbing energy) minus the sum of the energies of the bonds formed (an exothermic process releasing energy). By convention, an exothermic reaction has a negative enthalpy value but for the purposes of simplicity, all heat of combustion values in this paper are reported as positive numbers.

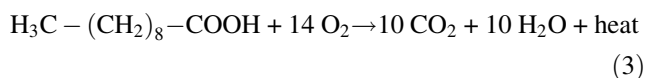
It is well known that alternative fuels and biodiesel that contain oxygenated compounds such as methyl esters and low molecular weight primary alcohols have a lower energy density than petroleum derived hydrocarbon fuels [17–19]. The fact that fatty acids and esters evolve less heat per mole than alkanes of similar weight or chain length can be understood in part by looking at the literature bond energies [13, 20, 21] in Table 3. At first, a simple approach was taken to estimate the gross heat of combustion by analysis of the bond energies of the products formed relative to the reactants consumed. Alkanes contain only C–C and C–H bonds. All fatty acids and esters include a C–O double bond (carbonyl group). Additionally, alkyl esters have two C–O single bonds and fatty acids have one C–O single bond and an O–H bond. While exact combustion mechanisms for alkyl esters found in biodiesel are not well known at this time, it is reasonable to conclude that any process that requires breaking these stronger bonds (relative to C–C and C–H bonds) would consume more energy and, therefore, reduce the overall net energy released from forming combustion products. Several published works have postulated that C–O bond scission to form methoxy radicals is one possible intermediate pathway [22–24], thus supporting this fundamental assumption. Furthermore,

Table 3 Bond energies relevant to the combustion of fatty acids and esters from literature and those calculated from the ARL group contribution method (ARL GCM)

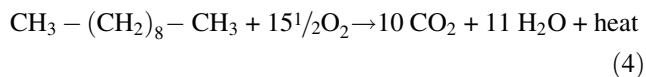
Bond	Literature bond energies (kJ/mol) [13, 20, 21]	Bond energy calculated from ARL GCM (kJ/mol)
C–C	296–385	351–356
C–H	363–435	384–393
C–O	385–464	397–451
O–H	464	464
O=O	498	498
C=C aliphatic	610	613–636
C=C aromatic	n/a	710–733
C=O	736	640–769
C=O (CO ₂)	803	803

Glaude et al. [23] presented a model that showed higher C–C and C–H bond energies (relative to hydrocarbons) when in the α or β position to the –COO– ester linkage. This assertion would reduce the gross heat evolved from combusting these functionalized materials.

Using the values in Table 3, we can compare the enthalpies of combustion for organic molecules. As an example, we calculated the heat of combustion when decanoic acid and decane are burned. Median bond energy values for the literature bond energies were chosen for these enthalpy calculations (Table 3, column 2). These values were 341, 399 and 425 kJ/mol for C–C, C–H and C–O bonds, respectively. The combustion of decanoic acid is described by Eq. 3. The bond energy enthalpy for this reaction was calculated to be 6,093 kJ/mol (35.37 kJ/g) net energy released.



The combustion of decane is described in Eq. 4. The bond energy enthalpy for this reaction was calculated to be 6,702 kJ/mol (46.77 kJ/g) net energy released.



The enthalpy change calculated from bond energies for the combustion of decanoic acid and decane shows that the hydrocarbon will yield 609 kJ/mol (11.40 kJ/g) more heat than the fatty acid. Experimental values for the combustion of decane and decanoic acid were 6,735 kJ/mol (47.38 kJ/g) and 6,114 kJ/mol (35.49 kJ/g), respectively, or 621 kJ/mol (11.89 kJ/g) more heat evolution for decane. This enthalpy calculation method was explored for the prediction of H_c for the fatty acids and esters used in this work; and it was found that published bond energies span fairly broad and overlapping ranges due to the fact that

bond energies vary with local molecular structure and composition [25, 26]. Using the selected mid-range values, we predicted heats of combustion that varied 3–5 % from experimental data for saturated fatty acids. Although the difference is not large for this limited subset of data, when this method is applied to the entire data set, the predicted values varied as much as 9.8 % from experimental results. The aromatic compounds produced the largest amount of error due to the fact that the bond energies found in the literature do not differentiate aromatic C=C bonds from aliphatic C=C bonds. Although resonance stabilization of a benzene ring has been estimated at 36 kcal/mol (150 kJ/mol) [16], it is difficult to assign a specific value to a single aromatic double bond. Furthermore, using bond energies to calculate the heat of combustion for a given molecule is not simple, partly because the combustion reaction must be balanced and then the total chemical bond energies of the reactants and products must be determined in order to estimate enthalpy differences.

Ultimately, we found it was easier and more accurate to use the GCM to predict heat of combustion than bond enthalpy calculations. The best fit to all the experimental data that could be achieved with the enthalpy calculation method had a sum of absolute error of 17.54, a sum of error² of 8.81 and an R^2 of 0.9964. When comparing these values to those for the ARL group contribution method in the last column of Table 4, it is apparent that the group contribution method led to better prediction of the experimental results with a sum of absolute error of 9.65, a sum of error² of 3.91 and an R^2 of 0.9982.

The GCM was used to calculate the theoretical heat of combustion (Q_c) for each structure. Initial heat values for the structural components within the model were taken from the Walters model [10] and are shown in column 2 of Table 4. Structures that were not included in the Walters model were estimated from the structures that were included. See the footnotes for Table 4 for the details of these estimations. Sagadeev et al. [27] published similar modeling of hydrocarbon fuels and derived slightly different heat values for methyl (–CH₃) and methylene (–CH₂–) structures. The Sagadeev model only provided molar heat values for methyl and methylene because their work was exclusively on hydrocarbons. The other structures in Table 4 were assigned the same estimated values from the Walters model to complete the Sagadeev model (column 3 of Table 4).

The accuracy of the Walters and Sagadeev models to predict the heat of combustion for the compounds in this study was evaluated by calculating the expected heat of combustion for each compound using the methodology described in the experimental section. Each calculated value for the heat of combustion was compared to the average experimental heat of combustion for a given

Table 4 Molar heat values, H_i (kJ/mol), for several group contribution methods and statistical data to quantify the accuracy of those values to predict the gross heat of combustion for the compounds in this study

Group	Walters [10]	Sagadeev [27]	ARL group contribution model			
			Saturated FA/FAME only	Add unsaturated FA and esters, diacids, diesters	Add branched FA, branched methyl esters, propyl and isopropyl esters	Add aliphatic and aromatic rings, hydro-carbons
CH ₃	775	779.9 ^f				
CH ₃ (–C–)			770	770	770	770
CH ₃ (–O–)			749	748	749	749
CH ₃ (dimethyl esters)				638	646	646
CH ₂	670	652.3 ^f				
CH ₂ (–C–)			647	647	647	647
CH ₂ (–O–)				550	610	610
CH	518	518				
CH (–C–)					535	524.2
CH (–O–)				455	482	481.8
C=C	781	781				
HC=CH	1,161 ^a	1,161 ^a		1,136	1,140	1,140
H	190	190				
COO ester	112	112	112	120	112	112
COOH	302 ^b	302 ^b	128	129	129	139.9
COOH diacids				104	104	103.6
Cyclohexane (+1 bond)	3,868 ^c	3,868 ^c				3,740
Furan (+1 bond)	2,000 ^d	2,000 ^d				1,828
Benzene	3,320 ^e	3,320 ^e				3,130
Benzene (+1 bond)	3,130	3,130				3,091
Benzene (+2 bonds)	2,871	2,871				2,972
$\sum \text{error} $	98.41	61.59	1.024	3.136	6.875	9.645
$\sum \text{error}^2$	165.65	81.78	0.155	0.709	2.052	3.914
m (slope of best fit line)	1.0391	1.0231	0.9996	0.9998	1.0008	1.0010
R^2	0.9820	0.9800	0.9986	0.9990	0.9978	0.9982

^a For the compounds in this paper HC=CH was a more logical grouping than adjusting values for C=C and H independently. H_i value was the sum of C=C and two times H

^b Carboxylic acid was not included in the Walters group contribution method. H_i value was the sum of an ester plus hydrogen

^c Cyclohexane with one substituent was not included in the Walters model. Starting H_i value was calculated by five times CH₂ plus CH

^d Furan with one substituent was not included in the Walters model. Starting H_i value was calculated by two times carbon–carbon double bond plus three times hydrogen plus oxygen with two single bonds (–132 kJ/mol)

^e Benzene was not included in the Walters model. Starting H_i value was calculated by addition of benzene (+1 bond) plus hydrogen

^f The Sagadeev model provided different values for CH₃ and CH₂ only. All other structures were given the Walters values or estimated values calculated by the authors

compound. The error of each theoretical prediction was calculated. The predictive quality of the model was determined by the sum of the absolute error ($\sum |\text{error}|$) for all molecules within the data set, as well as the sum of the squared error ($\sum \text{error}^2$) for the data set. Additionally, the theoretical heat of combustion calculated for each material was plotted as a function of the experimental heat of combustion. The slope, m , of the best fit line through this plot (with the y -intercept set at 0) and the R^2 value for each set of H_i values are reported in Table 4. A perfectly

predictive model would generate a best fit line with slope and R^2 equal to one.

Table 4 and Figure 6 show that the Walters model had significant error relative to the experimental results for fatty acids and fatty acid esters. This model was developed from the combustion of a diverse group of polymers encompassing a large array of structures. Using the Sagadeev values for methyl and methylene groups improved the predictive model only slightly. The Sagadeev model focused on hydrocarbons with no oxygen in the molecules

and, thus, was not optimized for fatty acids and esters. Despite this, the error using these group contribution methods was no more than that of the bond energy/enthalpy method. Yet, using the GCM was far simpler than the bond energy/enthalpy method to calculate the heat of combustion and, as a result, the GCM was used for the work presented here.

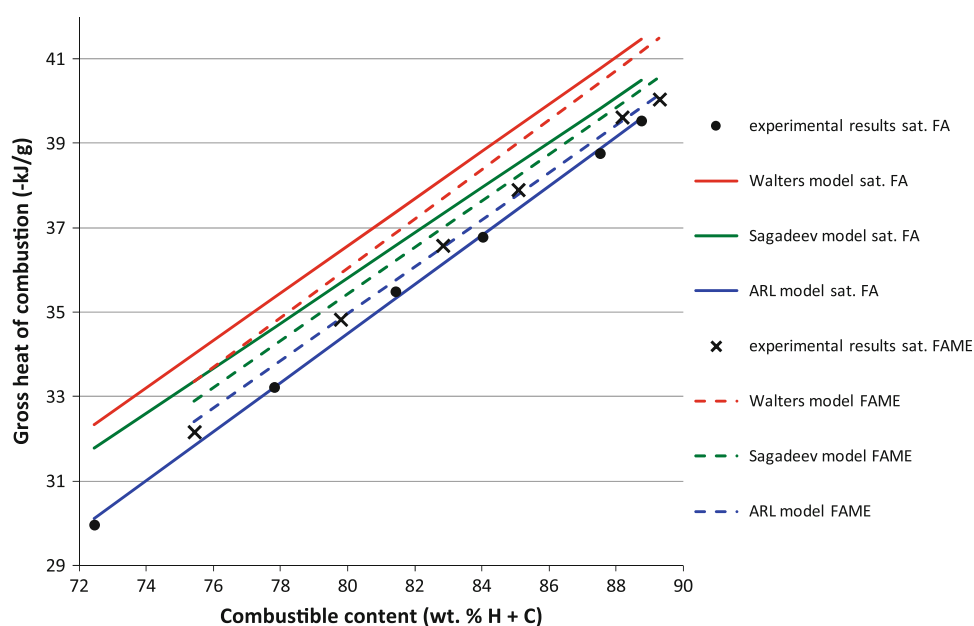
To enable the GCM to predict heats of combustion of fatty acids and alkyl esters to an extremely high degree of accuracy, including subtle differences for unsaturation, aromatic stabilization, etc., we modified the values of the molar heat values assigned to the various functional groups to optimize the results for our data set, using the existing group contribution models as starting points. Rough estimations for furoic acid, cyclohexanoic acid, benzoic acid and related esters were calculated from the Walters values as starting points. These estimated values were then optimized to best fit the experimental data.

In developing the ARL model for predicting the heat of combustion of FA and FAME, the methyl and methylene molar heat values of the Walters and Sagadeev models were compared. The methylene group was the most frequently occurring group in the set of compounds in this study followed by the methyl group. It was found that better predictions for FA and FAME were obtained when using the lower of the published values for each group. The correlation to experimental results became even better when the molar heat values were lowered even more than either of the two published models. In order to remain within reasonable limits of the previously published values, the molar heat values for methyl and methylene groups bonded to carbon (i.e., not attached to the ester group) were locked within 5 kJ/mol (<1 % difference) of the published

values. The CH_3 ($-\text{C}-$) and CH_2 ($-\text{C}-$) were set at 770 and 647 kJ/mol, respectively. By plotting % error of the predicted heat of combustion as a function of combustible content for each set of compounds, it was easy to identify the structures that had the most error in their molar heat values. Adjustments to the molar heat value of the most frequently occurring molecular group ($-\text{CH}_2-$) provided the largest impact on the total error for the data set. Adjustments were then made to the next most frequently occurring molecular group and so on in an iterative process until no further optimization could be made for that set of compounds. This procedure was first applied to the saturated FA and FAME molecule set because these are the simplest compounds to model and they are abundant in biodiesel [8, 9, 28–30]. Upon optimization of the model for that set, the model was modified to take into account unsaturation and diacids. Unsaturated fatty acid esters are common components of biodiesel because of their high prevalence in plant oils [29, 30]. The model was then optimized to account for the effect of larger ester groups and branched fatty acids and the methyl esters of branched fatty acids. Branched acids/esters have much lower melting temperatures, making these biodiesels especially useful in colder temperatures. Lastly, the model was optimized to account for cyclic and aromatic compounds. Although these types of molecules are not abundant in typical biodiesel, widespread research in lignin and cellulose as potential biodiesel sources is expanding and, thus, warranted inclusion in this study.

During the process of optimizing contributions for groups found in saturated FA and FAME, it became apparent that there were more logical chemical groups for our data set. It was found that better predictions could be

Fig. 6 Experimental H_c for straight chain saturated FA/FAME compared to values predicted by various models



made by distinguishing the methyl ester groups from the methyl groups in the terminal fatty acid position or branches of the fatty acid portion of the ester. Although the alkyl methyl group was maintained at values near that of the Walters and Sagadeev models, the methyl group bonded to oxygen (ester group) was considerably lower (749 kJ/mol) due to the increased bond strength of the C–O bond relative to the C–C bond of the alkyl methyl group. Assigning independent values for –COOH, as opposed to the sum of –COO– plus hydrogen made the model more adaptable to our experimental results. There was no advantage to having a separate value for –H as it became difficult to find a single value that would best satisfy the heat of combustion of carboxylic acids and unsaturated molecules. In fact, the calculated value of 302 kJ/mol for the carboxylic acid group (–COOH) from the Walters model as the sum of the ester (–COO–) plus hydrogen was the largest source of model error. Our results show that a much lower value (128 kJ/mol) is more appropriate for the small data set of saturated FA/FAME. These differences indicate that the adjacent electronic environment of the functional group affects the heat of combustion through differences in bond energies of C–C and C–O bonds as previously discussed. On the other hand, no modifications were necessary to optimize the contribution of the ester group once all the data were included in the model. Overall, Table 4 and Figure 6 show a very high level of matching between the experimental and theoretical results when optimizing the group contributions for saturated FA/FAME. In fact, the level of matching is better than that of the Walters or Sagadeev models.

Upon modifying the model to account for unsaturation and diacids, it again became apparent that a HC=CH group, as opposed to C=C plus 2 hydrogens, would be more useful for this molecule set. The initial H_i value we used was the sum of the Walters H_i values for C=C and 2 times H. In our model, the assigned H_i value for HC=CH (1,140 kJ/mol) relative to the Walters model (1,161 kJ/mol) is a fairly small change, but significant. The ARL model H_i value for the –COOH group in diacids was 25 kJ/mol lower than the value for the same group in a mono-functional carboxylic acid. This is likely due to hydrogen bonding stabilization of the diacid structure, which has been found to be very similar to this value [31]. No other group contribution modifications were required to optimize the results, indicating high consistency among sample sets.

Inclusion of branched fatty acids and larger ester groups resulted in some changes to the model. First, a value for the methine group (–CH–) needed to be determined. The Walters model uses 518 kJ/mol for this group contribution. In our sample set, the methine group can be bonded to three carbon atoms (in the case of branched fatty acids) or bonded to two carbon atoms and one oxygen atom (in the case of isopropyl esters). In the former case, the optimized value was 524.2 kJ/mol while in the latter case it was 481.8 kJ/mol. This again shows that groups bonded to oxygen have lower heats of combustion. Note, if we used a single value for the methine group, it would be close to that used in the Walters/Sagadeev models. Secondly, methylene groups (–CH₂–) needed to be broken out into groups bonded to two carbon atoms and groups bonded to one carbon and one oxygen. Again, the group bonded to

Fig. 7 Literature H_c and experimental H_c of hydrocarbons compared to the values predicted by various models

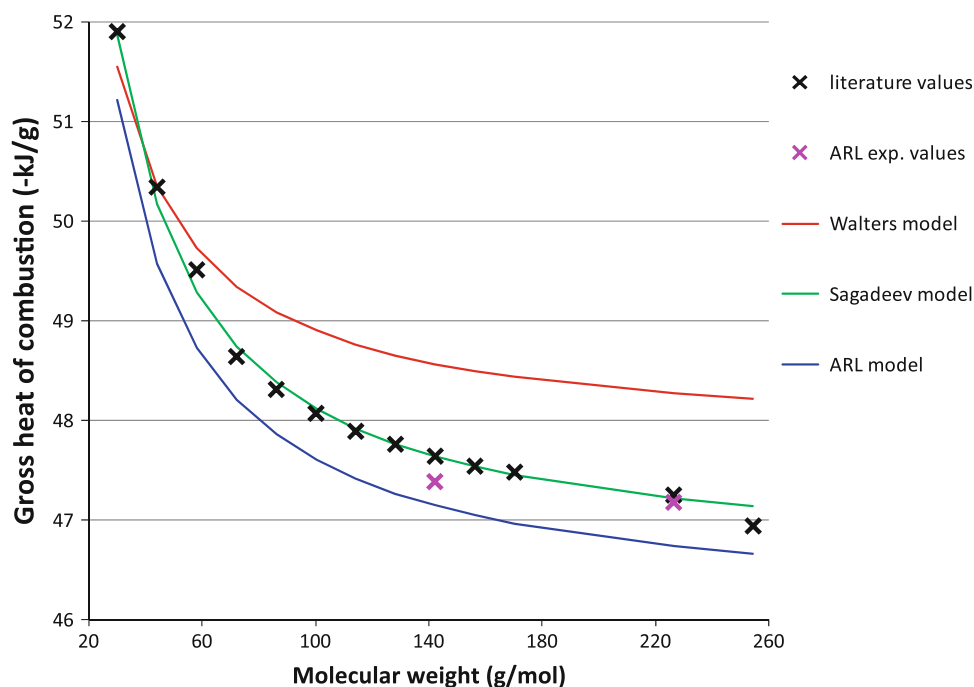


Table 5 Experimental H_c data (kJ/g) for all compounds in this study and the heats of combustion calculated from the ARL, Walters and Sagadeev models

	ARL experimental results		ARL GCM		Walters		Sagadeev	
	H_c (kJ/g)	% error	Predicted Q_c (kJ/g)	% error	Predicted Q_c (kJ/g)	% error	Predicted Q_c (kJ/g)	% error
Hexanoic acid	29.97	0.38	30.11	0.49	32.34	7.94	31.78	6.05
Octanoic acid	33.22	0.12	33.23	0.01	35.34	6.38	34.64	4.27
Decanoic acid	35.49	1.07	35.33	0.46	37.37	5.28	36.57	3.05
Dodecanoic acid	36.78	0.08	36.84	0.16	38.82	5.55	37.96	3.21
Palmitic acid	38.76	0.43	38.87	0.28	40.78	5.20	39.83	2.76
Stearic acid	39.54	0.03	39.59	0.13	41.47	4.89	40.49	2.41
Oleic acid, 90 %	39.51	0.13	39.33	0.48	41.13	4.09	40.27	1.92
Linoleic acid, 95 %	39.12	0.08	39.06	0.15	40.79	4.27	40.05	2.38
2-Propylpentanoic acid	33.23	0.23	33.23	0.01	35.02	5.40	34.60	4.12
2-Butyloctanoic acid	36.92	0.11	36.84	0.20	38.59	4.53	37.93	2.75
2-Hexyldecanoic acid	39.25	0.02	38.87	0.95	40.60	3.44	39.81	1.42
2-Methyloctadecanoic acid	39.52	1.74	39.90	0.96	41.61	5.29	40.75	3.12
Suberic acid	23.48	0.25	23.47	0.00	26.55	13.07	25.94	10.48
Sebacic acid	26.55	1.07	26.62	0.24	29.49	11.05	28.79	8.41
Dodecanedioic acid	29.05	0.08	28.99	0.19	31.72	9.18	30.95	6.53
Cyclohexanoic acid	30.34	0.13	30.27	0.22	32.54	7.24	32.54	7.24
2-Furoic acid	17.93	1.77	17.56	2.06	20.54	14.57	20.54	14.57
Benzoic acid	26.46	0.02	26.46	0.00	28.10	6.22	28.10	6.22
Methyl hexanoate	32.17	0.22	32.41	0.72	33.35	3.66	32.88	2.20
Methyl octanoate	34.84	0.12	34.84	0.00	35.91	3.06	35.30	1.32
Methyl decanoate	36.59	0.08	36.54	0.14	37.69	3.01	36.99	1.08
Methyl dodecanoate	37.91	0.01	37.79	0.31	39.01	2.91	38.23	0.85
Methyl palmitate	39.63	0.09	39.52	0.27	40.83	3.03	39.95	0.80
Methyl stearate	40.06	0.07	40.14	0.22	41.48	3.56	40.56	1.27
Methyl 5-cis dodecenoate	37.44	0.05	37.43	0.03	38.54	2.94	37.92	1.28
Methyl oleate	39.93	0.27	39.90	0.09	41.16	3.07	40.36	1.05
Methyl linoleate	39.65	0.06	39.65	0.00	40.83	2.99	40.14	1.25
Methyl 2-propylpentanoate	34.15	0.11	34.84	2.03	35.61	4.29	35.26	3.25
Methyl 2-butyloctanoate	37.57	0.09	37.80	0.60	38.79	3.25	38.20	1.68
Methyl 2-hexyldecanoate	39.72	0.08	39.52	0.50	40.65	2.34	39.92	0.50
Methyl 2-methylstearate	40.59	0.07	40.41	0.44	41.61	2.52	40.81	0.54
<i>n</i> -Propyl hexanoate	34.58	0.27	34.74	0.47	35.91	3.85	35.30	2.09
Isopropyl hexanoate	34.51	0.12	34.71	0.58	35.61	3.20	35.26	2.17
<i>n</i> -Propyl octanoate	36.51	0.13	36.45	0.16	37.69	3.24	36.99	1.30
Isopropyl octanoate	36.46	0.49	36.43	0.10	37.44	2.68	36.95	1.33
<i>n</i> -Propyl decanoate	37.76	0.42	37.72	0.10	39.01	3.32	38.23	1.25
Isopropyl decanoate	37.73	0.51	37.70	0.10	38.79	2.80	38.20	1.24
<i>n</i> -Propyl dodecanoate	38.87	0.09	38.69	0.46	40.03	2.97	39.19	0.82
Isopropyl dodecanoate	38.67	0.11	38.67	0.00	39.83	3.00	39.16	1.27
<i>n</i> -Propyl palmitate	40.21	0.14	40.09	0.29	41.48	3.17	40.56	0.89
Isopropyl palmitate	40.08	0.08	40.07	0.01	41.32	3.11	40.54	1.16
<i>n</i> -Propyl stearate	40.60	0.55	40.61	0.02	42.02	3.50	41.07	1.17
Isopropyl stearate	40.39	0.13	40.59	0.49	41.88	3.67	41.05	1.63
<i>n</i> -Propyl oleate	40.39	0.56	40.39	0.01	41.73	3.32	40.89	1.23
Isopropyl oleate	40.28	0.24	40.37	0.23	41.58	3.25	40.87	1.46

Table 5 continued

	ARL experimental results		ARL GCM		Walters		Sagadeev	
	H_c (kJ/g)	% error	Predicted Q_c (kJ/g)	% error	Predicted Q_c (kJ/g)	% error	Predicted Q_c (kJ/g)	% error
<i>n</i> -Propyl linoleate	39.83	0.05	40.16	0.84	41.44	4.04	40.70	2.19
Isopropyl linoleate	39.69	0.08	40.15	1.16	41.29	4.04	40.68	2.50
Dimethyl suberate	26.69	0.18	26.69	0.00	28.65	7.34	28.17	5.55
Dimethyl sebacate	28.79	0.54	29.06	0.95	30.98	7.61	30.40	5.62
Dimethyl dodecanedioate	31.31	0.10	30.91	1.27	32.80	4.76	32.15	2.69
Dipropyl suberate	31.19	0.09	31.58	1.28	32.80	5.18	32.15	3.10
Diisopropyl suberate	31.55	0.03	31.54	0.03	32.44	2.80	32.10	1.74
Diisopropyl sebacate	32.84	0.11	32.97	0.40	33.94	3.34	33.51	2.04
Methyl cyclohexanoate	32.32	0.22	32.36	0.11	33.44	3.46	33.47	3.57
<i>n</i> -Propyl cyclohexanoate	34.49	0.12	34.53	0.11	35.80	3.79	35.62	3.27
Isopropyl cyclohexanoate	34.51	0.12	34.50	0.01	35.52	2.95	35.58	3.12
Methyl furoate	21.32	0.07	21.32	0.01	22.89	7.35	22.93	7.54
Isopropyl furoate	25.39	0.10	25.70	1.21	27.11	6.79	27.18	7.04
Methyl benzoate	28.92	0.27	29.03	0.38	29.50	2.03	29.54	2.15
<i>n</i> -Propyl benzoate	31.92	0.05	31.85	0.22	32.62	2.20	32.44	1.62
Isopropyl benzoate	31.86	0.10	31.82	0.12	32.34	1.51	32.40	1.70
Decane	47.38	0.21	47.20	0.39	48.57	2.49	47.64	0.54
<i>n</i> -Hexadecane (cetane)	47.18	0.02	46.80	0.79	48.27	2.31	47.22	0.09
Benzene	40.08	0.30	40.07	0.01	42.50	6.06	42.50	6.06
Toluene	40.69	1.35	41.90	3.00	42.38	4.17	42.44	4.30
Xylene	42.50	0.07	42.50	0.01	41.64	2.02	41.74	1.81

oxygen was lower (610 kJ/mol) than the methylene bonded to two carbons (647 kJ/mol), which, as you will recall, was held at this value because of the accuracy of the Sagadeev model for alkanes.

Lastly, addition of cyclic aliphatic (cyclohexane with one substituent) and aromatic ringed molecules (2-furoic and benzoic acid with one substituent) and hydrocarbons completed the data set. This last leg of the data included benzene and benzene with methyl substituents (i.e., toluene and xylene). Aromatic stabilization lowered the gross heat of combustion relative to that which would be predicted for a linear, non-conjugated arrangement. This result is due to the higher amount of energy needed to break these rings apart than non-conjugated double bonds. The more energy needed to break apart the chemical bonds of the reactants will result in a lower gross heat released upon formation of combustion products. Per the Walters model, benzene group contributions were dependent on the number of substituent bonds connected to the benzene ring. For pure benzene, our model had a lower contribution (3,130 kJ/mol) relative to that predicted from the Walters model (3,320 kJ/mol), based upon benzene with one substituent plus hydrogen. Considering the Walters model did not actually account for this molecule unit itself, this difference is likely an artifact of the Walters model, not our model.

Similarly, our model had a lower value (3,091 kJ/mol) versus that of the Walters model (3,130 kJ/mol) for benzene with one substituent. As shown before, the electronic structure clearly affects the bond energy and, consequently, heat of combustion. Our benzene structures were bonded to carboxylic acid and ester functional groups, while the Walters model accounted for benzene bonded to many different chemical structures, thus accounting for the discrepancy. Although our result (2,972 kJ/mol) for benzene plus two substituents is higher than that for the Walters model (2,871 kJ/mol), this is again likely due to the variety of benzene structures used in the Walters model. Furan plus one bond was also optimized for our model (1,828 kJ/mol) and again found to be lower than the Walters model estimation (2,000 kJ/mol). These results are fairly similar, considering the furan with one substituent was not included in the Walters model. The starting H_i value for the Walters furan group was calculated as two times the carbon–carbon double bond plus 3 times hydrogen plus oxygen with two single bonds (−132 kJ/mol). Cyclohexane with one substituent was not included in the Walters model. The starting H_i value (3,868 kJ/mol) was calculated by five times CH_2 plus CH . This was slightly higher than our optimized result of 3,740 kJ/mol and likely due to artifacts in the Walters model for calculating this particular structure. The

carboxylic acid group contribution slightly increased to 139.9 kJ/mol, but was still far lower than the Walters number.

A fine tuning of the model including all data was done to provide the best possible fit to the experimental data. These values are presented in the last column in Table 4. The sum of the absolute error and the sum of the squared error steadily increases for each iteration of the ARL model but that is expected due to the successively larger data sets used in each iteration, whereas R^2 remained fairly constant with each iteration showing that each version did an excellent job of predicting the heat of combustion for its respective data set.

To compare the quality of the ARL model to those published by Walters and Sagadeev, a plot of all linear, straight chain, saturated FA/FAME experimental data and the values predicted by each model is presented in Fig. 6. This plot shows that the Walters model has the most error in predicting the heat of combustion of FA/FAME as expected since it is derived from the polymer heat of the combustion results. The Sagadeev model is closer to the actual experimental values than the Walters model, as expected since this model fine-tuned the methyl and methylene group values for small molecules. The ARL model does the best job predicting the heat of combustion for FA/FAME than the other models discussed in this paper. This was an expected result as the ARL model was developed to fit the FA/FAME experimental data and, as such, reflects energetic differences between carbon–oxygen bonds and carbon–carbon bonds better than the other models.

The three models were compared in prediction of the heat of combustion of saturated aliphatic hydrocarbons and graphed in Fig. 7. The literature hydrocarbon values were obtained from the CRC Handbook of Chemistry and Physics, 92nd edition. As expected, the Sagadeev model, developed from the combustion data of hydrocarbons, was the best fit to the literature and experimental data for H_c of hydrocarbons. The ARL experimental results for decane and hexadecane fall in line fairly well with the literature values and the Sagadeev model. The ARL model is somewhat inaccurate for the prediction of hydrocarbon heat of combustion but more accurate than the Walters model for hydrocarbons of five or more carbon atoms in length. This is further confirmation that local electronic structure affects heat of combustion. Thus, to obtain the most accurate prediction of heat of combustion, a model derived from compounds related to the compound(s) of interest should be used. Furthermore, even with our model, we would recommend using the simplest model that uses the functional groups of interest to the compound of interest. In other words, if it was desired to predict the heat

of combustion of a particular saturated FAME, we would recommend using the group contribution numbers from column 4 of Table 4. If instead, the heat of combustion for a branched FAME is desired, column 6 of Table 4 should be used. Table 5 reports all ARL experimental results along with the predicted values calculated from each of the three models discussed here.

Bond Energy Calculations

After determining the optimized molar heat values for the chemical groups in the ARL GCM from the experimental data, the apparent bond energies within each group were calculated and presented in column 3 of Table 3. Ranges were provided in column 3 as we found some variation in the apparent bond energies depending on which group was used to calculate them.

The bond energy calculations were done by solving the chemical combustion equation for each group's bond enthalpy. The chemical group from the model combined with oxygen yields some amount of carbon dioxide, water and heat equivalent to the molar heat value assigned in the model. The bond energies of O_2 , H_2O and CO_2 were taken from the literature values in Table 3. Once the bond enthalpy of each group was calculated, algebraic equations were written setting the sum of bond energies in each group equal to the total bond enthalpy determined from the combustion equation. For example, the methyl group ($-CH_3$) contains three C–H bonds and one half of a C–C bond. The bond enthalpy for the methyl group calculated from the ARL molar heat value and the combustion equation for the methyl group told us that three C–H bonds and one half of a C–C bond equals 1,356.5 kJ/mol. By deriving an algebraic relationship of bonds and bond enthalpy for each group in the ARL model, values for individual bond energies were calculated and reported in column 3 of Table 3. These calculated bond energies are more appropriate for the FA/FAME compounds in this study or similar compounds than the broader ranges published in various literature sources. The various errors between the bond energy predicted heats of combustion and the experimental values were calculated. The results showed that the error in the heats of combustion for fatty acids/esters calculated from these bond energies was low ($\sum|\text{error}| = 17.5$, $\sum\text{error}^2 = 8.8$, $R^2 = 0.9964$), but higher than that determined for the group contribution method. However, the error in the heat of combustion for these predicted bond energies was significantly lower than that obtained using the lowest, highest or mid-point of the literature bond energy ranges where the error had the following range: $\sum|\text{error}| = 31\text{--}431$ ($\sum\text{error}^2 = 47\text{--}2864$, $R^2 = 0.978\text{--}0.911$, where the mid-point value tended to give the better prediction relative to the lowest or highest bond energy values.

Conclusions

An increase in combustible content (total wt% of carbon and hydrogen) in biodiesel esters produced higher gross heat of combustion (kJ/g). Heat of combustion (kJ/g) decreased as the molar content of oxygen increased. Alkyl esters have lower gross heats of combustion than hydrocarbons of similar molecular weight or number of carbon atoms. This is due to higher bond energies of the C–O single bond in the ester group and the higher bond energies of the C–C and C–H bonds adjacent to the –COO– ester group relative to C–C and C–H bonds in hydrocarbons. These higher energy bonds require more energy to break before yielding energy upon the formation of combustion products. Diacids and diesters with greater degrees of hydrogen bonding than acids and esters with single functionality have lower gross heat of combustion. Aromatic stabilization of molecules also leads to lower gross heat of combustion. None of the fatty acids or synthesized esters produced enough energy upon combustion with oxygen to meet the JP-8 specification. The results show that a FAME of more than 40 carbon atoms would be necessary to achieve that property, but fatty acids of that length are rare and are not useable in liquid fuel applications because of their high melting temperature. While biodiesel may meet some of the energy needs of the civilian population, oxygenated fuels prove to be lacking sufficient energy density to satisfy military requirements. The authors were able to modify existing group contribution methods to predict more accurately the gross heat of combustion of fatty acids and esters and account for various molecular effects including unsaturation, branching, cyclization, and aromaticity. This model is better than published models for predicting the heat of combustion of fatty acids and fatty acid esters with 59 of 66 compounds in this study having <1 % error in their predicted values. The Walters and Sagadeev models had as much as 15 % error in predicting experimental heat of combustion for some diacids/diesters and aromatic acids and esters. In addition, the ARL GCM was able to accurately predict the organic bond energies for these compounds.

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