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Determination of calorific values of some renewable biofuels

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Abstract

Thermal methods such as differential scanning calorimetry (DSC), and elemental analysis (EA) were employed to determine the calorific values of some renewable biofuels either directly or indirectly. The biofuels tested were the common milkweed, dogbane, kudzu, and eucalyptus tree. The purpose of this work was to optimize the experimental conditions for DSC analysis of biofuels, improve the calorific values by adding metal oxides as catalysts, and compare the heat values between DSC and EA analyses.

Keywords: Biofuels; Calorific values; Thermal methods

1. Introduction

The determination of the calorific values as well as the percentages of C, H, N, S, and O of biofuels are important in considering their suitability as environmentally safe energy sources. The biofuels tested such as the common milkweed, dogbane, kudzu, and eucalyptus tree can be replenished, unlike fossil and petroleum-based fuels. They are fast-growing renewable energy sources with recovery periods for harvesting ranging from less than a year [1–3] for the weed and vine-type plants [4, 5], and up to seven years for eucalyptus tree [6]. The above biomass materials can be converted to synthetic liquid fuels [7, 8] and chemical feedstocks [9, 10]. Other benefits of these plants are that they can be used to stop erosion and can be utilized in heating. Currently, about two percent of the U.S. energy consumption comes from woods, agricultural crops with their residues, and municipal and animal wastes plus other

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sources of biomass [11, 12]. The majority of the energy from biomass comes from its use in the forest industry [13, 14]. By the year 2000 up to twenty percent of the U.S. energy consumption could be furnished by biomass [15].

Thermal methods such as differential scanning calorimetry (DSC) and elemental analysis (EA) were employed to determine calorific values of biofuels either directly or indirectly. The biofuels tested were the common milkweed, dogbane, kudzu, and eucalyptus tree. All the biofuels tested were mainly composed of lignocellulosic polymers (hemicellulose, cellulose, and lignin). The milkweed and dogbane contained some latex (liquid hydrocarbons) while kudzu and eucalyptus contained high molecular weight resins and oils respectively.

The direct determination of calorific values of fuel materials by differential scanning calorimetry (DSC) was introduced by Fyans in 1977 [16]. This technique measures heat flow as a function of temperature with the total area under the curve being proportional to the heat of combustion. A typical thermocurve shows a two-step decomposition with the first peak relating to the combustion of volatiles and the second to the fixed carbon in the sample. Earnest has reported calorific values for coal samples that are in close agreement with the values published by ASTM [17, 18]. Earnest and Fyans [19, 20] determined the calorific values of coal and coke specimens from the percentage of volatile matter and fixed carbon using a thermogravimetric technique. A method for calculating the calorific values from the elemental composition has been introduced by Culmo [21]. Percents of carbon, hydrogen, oxygen, sulfur, moisture and ash were used to calculate the calorific values from the Dulong equation. Giazzi and Colombo introduced a modification of this equation for calculating gross and net heat values [22]. Calorific values of standard coal samples determined by DSC and elemental analysis in our laboratory were compared to ASTM values of the same samples. The biofuels were analyzed under the same conditions as the standard coal samples and the calorific values of direct and indirect determinations were compared.

2. Experimental

2.1. Instruments and materials

A Mettler DSC 20 with measuring cells containing medium-sensitivity sensors was used to determine calorific values of standard coal samples and biofuels. The instruments were calibrated as per the instructions in the manuals. Determination of C/H/N/S/O was made on a Carlo Erba Elemental Analyzer (EA), Model 1106. A microbalance, Cahn C-31, and an IBM computer were interfaced with the instrument. Eager 100 software of Carlo Erba was used for operating the system and data analysis. The Mettler TG-50 Thermogravimetric Analyzer was used to dry the samples.

All gases used were 99.9% pure or better from National Speciality Gases, a division of National Welders Supply. Transparent traps filled with anhydrous and ascarite were added to the lines to absorb traces of moisture and CO₂. Nitrogen used for drying was purified with a Supleco High Capacity Heated Carrier Gas Purifier, catalogue # 2-3802. The standards, sulfanilamide for C/H/N/S and dextrose for oxygen analysis, were provided with the instrument for the standardization and calibration of the instrument.

Chemicals to pack the combustion and pyrolysis reactors and other consumables like tin containers were obtained from Erba Company. The coal standards from National Bureau of Standards (NBS) (numbered 2684), a set of 8 premium coal samples from Argonne National Laboratories (ANL), and dextrose sugar were used throughout this work. Due to the decomposition of coal samples after the exposure to atmospheric conditions, a synthetic standard made of microanalytical chemicals was used to calibrate the elemental analyzer. Magnesium oxide, lead chromate (Analytical Reagent, Mallinckrodt), silver oxide (Baker and Adamson), praseodymium oxide, copper oxide (certified ACS, Fisher), and lead dioxide (Fisher) were used as received.

2.2. Sample collection and preparation

Plants were collected in Winston-Salem, Kernersville, Greensboro, and Hillsborough, North Carolina. Coal standards were acquired from NBS and the Premium Coal Samples came from ANL. Several whole green plants of milkweed, dogbane, kudzu, and eucalyptus were selected. They were dried separately in a gravity oven (70–120°C for several hours), ground in a Waring blender, and sieved to obtain 100 mesh size samples. The portions that did not pass 100 mesh were kept as coarse ground. Leaves of the biofuels were cut into small pieces for analysis.

2.3. Procedure

The Mettler TG-50 was used to dry about 10 mg of the sample in a tared platinum container in the furnace with dry, oxygen-free nitrogen flowing at 300 ml min⁻¹. The sample was dried by slowly heating from 35 to 135°C and held isothermally for either 2 or 5 min depending on the moisture content. If the thermocurve indicated insufficient drying, the isothermal drying was repeated. The samples were then stored in nitrogen atmosphere for further analysis.

A screening procedure recommended in the instrument manual for determining the calorific values by DSC was stored on the TC-10A processor. This included a 10°C min⁻¹ heating rate from room temperature to 600°C. The experimental conditions were optimized using a standard coal sample as outlined in Table 1. The sample holders are 40 µl in capacity and each hole is about 0.50 mm in size. Sample weights of about 0.50 mg of coal samples (200 mesh) and biofuels (100 mesh) were integrated over a baseline starting at 105°C to the end of the run. Among the additives (catalysts) tested, a 1 : 1 (by weight) magnesium oxide to silver oxide mixture improved the calorific values of both coal and the biofuels (Fig. 1).

A Carlo Erba Elemental Analyzer was used to simultaneously analyze the samples for carbon (C), hydrogen (H), nitrogen (N), and sulfur (S). Due to the large differences in the elemental composition of sulfanilamide standards, a synthetic standard was made and used for calibration. The elements, C, H, N and S, were combusted to their respective oxides first. The nitrogen oxides were then reduced to nitrogen and sulfur trioxide to sulfur dioxide by metallic copper in the reactor. The gas chromatographic separation of N₂, CO₂, H₂O and SO₂ is shown in Fig. 2. After separation, the gases pass through a detector which sends a signal to an integrator. The integrated values

Table 1

Effect of DSC variables on the accuracy of heat value (using a demineralized bituminous coal standard, h.v. of 35672 J g⁻¹)

Exp. conditions	Variable studied	HV/J g ⁻¹
	Heating rate/°C min ⁻¹	
Mass approx. 1 mg, open container, and 80 ml min ⁻¹ O ₂ flow rate	1	25844
	2.5	25114
	5	28130
	10	27316
	25	23712
	50	21294
	Holes in container cover	
Mass approx. 0.75 mg, 10°C min ⁻¹ heating rate, and 80 ml min ⁻¹ flow rate	1 holes	27737
	2 holes	29282
	4 holes	30489
	7 holes	28604
	8 holes	29885
	No cover	27191
	Sample mass/mg	
10°C min ⁻¹ heating rate, 80 ml min ⁻¹ flow rate, no cover	1.092	27316
	0.830	28604
	0.432	34287
	0.393	30702
	O ₂ flow rate/ml min ⁻¹	
Mass approx. 0.8 mg, heating rate 10°C min ⁻¹ , no cover	40	32392
	80	27191
	240	31370
	320	29404

were used to prepare the calibration curves which were then used to calculate the percentages of the various elements present. The analysis of oxygen was carried out in an inert gas stream with the pyrolysis of sample over a catalytic layer of nickel-plated carbon. The oxygen was converted to carbon monoxide (CO) and was separated from any nitrogen on a chromatographic column, Fig. 3. The signal was recorded and integrated as above. Dextrose was used as a standard for oxygen. The gross heat value (GHV) of both coal standards and biofuels were calculated using the equation recommended by Giuzzi and Columbo (Table 2). The effect of particle size of the biofuels on the calorific values was also studied to choose the best mesh size of the sample, Table 3.

3. Results and discussion

The Mettler TG-50 equipped with TC10 TA controller/processor was used for drying the coal samples and biofuels. The Mettler processor was changed from TC10 to

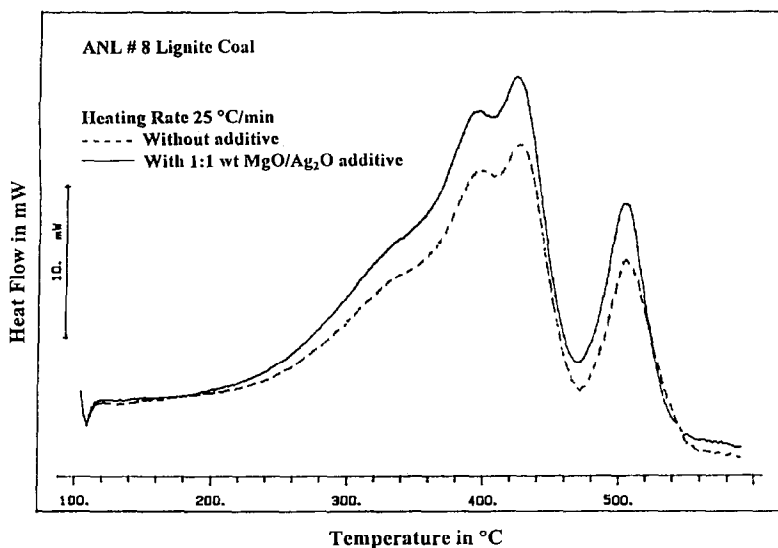


Fig. 1a. DSC curves of a standard coal sample.

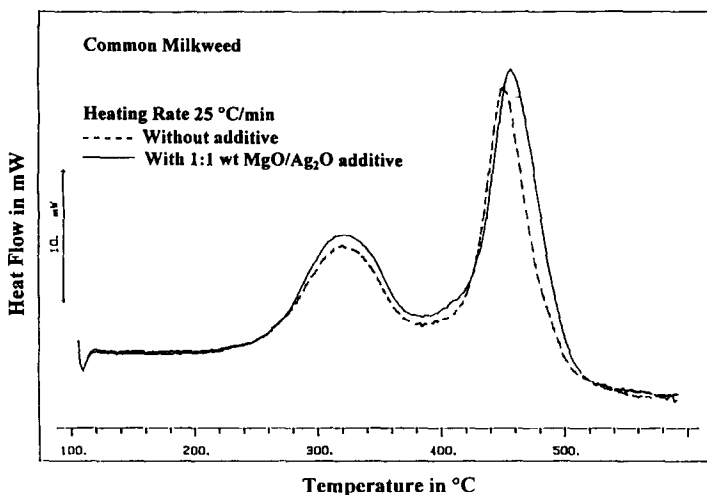


Fig. 1b. DSC curves of common milkweed.

TC10A and connected to an IBM/PC. This modification made the storage of raw data feasible and reduced the 4 linked methods to 2. This processor was tested with standard premium coal samples from ANL and then used for the biofuels. The samples were dried as described in the procedure and then used in DSC and EA.

The optimized experimental conditions for DSC, based on the data on Table 2 are: $5^{\circ}\text{C min}^{-1}$ heating rate, 4 holes in the container cover, about 0.40–0.50 mg of sample,

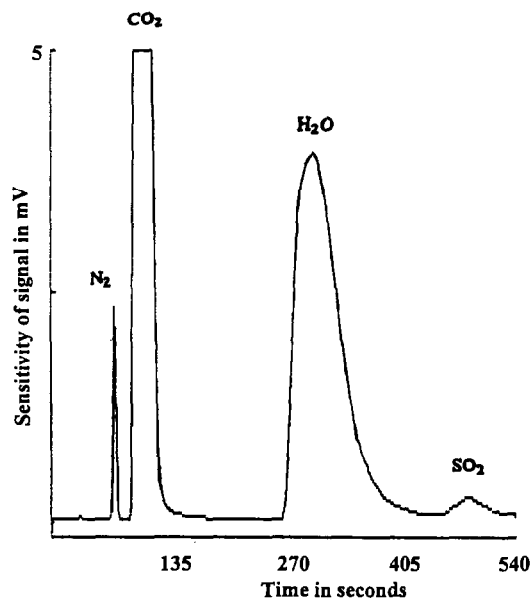


Fig. 2. Simultaneous determination of C, H, N, S.

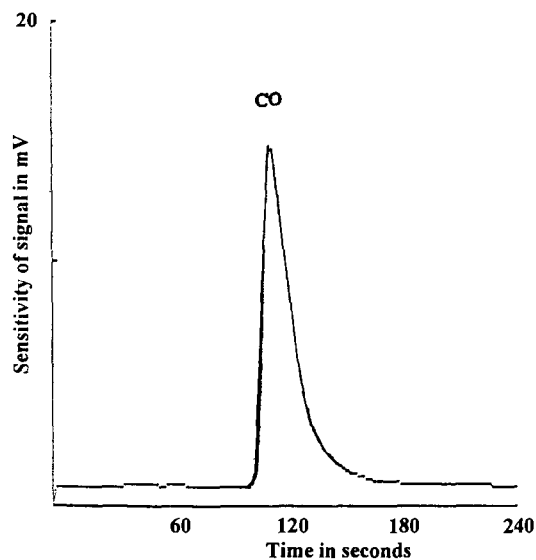


Fig. 3. Determination of oxygen by pyrolysis.

and 40 ml min^{-1} oxygen flow rate. Four holes were better than one because more holes allowed sufficient oxygen to enter into the container for better combustion. Since it took several hours to complete one analysis at a heating rate of 5°C min^{-1} , the experimental conditions were slightly modified to a heating rate of $25^\circ\text{C min}^{-1}$ with

Table 2
Elemental analysis of standard coal samples and biofuels

Sample ID	%C		%H		%N		%S		%O		J g ⁻¹
	ASTM	E.A.	ASTM	E.A.	ASTM	E.A.	ASTM	E.A.	ASTM	E.A.	
ANL # 3	65.7	64.4	4.2	1.2	1.2	1.4	4.8	4.5			27798
ANL # 4	75.5	75.0	4.8	5.0	1.5	1.5	2.2	2.2			31701
ANL # 5	86.7	85.7	4.2	4.4	1.3	1.2	0.7	0.7			34946
ANL # 7	66.2	66.3	4.2	4.3	1.3	1.2	0.7	0.7			27470
ANL # 8	65.8	65.7	4.4	4.4	1.0	0.9	0.8	0.9			25588
Milkweed		46.1		6.1		1.8				42.47	17298
Dogbane		48.4		6.0		1.8				38.77	18201
Kudzu		48.4		5.8		2.0				42.23	17273
Eucalyptus Gl.		48.3		5.8		0.6				39.71	17652

Table 3
Effect of particle size of the biofuels on the calorific value

Sample ID ^a	%N	%C	%H	%O	J g ⁻¹
Milkweed (C)	1.45	45.81	6.00	43.46	16354
Milkweed (F)	2.17	46.46	6.08	39.55	17392
Milkweed (L)	4.91	45.89	6.23	34.98	18238
Dogbane (C)	1.78	48.50	6.05	39.26	18094
Dogbane (F)	1.75	49.07	6.16	38.37	18606
Dogbane (L)	4.10	45.54	6.37	37.06	17947
Kudzu (C)	1.49	45.91	5.86	42.64	16333
Kudzu (F)	3.26	45.76	5.84	35.98	17452
Kudzu (L)	4.72	44.63	5.99	35.82	18082
Eucalyptus Gr(LF)	1.66	47.90	5.47	39.33	17043
Eucalyptus Gr.(C)	0.62	48.43	5.80	43.30	16982
Eucalyptus Gl.(L)	2.53	49.59	6.87	35.41	20336

^a C, coarse ground > 100 mesh; F, fine ground < 100 mesh; L, leaf section; LF, leaves ground to < 100 mesh; Gr., Grandis; Gl., Globulus.

one hole in the cover. Varhegyi et al. [23] showed that DSC curves reveal considerably less energy release than the true heat of combustion due to experimental conditions. To correct this problem they proposed the use of catalysts as aids to combustion in DSC. In an effort to improve the DSC techniques for our samples, several metal oxides alone and in mixtures of various proportions were tested with a standard coal sample. Among the choices, 1:1 magnesium oxide (MgO) to silver oxide (Ag₂O) (by weight) proved to be the best mixture. Magnesium oxide aids the combustion of the volatile matter and also catalyzes the oxidation of carbon monoxide (CO) to carbon dioxide (CO₂). Silver oxide catalyzes the combustion of fixed carbon in the sample as well as converting any CO to CO₂. Formation of CO₂ releases approximately four times the amount of heat as the formation of CO from the same amount of carbon [24]. The effect of the catalyst on a coal sample and a biofuel is presented in Fig. 1.

The simultaneous determination of C, H, N, and S in organic compounds [25] and oxygen [26] has been done by Pella and Colombo using a Carlo Erba Elemental Analyzer, Model 1106. Sadek and deBot [27] have determined C, H, N, and S simultaneously along with oxygen (O) in coal samples using the same Model 1106 Elemental Analyzer whereas we used it for biofuels. A typical gas chromatographic separation is shown in Fig. 2. The Eager 100 computer program on an IBM personal computer interfaced to the Elemental Analyzer was used to run the instrument, calculate and store the results, as well as give the actual time plot showing the quality of the chromatographic separation. The regression analysis for C, H, N, S, and O was done by the computer using the Eager program. Also, the program uses a modified Dulong equation introduced by Giuzzi and Colombo to calculate the gross and net heat values of each sample. The calculated calorific values were then compared to the ASTM values derived using a bomb calorimeter. The results show good agreement with those

Table 4
Comparison of heat values (J g^{-1}) from DSC and EA

Sample ID	DSC ^a	EA	Difference
ANL # 3	27798	27130	+ 668
ANL # 4	31331	31829	- 498
ANL # 7	27470	27607	- 137
ANL # 8	25588	25556	+ 32
Milkweed	18236	17815	+ 421
Dogbane	18566	18201	+ 365
Kudzu	17480	17273	+ 207
Eucalyptus gl. [c]	17052	17652	- 600

^a With MgO/Ag₂O 1:1 mixture.

generated by ASTM methods as presented in Table 2. The presence of sulfur was found to be below 0.20% or the limit of detection of the instrument and so considered to be negligible.

The results listed in Table 3 reflect the effect of particle size on the calorific values. The finely ground sample (with larger surface area) reacted with the catalyst more effectively and released more heat than the coarse and leaf samples. At the same time, the fine grinding resulted in a loss of some heat and made the sample vulnerable to air oxidation.

4. Summary and conclusion

The calorific values of the ANL premium coal samples as well as the biofuels determined by direct (DSC) and indirect (EA) methods (Table 4) are within $\pm 668 \text{ J g}^{-1}$. The difference is below the ASTM specified range of $\pm 837 \text{ J g}^{-1}$ ($\pm 360 \text{ Btu/lb}$) for repeatability. Since the same methods and instruments were used to study the biofuels, the calorific values determined are considered to be accurate and reliable. The addition of the catalyst, 1:1 (by weight) MgO : Ag₂O mixture, improved the calorific values of the samples. The standard deviation of the elemental analysis of the biofuels ranged from 0.42 to 0.89 indicating that the results generated are reliable.

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