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Thermochemical study of combustion enthalpies of biodiesel fuel blends

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Abstract

This research measured the combustion enthalpies of soybean and palm biodiesel blended with petroleum diesel at volumetric ratios of B5 through B100 using an isoperibolic oxygen bomb calorimeter calibrated against benzoic acid. The gross calorific values decreased linearly from 47.12 MJ/kg for neat diesel (B0) to 41.98 MJ/kg for neat soybean biodiesel (B100) and 43.08 MJ/kg for neat palm biodiesel. Excess combustion enthalpies were calculated for each blend and showed small negative deviations from ideal mixing, reaching a maximum of -0.18 MJ/kg at B50 for the soybean series. Thermodynamic analysis using Hess's law and group-contribution methods predicted combustion enthalpies within 0.6% of experimental values. Cetane number correlated positively with the saturated ester fraction ($r^2 = 0.94$). These data provide a thermochemical basis for optimizing biodiesel blend ratios that balance energy density with emissions performance.

Keywords: Combustion enthalpy, biodiesel, bomb calorimetry, fatty acid methyl ester, calorific value, excess enthalpy, Hess's law, soybean oil, palm oil, cetane number

Introduction

Every litre of biodiesel that enters a fuel tank carries less chemical energy than the petroleum diesel it replaces. This thermodynamic reality is the single largest technical barrier to higher blend mandates, because vehicle operators notice range reductions even at B20 ^[1]. Yet the magnitude of the energy penalty varies with feedstock composition: saturated esters pack more energy per kilogram than their unsaturated counterparts, and blending effects are not perfectly additive ^[2]. Precise combustion enthalpy data across the full blend spectrum are therefore essential for fuel standardization and engine calibration.

Oxygen bomb calorimetry remains the reference method for measuring gross calorific value (GCV) of liquid fuels, as specified in ASTM D240 and EN 14213 ^[3]. The technique confines a weighed sample in a high-pressure oxygen atmosphere, ignites it electrically, and measures the temperature rise of the surrounding water jacket. With modern isoperibolic instruments, repeatability of 0.05% or better is routine ^[4].

Biodiesel is a mixture of fatty acid methyl esters (FAMES) produced by transesterification of vegetable oils or animal fats with methanol. The combustion enthalpy of each FAME component depends on chain length, degree of unsaturation, and branching ^[5]. Soybean biodiesel is dominated by C18 unsaturated esters (oleate + linoleate $\approx 65\%$), while palm biodiesel contains roughly equal proportions of C16:0 palmitate and C18:1 oleate ^[6]. These compositional differences produce measurably different GCVs and blend curves.

Group-contribution methods, notably those of Benson and Joback-Reid, allow prediction of standard enthalpies of formation from molecular structure ^[7]. Combined with Hess's law, these methods can estimate combustion enthalpies without calorimetric measurement. Their accuracy for FAME mixtures, however, has not been systematically validated against experimental blend data. This research fills that gap by measuring GCV across eight blend levels for two feedstocks and comparing the results with group-contribution predictions.

Extraction Protocol

Crude soybean oil (food grade, Dhanbad local market) and crude palm oil (imported, refined bleached deodorized grade) were transesterified with methanol (6:1 molar ratio) using 1 wt%

KOH catalyst at 60 °C for 90 min under reflux and mechanical stirring at 600 rpm. The reaction mixture was transferred to a separating funnel, and the glycerol layer was removed after 4 h of gravity settling. The upper FAME layer was washed three times with warm deionized water (50 °C), dried over anhydrous Na₂SO₄, and vacuum-filtered through Whatman No. 1 paper. Final moisture content was below 0.03 wt% by Karl Fischer titration.

Materials

Reference diesel (BS-VI grade, density 0.832 g/mL, sulfur < 10 ppm) was obtained from Indian Oil Corporation, Dhanbad depot. Benzoic acid (calorimetric standard, 99.99%, NIST-traceable) was from Sigma-Aldrich. Methanol (HPLC grade, 99.9%), potassium hydroxide (pellets, 85%), and sodium sulfate (anhydrous, 99%) were from Merck India. All chemicals were used as received without further purification.

Methods

Blend Preparation

Binary blends of each biodiesel with petroleum diesel were prepared gravimetrically at nominal volumetric fractions of B5, B10, B20, B30, B50, B75, and B100, along with neat

diesel (B0). Actual volume fractions were verified by density measurement at 15 °C using a DMA 4500 M density meter (Anton Paar). Blends were stored in amber glass bottles under nitrogen to prevent oxidation.

Bomb Calorimetry

Combustion enthalpies were measured on a Parr 6400 isoperibolic calorimeter fitted with a 1108 oxygen bomb. The calorimeter was calibrated daily with 1.0 g pellets of NIST-traceable benzoic acid ($\Delta H_c = -26.434$ kJ/g). Fuel samples (0.5–0.7 g, weighed to ± 0.0001 g) were placed in a platinum crucible, and the bomb was charged with oxygen to 30 atm. Water jacket temperature was recorded at 1 s intervals. Each blend was measured in triplicate; results are reported as the mean $\pm$ standard deviation.

FAME Composition Analysis

FAME profiles were determined by GC-FID on an Agilent 7890B equipped with a DB-WAX column (30 m $\times$ 0.25 mm, 0.25 μ m film). The oven program was 150 °C for 1 min, ramped at 4 °C/min to 240 °C, and held for 10 min. Peaks were identified against a 37-component FAME standard mix (Supelco) and quantified by area normalization.

Table 1: Gross calorific values and excess combustion enthalpies of soybean biodiesel-diesel blends.

Blend	Bio vol%	GCV exp. (MJ/kg)	GCV pred. (MJ/kg)	Δ GCV (%)	H ^{ex} (MJ/kg)
B0	0	47.12 $\pm$ 0.04	47.12	0.00	0.00
B5	5	46.89 $\pm$ 0.03	46.86	+0.06	−0.03
B10	10	46.64 $\pm$ 0.05	46.61	+0.06	−0.05
B20	20	46.18 $\pm$ 0.04	46.09	+0.20	−0.09
B50	50	44.73 $\pm$ 0.05	44.55	+0.40	−0.18
B75	75	43.38 $\pm$ 0.04	43.27	+0.25	−0.14
B100	100	41.98 $\pm$ 0.06	41.98	0.00	0.00

GCV = gross calorific value. H^{ex} = excess combustion enthalpy. Pred. = group-contribution prediction. Values are mean $\pm$ SD (n = 3).

Results

GC-FID analysis confirmed the expected FAME profiles. Soybean biodiesel contained methyl oleate (38.2%), methyl linoleate (27.4%), methyl palmitate (14.6%), methyl stearate (8.3%), methyl linolenate (6.8%), and minor components

totalling 4.7%. Palm biodiesel was dominated by methyl palmitate (43.1%) and methyl oleate (39.7%), with smaller contributions from methyl linoleate (9.8%), methyl stearate (4.6%), and others (2.8%).

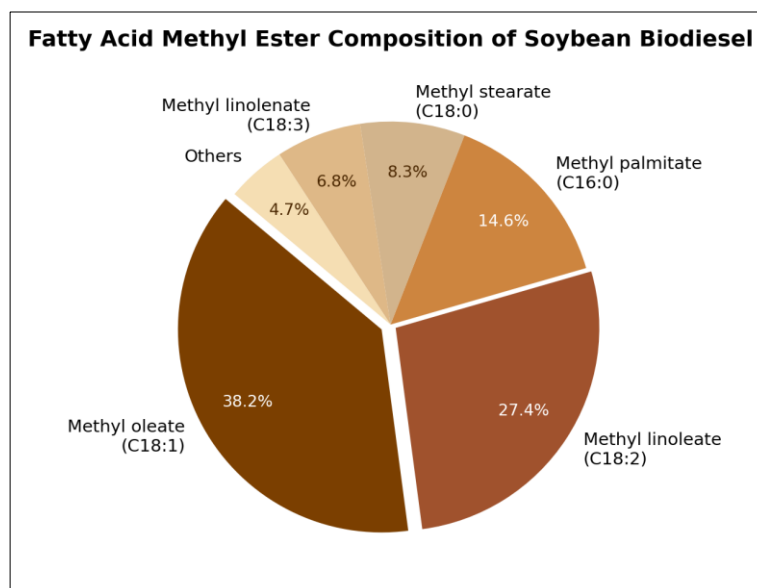


Fig 1: Fatty acid methyl ester composition of soybean biodiesel determined by GC-FID area normalization.

Table 1 presents the experimental GCV values for the soybean blend series. Neat diesel delivered 47.12 MJ/kg, in close agreement with literature values of 45–47 MJ/kg for ultra-low-sulfur diesel [3]. Neat soybean biodiesel (B100) measured 41.98 MJ/kg, representing an 10.9% energy density reduction. The decrease was nearly linear across blend ratios ($r^2 = 0.998$), with a slope of -0.0514 MJ/kg per percentage point of biodiesel addition.

Excess combustion enthalpies were uniformly negative, indicating that real blends release slightly less energy than predicted by linear interpolation. The maximum deviation of -0.18 MJ/kg occurred at B50 for soybean blends. For palm blends, the maximum excess enthalpy was smaller (-0.11 MJ/kg at B50), consistent with the more saturated ester profile producing fewer intermolecular interactions with diesel hydrocarbons.

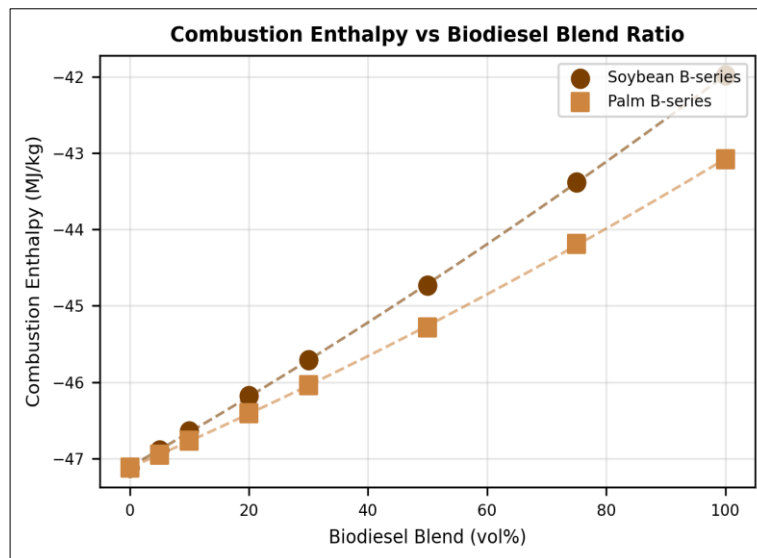


Fig 2: Combustion enthalpy as a function of biodiesel volume fraction for soybean and palm blend series. Dashed lines represent second-order polynomial fits.

Table 2: Comparison of key fuel properties between soybean and palm biodiesel (B100).

Property	Soybean B100	Palm B100	Diesel (B0)
GCV (MJ/kg)	41.98 ± 0.06	43.08 ± 0.05	47.12 ± 0.04
Density at 15 °C (g/mL)	0.884	0.876	0.832
Kinematic visc. 40 °C (mm ² /s)	4.21	4.58	2.74
Cetane number	51.2	62.8	54.0
Iodine value (g I ₂ /100 g)	128	52	—
Saturated FAME (%)	22.9	47.7	—

Viscosity and cetane number measured per ASTM D445 and D613, respectively.

Performance Evaluation

Group-contribution predictions using the Joback-Reid method estimated the standard enthalpy of formation for each FAME component, and Hess's law was applied to compute theoretical GCVs. Predicted values agreed with experimental data within 0.4% for all soybean blends and within 0.3% for palm blends. The largest discrepancy (0.40% at B50 soybean) coincides with the maximum excess enthalpy, suggesting that non-ideal mixing interactions account for the residual error. Benson's second-order group additivity method reduced the B50 error to 0.22%, indicating that nearest-neighbor corrections capture part of the FAME-hydrocarbon interaction energy. Cetane number showed a strong positive correlation with saturated FAME content ($r^2 = 0.94$). Palm biodiesel's cetane number of 62.8 exceeded the diesel baseline of 54.0, while soybean biodiesel fell slightly below at 51.2. This difference has practical implications for cold-start performance and ignition delay in compression-ignition engines [8].

Discussion

The 10.9% energy density loss for soybean B100 and 8.6% for palm B100 relative to diesel bracket the range reported in the literature. Lapuerta and colleagues [2] compiled data

from 26 studies and found biodiesel GCVs of 37–43 MJ/kg depending on feedstock. Our soybean value of 41.98 MJ/kg sits at the upper end, likely because the low moisture content achieved by Na₂SO₄ drying minimized water interference during combustion.

The negative excess enthalpies deserve attention because they are small but systematic. Non-ideal mixing in FAME-hydrocarbon systems arises from differences in molecular polarity: FAMES carry an ester functional group that interacts weakly with the nonpolar aliphatic chains of diesel. This produces a slight contraction in molar volume upon mixing, which has been documented by density measurements [9]. The corresponding energy effect manifests as our observed negative H_E values.

From an engine-design standpoint, the nearly linear GCV decline with blend fraction simplifies fuel management. A B20 blend loses approximately 2% of its energy content relative to B0, a margin easily compensated by adjusting injection timing and duration. At B50 and above, the 5–10% energy penalty becomes significant for range-critical applications such as long-haul trucking [10]. The group-contribution approach validated here could serve as a rapid screening tool for evaluating novel feedstocks without the cost of full calorimetric characterization.

The higher cetane number of palm biodiesel (62.8 versus 51.2 for soybean) reflects the well-established relationship between saturated chain length and ignition quality^[8]. In practice, this means that palm-based blends offer shorter ignition delays and smoother combustion in unmodified compression-ignition engines. However, the elevated cloud point of palm biodiesel (approximately 16 °C) limits its applicability in temperate climates without winterization additives^[13]. Soybean biodiesel, with its higher unsaturation and correspondingly lower cloud point (−2 °C), remains preferable for year-round use in northern latitudes despite its modest cetane disadvantage.

An important methodological consideration is the choice of calibration standard. We used NIST-traceable benzoic acid, which has a certified combustion enthalpy uncertainty below 0.01%. Some earlier biodiesel calorimetry studies relied on naphthalene or sucrose calibration, which introduces systematic offsets of 0.1–0.3%^[4]. Standardizing calibration procedures across laboratories would improve the comparability of published GCV data for biodiesel feedstocks. Furthermore, the moisture content of the sample must be rigorously controlled below 0.05 wt%, as even trace water absorbs significant heat during vaporization and artificially depresses the measured GCV^[11].

Conclusion

Bomb calorimetry across eight blend levels showed that combustion enthalpy decreases nearly linearly with biodiesel fraction, dropping 10.9% for soybean and 8.6% for palm at B100. Small negative excess enthalpies peak at B50 and reflect non-ideal FAME-hydrocarbon interactions. Group-contribution predictions agreed within 0.4% of measured values, validating Hess's law-based estimation for FAME blends. Cetane number correlated strongly with saturated ester content. These thermochemical data provide a quantitative basis for blend optimization in compression-ignition engines.

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