



5th International Conference
"Computational Mechanics and Virtual Engineering "
COMEC 2013
24- 25 October 2013, Braşov, Romania

EXPERIMENTAL INVESTIGATION ON ENERGY DENSITY OF BIO-FUELS

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Abstract: *This paper presents the results obtained in investigation on energy density of bio-fuels. There are analyzed five kinds of bio-fuel candidates like sunflower oil, waste used oil and canola oil.. Measuring of energy density (heat of combustion) of bio-fuels was done using the Parr oxygen bomb calorimeter. There are presented the sample preparation, the testing procedure, the comparative results on the mixed and separated fuels and also the conclusions of the experiment. Even the energy density of bio-fuels studied decreases after mixing with diesel fuel, the fuels could be effectively used for energy generation by car engines.*

Keywords: *energy density; Parr oxygen calorimeter; biodiesel, bio-fuel*

1. INTRODUCTION

The use of so called bio-fuels is not new. Since 1990 engineers and researchers have been experimenting with using vegetable oils as fuel for a diesel engine. The rise of the price for regular fuels determined recently that it is necessary to investigate the bio-fuel properties and engine parameters for reliable operation.

The main form of used vegetable oil (UVO), waste vegetable oil (WVO) used in the UK is rapeseed oil (also known as canola oil, primarily in the United States and Canada) which has a freezing point of -10°C. However the use of sunflower oil, which gels at around -12°C,[10], is currently being investigated as a means of improving cold weather starting. Unfortunately oils with lower gelling points tend to be less saturated (leading to a higher iodine number) and polymerize more easily in the presence of atmospheric oxygen [8].

Recycled vegetable oil, also termed UVO, WVO, used cooking oil, or yellow grease is recovered from businesses and industry that use the oil for cooking.

As of 2000 [8], the United States was producing in excess of 11 billion liters (2.9 billion U.S. gallons) of recycled vegetable oil annually, mainly from industrial deep fryers in potato processing plants, snack food factories and fast food restaurants. If all those 11 billion liters could be recycled and used to replace the energy equivalent amount of petroleum, almost 1% of US oil consumption could be offset.[8]

Taxation on SVO/PPO as a road fuel varies from country to country, and it is possible the revenue departments in many countries are even unaware of its use, or feel it too insignificant to legislate. Germany used to have 0% taxation, resulting in it being a leader in most developments of the fuel use. However SVO/PPO as a road fuel began to be taxed at 0,09 €/liter from 1 January 2008 in Germany, with incremental rises up to 0,45 €/liter by 2012. However, in Australia it has become illegal to produce any fuel if it is to be sold unless a license to do so is granted by the federal government.[8]

All most diesel car engines are suitable for the use of straight vegetable oil, also commonly called pure plant oil (PPO), with suitable modifications. Even, Rudolf Diesel the fathers of the engine, the first attempts were to design an engine to run on coal dust, but later designed his engine to run on vegetable oil. Principally, the viscosity and surface tension of the SVO/PPO must be reduced by preheating it, typically by using waste heat from the engine or electricity, otherwise poor atomization, incomplete combustion and carbonization may result.

The relatively high kinematic viscosity of vegetable oils must be reduced to make them compatible with conventional compression-ignition engines and fuel systems. Cosolvent blending is a low-cost and easy-to-adapt technology that reduces viscosity by diluting the vegetable oil with a low-molecular-weight solvent.[11] This blending, has been done with diesel fuel, kerosene, and gasoline, amongst others; however, opinions vary as to the efficacy of this. Noted problems include higher rates of wear and failure in fuel pumps and piston rings when using blends.

2. MATERIALS AND METHODS

2.1. Materials

The tested bio-fuels come from main three sources: regular diesel fuel for cars, sunflower oil and canola oil. A supplemental source was used to investigate energy density because there are large quantities of waste oil, including commercial and industrial activities. Mainly, bio-fuels are prepared in samples at the Transilvania University automotive facility from Braşov County, Romania.

The Biodiesel samples were filtered and separated in two kinds of samples. First kind is pure vegetable oil, like Biodiesel 1: Sunflower oil and Biodiesel 2: Used vegetable oil. The second kind is a mixture of diesel fuel and vegetable oil, namely canola oil, also known as rapeseed oil. There are three volume fractions used in the sample mixture with diesel fuel, the 5%, 10% and 20% rapeseed oil.

For each kind of sample were prepared three probes. After filtering, the samples were weighed using a precision 0.1 mg. Each sample weight was approximately 1.4 gram.

2.2. Experimental System & Calibration

The equipments used for the energy density tests were: XRY-1C Oxygen bomb calorimeter, Figure 1, XRY-1C software and Kern & Sohn ABJ 220-4M analytical balance.



Figure 1: XRY-1C experimental system

Technical specifications for Oxygen bomb calorimeter are:

- Calorimeter capacity: 11000~15000 [J/K];
- Temperature measuring domain: 10-35[°C];
- Temperature reading resolution: 0.001 [°C];
- BIAS ≤ 0.2% [°C];
- Oxygen maximum pressure: 20 [MPa];
- Normal functioning temperature: 15-28 [°C]; temperature variation during experiments < 1 [°C];
- Relative humidity: < 85 [%];

Before determinations of the calorific value of samples, it is necessary to do the calibration of oxygen bomb calorimeter. This consists in a reverse procedure. Having the heat of combustion of benzoic acid as $H_e = 26454$ [J/g], it is determined by the same kind of test the thermal capacitance of the calorimeter, W [J/K], burning in crucible the benzoic acid and knowing its mass, m_e [g] using equation (1).

$$W = \frac{H_e \cdot m_e - (Q_{wc})}{(t_f - t_i)} \quad (1)$$

where, for calibration:

m_e - benzoic acid and knowing its mass = 1.0018 [g]

Q_{wc} - the heat correction for the wire's burning and for the cotton's burning, $Q_{wc} = 131.36$ [J]

t_f - the final temperature from the main stage, $t_f = 20.538$ [°C]

t_i - the initial temperature from the main stage, $t_i = 18.405$ [°C].

The burning process of benzoic acid in the calorimeter during calibration can be seen in Figure 2. After calibration the calculated thermal capacitance of the calorimeter is $W = 12328$ [J/K].

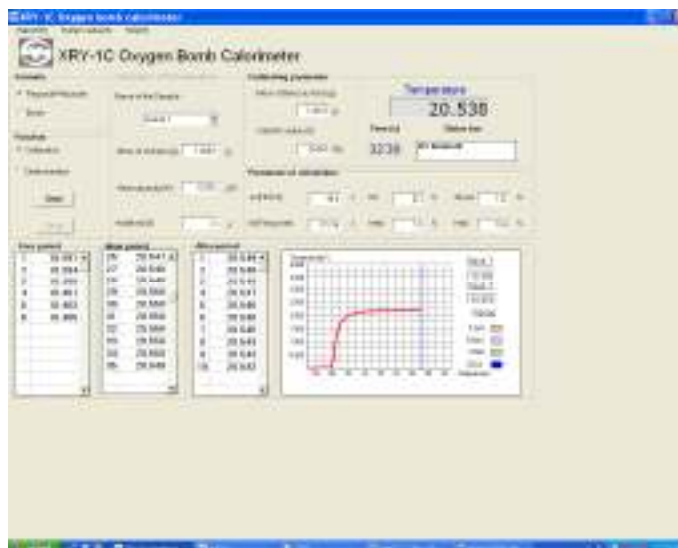


Figure 2: Calibration screen for XRY-1C.

Mass of sample = 1.0018 g, cotton wire mass = 0.0061 g, burning wire mass = 0.0040 g,
cotton burning heat = 108.49 J, wire burning heat = 22.87 J

2.3. Heat of Combustion

Because the tested material is a fuel, the energy density measurement means the determination of the heat of combustion. The heat of combustion is the energy released as heat when a compound undergoes complete combustion with oxygen in an enclosure of constant volume.

The gross calorific value at constant volume (named also as higher heating value or gross energy or upper heating value or higher calorific value) is the absolute value of the specific energy of combustion, in Joule, for the unit mass of a solid recovered fuel burned in oxygen in a calorimetric bomb under the conditions specified. The products of combustion are assumed to consist of gaseous oxygen and nitrogen (coming from the gaseous atmosphere of burning), of carbon dioxide and sulphur dioxide, of liquid water (in equilibrium with its vapor) saturated with carbon dioxide under the conditions of the bomb reaction, all at the reference temperature [4]. The equation used to calculate gross calorific value in adiabatic conditions, $Q_{gr,ad}$, is presented in equation (2).

$$Q_{gr,ad} = \frac{W \cdot (t_f - t_i - t_\alpha) - (Q_1 + Q_2 + Q_3 + Q_4)}{m_c} \quad (2)$$

where: W - calorimetric factor [J/K], determined by calibration of calorimeter;

- m_c - the fuel sample's mass [g];

- t_f - the final temperature from the main stage [°C]

- t_i - the initial temperature from the main stage [°C]

- t_α - the temperature correction caused by exterior heat losses [°C];

- Q_1 - the heat correction for the wire's burning and for the cotton's burning [J]

- Q_2 - the heat correction when the nitric acid is formed $Q_2 = 40$ [J].

- Q_3 - the heat correction when the sulfuric acid is formed $Q_3 = 1298 m_1$ [J].

- Q_4 - the heat correction for the benzoic acid's combustion, if the fuel has been mixed with this acid for plasticization.

The net calorific value at constant volume (lower calorific value) is the absolute value of the specific energy of combustion, in Joules, for the unit mass of a solid recovered fuel burned in oxygen under conditions of constant volume and such that all the water of the reaction products remains as water vapor (in a hypothetical state at 0.1 MPa), the other products being, as for the gross calorific value, all at the reference temperature [4]. With the bomb calorimeter is measured the gross calorific value. The testing procedure is presented in [1, 2, 3].

3. RESULTS AND DISCUSSION OF CALORIMETRIC ANALYSIS

For each sample, in the XRY-1C software there were introduced the input data: the mass of ignition wire in grams; the mass of cotton fuse in grams; the calorific value of wire [J/g]; the calorific value of cotton [J/g] and the mass of

test sample in grams. These input data values are weighted for each sample with a precision Kern & Sohn ABJ 220-4M analytical balance by a 0.01mg resolution.

After burning the software plotted the graph temperature-time as shown in Figure 3, and calculates the gross calorific value using the Regnault-Pfaudler[2], [3] method as shown in Table 1.

Table 1: Calorimeter Temperature vs. Time for Biodiesel 1, sample 2

Determination		Time:	9/20/2012 4:43:27 PM
SampleMass[g]	1.3819	Mad[%]	1.9
Capacity[J/K]	12328.00	Sb _{ad} [%]	1.32
SampleName	moto7_2	Had[%]	1.54
		Formula	R-P
		Temperature [°C]	
AutoID	Fore period	Main period	After period
1	23.932	24.560	27.602
2	23.929	25.835	27.601
3	23.926	26.562	27.599
4	23.923	26.905	27.596
5	23.921	27.093	27.594
6	23.919	27.213	27.591
7		27.296	27.588
8		27.353	27.584
9		27.402	27.581
10		27.437	27.577
11		27.469	
12		27.494	
13		27.515	
14		27.534	
15		27.549	
16		27.561	
17		27.572	
18		27.581	
19		27.587	
20		27.592	
21		27.597	
22		27.600	
23		27.602	
24		27.603	
25		27.604	
26		27.604	
27		27.603	
Q_{b,ad}[J/g]	Q_{gr,ad}[J/g]	Q_{net,ad}[J/g]	
33402	33224	32720	

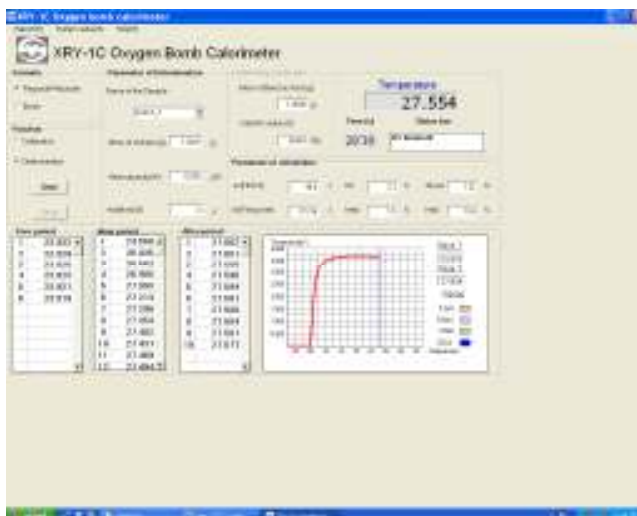


Figure 3: Measurements for Biodiesel 1-Sunflower Oil, sample 2, Mass of sample = 1.3819 g, cotton wire mass = 0.0062 g, burning wire mass = 0.0039 g, cotton burning heat = 108.5 J, wire burning heat = 22.86 J, thermal capacitance of the calorimeter, $W = 12328 \text{ J/K}$

The results obtained for pure and mixtures of bio-diesel fuels are presented in Table 2. $Q_{b,ad}$ is burning calorific value, in adiabatic conditions, $Q_{gr,ad}$ is gross calorific value and $Q_{net,ad}$ is net calorific value, in adiabatic conditions. These values are compared with diesel fuel which was also tested. For each kind of sample were tested three probes, the value for heat of combustion is a mean value with tolerance.

Table 2: Results for Heat of Combustion of bio-fuels

Column 1	$Q_{gr,ad}$ [MJ/kg]	$Q_{net,ad}$ [MJ/kg]
Biodiesel 1-Sunflower Oil	33.224 ± 0.13	32.720 ± 0.13
Biodiesel 2-Waste Oil	19.805 ± 0.54	18.867 ± 0.54
Diesel Fuel	45.961 ± 0.14	45.404 ± 0.14
Diesel Fuel +5% Canola Oil	43.006 ± 0.38	42.461 ± 0.38
Diesel Fuel +10% Canola Oil	43.341 ± 0.34	42.795 ± 0.54
Diesel Fuel +20% Canola Oil	42.802 ± 0.22	42.259 ± 0.22

From Table 2 it could be seen that the heat of combustion of the Bio-fuels compared with the heat of combustion of the Diesel fuel are smaller with 27.71% for Biodiesel 1, with 56.90% for Biodiesel 2, with 6.43% for Biodiesel 3, with 5.70% for Biodiesel 4 and with 6.97% for Biodiesel 5.

It can be observed a small variation of heat of combustion value, even the Biodiesel 3, diesel fuel with 5% canola oil, the Biodiesel 4, diesel fuel with 10% canola oil, and the Biodiesel 5, diesel fuel with 20% canola oil, around 43.00 MJ/kg, which is about 6.4% smaller value than usual Diesel fuel.

Table 3: Heat of Combustion for fuels [4],[7]

Fuel	$Q_{gr,ad}$ [MJ/kg]	$Q_{net,ad}$ [MJ/kg]
Crude oil	45.60	42.60
Gasoline	46.60	43.50
Diesel fuel	45.70	42.80
Jet Fuel, JP-4	46.60	
Methanol	22.90	20.10
Ethanol	29.80	26.90
Liquefied petroleum gas	50.10	46.60
Liquefied natural gas	55.20	48.60
Liquid hydrogen	141.00	120.00
Residual oil	42.20	39.50

An interesting result is the increasing of the heat of combustion value for the Biodiesel 4, diesel fuel with 10% canola oil comparing with the bio-fuels with 5% and 20% canola oil.

The results are in agreement with the data from the literature, as it could be seen in Table 3. Because the heat of combustion of bio-fuels, such as Biodiesel 3, Biodiesel 4 and Biodiesel 5 is close to Diesel fuel heat of combustion, the use of these fuels is justified. But, if it is considered the price for Diesel fuel and the price for vegetable oil than the use of bio-fuels is tempting, even a decrease with 30% on heat of combustion for Biodiesel 1.

3. CONCLUSION

The calorimetric analysis reveals a comparable heat of combustion of the mixed vegetable oil with diesel fuel to be used as fuel. The calorific power of those materials has a reasonable level, compared to those of petroleum derivatives. The Biodiesel 3, Biodiesel 4 and Biodiesel 5 have a comparable calorific power compared with common diesel fuel, because the polymers in these kinds of products are present especially as resins for composite materials, rather than single material.

Even for pure vegetable oil, the calorific power is still greater than those of different sorts of coals, the smaller amount of sulphur compounds makes them as environmentally friendly and the price of acquisition can be a way to use these bio-fuels to obtain a reasonable amount of energy.

REFERENCES

- [1] European Committee for Standardization, Solid recovered fuels - Methods for the determination of calorific value, DD CEN/TS 15400:2006, 2006.
- [2] *** - SR ISO 1928/95 – Determinarea puterii calorifice superioare și inferioare a combustibililor solizi.
- [3] *** - DIN 51900-1/2000 Determining the gross calorific value of solid and liquid fuels using the bomb calorimeter, and calculation of net calorific value - Part 1: General information.
- [4] V.B. Ungureanu, Gh.Băcanu, D. Șova, V.Sandu, L.Costiuc - Termodinamica. Aplicatii practice/ Thermodynamics. Practical works. Editura Universitatii Transilvania, Brasov, 2010, 404 pag. ISBN 978-973-598-832-6
- [5] Costiuc, L., Popa, V., Serban, A., Lunguleasa, A., Tiorean, M.H., Investigation on heat of combustion of waste materials, Proceedings of the International Conference on Urban Sustainability, Cultural Sustainability, Green Development Green Structures and Clean Cars, Malta, September 15-17, 2010, Published by WSEAS Press, ISSN: 1792-4781, ISBN: 978-960-474-227-1, pag. 165-168.
- [6] Costiuc, L., Lunguleasa, A., Improving measurement accuracy of biomass heat of combustion using an oxygen bomb calorimeter, Bulletin of the Transilvania University of Brasov, vol.2(51)-2009, ISSN 2065-2119(print), ISBN- 978-973-598-521-9, pag. 467-474.
- [7] Walters, R.N., Hackett, S.M., Lyon, R.E., Heats of combustion of high temperature polymers, <http://large.stanford.edu/publications/coal/references/docs/hoc.pdf>.
- [8] http://en.wikipedia.org/wiki/Vegetable_oil_fuel, accessed 20/09/2013
- [9] Lunguleasa, A., Costiuc, L., ș.a. Combustia ecologică a biomasei lemnoase. Editura Universității TRANSILVANIA din Brașov, 2007. print+CD, ISBN 978-973-598-194-5
- [10] Altin, R., S. Cetinkaya, and H. S. Yucesu. 2001. The potential of using vegetable oil fuels as fuel for diesel engines. Energy Conversion and Management 42, no. 5 (March): 529-538. doi:10.1016/S0196-8904(00)00080-7
- [11] Knothe, Gerhard (2001). "Historical Perspectives on Vegetable Oil-Based Diesel Fuels" (PDF). Inform 12 (11): 1103–1107. Retrieved 2009-06-24