

Energetic Study on Animal Fats and Vegetable Oils Using Combustion Bomb Calorimeter

**Ioannis GRAVALOS, Theodoros GIALAMAS, Zisis KOUTSOFITIS, Dimitrios KATERIS,
Zisis TSIROPOULOS, Panagiotis XYRADAKIS, Anastasios GEORGIADES**

Technological Educational Institute of Larissa, Faculty of Agricultural Technology,
Department of Agricultural Machinery & Irrigation, 41110 Larissa, Greece
gravalos@in.gr

Abstract: The excessive use of traditional fossil fuels produces serious economical and environmental problems. Moreover fossil fuels are constricted, which makes the search for alternative fuels a priority objective, all over the world. Animal fats and vegetable oils can be used as alternative fuels directly or can be converted into other forms of liquids (various blends of oil and diesel or methyl esters). This paper is focused on the energetic evaluation of the animal fats and vegetable oils. Calorific Values (CV) of various fats and oils are reported. The values were measured by combustion bomb calorimeter (IKA C 5000). Data were obtained by user-friendly software C5040 CalWin. The tests and the methodology of tests in the calorimeter are validated according to ASTM D240. Calorific values of fat and oil samples were approximately 12-14% lower than those of diesel. Additionally, oil methyl esters and various blends with diesel gave higher calorific values.

Key words: Animal fats, vegetable oils, alternative fuels, calorific value, combustion bomb calorimeter.

INTRODUCTION

The fats and the oils are mixed glycerides, that is to say triesters that take shape with the reaction of three molecules of fatty acids with a molecule glycerol. When the three fatty acids are similar, the product that results from the reaction it is one simple triglyceride. When two different acids at least exist, the product is one mixed triglyceride. The natural fats contain fatty acids with an even number of carbon atoms. Units with two carbon atoms build these acids. Initially, the supremacy of fatty acids with 18 atoms of carbon led to the affair that the fats emanated from 3 molecules of glucose (carbohydrate with 6 atoms of carbon) later however their biosynthesis will be found to the acetic teams that have 2 atoms of carbon. Provided that the acetic team can be shaped from fats, proteins or carbohydrates with their reaction with oxygen, it is likely that the fats are composed indirectly by anyone of these substances. The shaping multiple (double) beams between the atoms of carbon in the fats that are composed by acetic teams are achieved with addition or abstraction of carbon atoms, which becomes via ferments. The natural fats are mainly composed from glycerides, but contain also a lot of other lipids in smaller quantities (Harrington, 1986).

The fatty acids constitute the 94% ÷ 96% of total weight of various fats and oils. Because their sovereign weight in the molecules glycerides and because they also contain the active department of molecules, the fatty acids influence to a large extent so much the natural what chemical character glycerides. Most of the oils and the fats are based on one roughly dozen of fatty acids. Taking into consideration the glyceride composition, it is particularly important to make discrimination between the saturated acids (e.g. palmitic, stearic) with relatively high temperatures of fusion and unsaturated acids (e.g. linoleic, oleic), which fuse in low temperatures and are much more chemically active. In the line of saturated acids, the point of fusion is increased progressively by temperatures lower than the temperature of room, for acids with a small molecular weight, up to a firmly high point of fusion for the longest carbonic chains. The unsaturated acids can contain up to 6 double bonds where as the degree of unsaturation is increased the point of fusion lowers. Glycerides composed mainly by unsaturated acids, for example soybean oil, are liquids. Glycerides containing a high percentage of saturated acids, like the beef fat, are steady. The carbon atoms in fatty

acids are ordered in straight line chains and the first place of double bond in most unsaturated acids are presented between the 9th and 10th atom of carbon, if the numeration begins from the final carboxylic team. The specialisation of place of double bond in fatty acids of so many plants of what animals implies shaping from a related enzymatic mechanism of dehydrogenisation.

Animal fats and vegetable oils can be used as alternative fuels directly or can be converted into other forms of liquids (various blends of oil and diesel or methyl esters). The vegetable oils are very viscously so as they can be used in modern machines. Nevertheless, various researches have given three methods according to which the use oils will be possible: a) mixture of vegetable oil with lighter fuels, as is the kerosene, b) heating of oil before it reaches the injector, c) chemical split of oil in smaller components.

The calorific values of the animal fats and vegetable oils will provide a measure of the energy available from these alternative fuels. Thus, the calorific value is the main power characteristic of a fuel quality. There exist two main groups of methods for its determination: a) theoretical and b) calorimetric. The first method is analytical and requires preliminary chemical analysis of the elemental composition of the fuel, and do not provide high accuracy. Elemental analysis is expensive and tedious and needs skilled workers to carry out the analysis. The second method based on experimental determination of the calorific value is most reliable and accurate. Two calorific values must be considered: a) the gross calorific value is the amount of energy released by complete combustion of a mass unit of fuel sample, at constant volume in an oxygen atmosphere, assuming that the final products of combustion consist of O₂, CO₂, SO₂, and N₂ in gas phase together with water, that the sample contains and that is generated from the combined hydrogen, in a liquid form, and b) the net calorific value, that can be calculated from gross calorific value assuming that water in the products remains in the form of vapour. Knowing net calorific value is very helpful to evaluate fuel resources from the energetic point of view. Combustion bomb calorimeters, characterized by large values of the heat release (40 kJ) and a relatively high

accuracy have been developed for measurements of the calorific value (Hill, 1994), (Vorob'ov et al., 1997), (Korchagina, 1998).

This paper is focused on the energetic evaluation of the animal fats and vegetable oils so as these products can be used as alternative fuels (raw or after their transesterification) in diesel engines.

LITERATURE REVIEW

Thermal analysis techniques have been applied to study organic "energy storage" materials. Wesolowski and Erecinska (1998) have presented the evaluation of the applicability of thermoanalytical methods to the assessment of the quality of refined rapeseed oils. Density, refractive index, and saponification, iodine and acid numbers of rapeseed oils were determined as part of the study. By correlating the data obtained from the temperatures of initial, final and successive mass losses determined from the thermogravimetric curves, strong relations were observed. The possibility of a practical utilization of regression equations for the assessment of the quality of refined rapeseed oils was indicated. The results of principal component analysis indicate that thermogravimetric techniques are very useful in defining the quality of rapeseed oils compared with chemical analyses. Giannelos et al. (2002) have investigated the physical, chemical and fuel related properties of tobacco seed oil. These properties were comparable to those of other vegetable oils and to current European specifications for automotive diesel fuel. This study suggests that this non-edible oil may be an appropriate substitute for diesel fuel. The HHV of tobacco seed oil was calculated using the Demirba equation, showed a difference of 0.032% from the measured value. The energy content of this oil was 39.4 MJ/kg. This value was almost the same with other vegetable oils. The energy contents of most vegetable oils are approximately 12% lower than that of the automotive diesel fuel used in Greece. Tan and Che Man (2002) study the thermal behaviour of coconut oil and palm oil and products based on them, by monitoring peak transition temperatures, transition enthalpies, offset-(Toff) and onset-temperatures (Ton) by differential scanning calorimetry (DSC) at different scanning rates. Some chemical and fuel properties of 17 vegetable oils (from 12 crop and 5 kernel samples)

were determined and compared (Demirbas, 2003). The HHV (Higher Heating Value) determination was based on the analytical method. Different mathematical equations have been used based on data from physical or chemical compositions. HHVs of the oil samples range from 39.3 to 39.8 MJ/kg. The HHVs of the vegetable oils are approximately 88% of those of diesel fuels. Kerihuel et al (2005) presented a detailed analysis on different properties of two kinds of animal fats and their suitability of using them as fuel in diesel engines. Physical and chemical properties (viscosity, low heating value (LHV), and chemical compositions) of animal fats are obtained experimentally. The results obtained from calorimeter test are, respectively, about 38.300, 28.200 and 42.500 kJ/kg with animal fat AF1, animal fat AF2 and standard diesel. It is seen that the LHV of AF1 is more than that of AF2. The higher LHV of AF1 can be explained by the presence of more carbon than AF2. As expected, the presence of chemically bound oxygen in the fats lowers LHV of the fats as compared to diesel. Santos et al. (2005) have been proposed conventional methods to determine thermal properties of edible vegetable oils. The evaluation of the applicability of DSC and microwave oven (MO) methods to determine the specific heat capacities of the edible vegetable oils was performed. It was observed that the specific heat capacities of each edible oil increased as a function of the saturation of the fatty acids. Conceicao et al (2007) provided a thermoanalytical and physical chemistry characterization of castor oil and biodiesel. The calorific capacity of castor oil and biodiesel in the interval of 55–125 °C was 2.718–2.680 and 1.855–2.179 J/g/K, respectively. It was verified that the castor oil presented a higher capacity of transference of heat compared to biodiesels'. The knowledge of the calorific capacity of castor oil and biodiesel is of great practical importance in the engineering branch. Higher heating values (HHVs) of fatty acids (C4–C18) were measured and correlated using linear least square regression analysis (Sadrameli et al., 2007). Equations were developed for the estimation of the HHVs of saturated fatty acids from their molecular weight (Mw), density (DN) and carbon number (CN). These equations are $HHV = 0.0518 Mw + 29.76$, $HHV = 93.4 DN + 122.67$ and $HHV = 0.7271 CN + 31.419$

with R2 values of 0.9895, 0.9798, and 0.9895, respectively. The correlations may be used for HHV estimation of mixtures of fatty acids developed from vegetable oils.

MATERIALS and METHODS

A diverse group of animal fat and vegetable oil samples was used in this study including cottonseed oil (CoO), corn oil (CnO), cardoon oil (CaO), olive oil (OeO), rapeseed oil (RaO), sesame oil (SeO), soybean oil (SoO), sunflower oil (SuO), beef fat (BeF), Pork fat (PoF) and sheep fat (SeF). For transesterification of the above fats and oils was used the following procedure: A sample of 500 g of each animal fat and vegetable oil was placed in a 1000 ml flat-bottom flask equipped with a mechanical stirrer, thermometer and condenser. The fat and oil was stirred and heated to 60°C. In another beaker, 111.6 g of methanol was mixed with 5.55 g of sodium hydroxide (1% by weight assuming 90% pure NaOH). A 6:1 molar ratio of methanol to fat or oil was used for better esterification. The mixture of methanol and NaOH was heated to 60°C and stirred until all of the NaOH was dissolved. This mixture was then added to the fat or oil, stirred rigorously, and further heated to 70–75°C. Heating and stirring continued for 2 h. The mixture was then allowed to cool to room temperature, and the ester and glycerol layers were separated in a separator funnel. Excess methanol was removed from the ester by distillation. Washing three times with distilled water and drying under vacuum purified the ester.

Bomb calorimeter (Model C5000 Adiabatic Calorimeter, IKA®-Werke, Staufen, Germany) was used to determine the gross energy of vegetable oil and animal fat samples. The calorimeter bomb and the metal container surrounding it form the kernel of the calorimetric system, which is placed in a thermally insulated jacket. A primary temperature transducer, placed inside the unit, records the change in the system temperature due to the combustion of the fuel in the bomb. The calorimeter also contains a cooling system. The bomb calorimeter enables a rapid analysis to be carried out, the basic time of which cannot be reduced, since it is related to the fuel combustion process itself. The following mathematical formulas are used to calculate results of

measurements. The calorimeter system acquires the data required for the measurements partially during the combustion process and the data is partially the results of analyses of examination on fuel samples or on combustion products. The calculations correspond to the applicable standards (DIN 51900, ASTM 240D, ISO 1928, BSI) for gross calorific values and net calorific values:

$$H_{Oan} = \frac{C \times \Delta T - Q_z}{m} \quad (1)$$

where: H_{Oan} is the gross calorific value in reference state analysis moist [J/g] (this is the provisional gross calorific value without acid or water correction), C is the heat capacity of the calorimeter [J/K], ΔT is the increase in temperature of the calorimeter system during a combustion experiment [K], Q_z is the extraneous energy from ignition, combustion of the cotton thread, combustion aids [J], and m is the mass of the fuel sample [g].

A calculated net calorific value for the oil and fat samples was determined by the following formula:

$$H_{Uan} = H_{Oan} - (H_2O \times 24,41) \quad (2)$$

where: H_{Uan} is the net calorific value in reference state analysis moist [J/g], H_2O is the percentage [%] of water in the fuel sample, as determined by elementary analysis.

RESEARCH RESULTS and DISCUSSION

Among the renewable fuels being considered are various types of fats and oils derived from animal and plant sources. These fats and oils have potential as diesel engine fuels but there is a need for continued and concentrated research. This research is part of a continuing program to obtain precise thermo-chemical data of fats and oils.

Table 1 lists the gross calorific values H_{Oan} [J/g] of various animal fat and vegetable oil samples. Calorific values of the fat and oil samples range from 39.060 to 39.693 J/g. Cardoon oil has exceptional low value (39.060 J/g). Also, sunflower has low calorific value 39.179 J/g concerning the values that are reported in the international bibliography 39.600 J/g (Demirbas, 2003). Obviously, it will be owed in the quality of particular sunflower oil. Finally, it confirms that the

animal fats and vegetable oils calorific values are approximately 86% to 88% of those of diesel.

Table 1. Gross calorific values of the animal fat and vegetable oil samples

Sample	H_{Oan} [J/g]
Cottonseed oil	39.420
Corn oil	39.407
Cardoon oil	39.060
Olive oil	39.675
Rapeseed oil	39.638
Sesame oil	39.406
Soybean oil	39.455
Sunflower oil	39.179
Beef fat	39.513
Pork fat	39.693
Sheep fat	39.548

It is generally accepted that fuel consumption is proportional to the volumetric energy density of the fuel based upon the lower or net calorific value. Lower calorific values determine higher fuel consumption, because for ensuring of the same load (torque) it is necessary to combust more fuel. Table 2 reports the net calorific values of the animal fat and vegetable oil samples. Net calorific values of fats and oils range between 36.247-37.294 J/g and they are 6-8% less than the above gross calorific values.

Table 2. Net calorific values of the animal fat and vegetable oil samples

Sample	H_{Uan} [J/g]
Cottonseed oil	36.975
Corn oil	36.687
Cardoon oil	36.247
Olive oil	37.294
Rapeseed oil	37.220
Sesame oil	36.805
Soybean oil	36.929
Sunflower oil	36.475
Beef fat	36.984
Pork fat	37.271
Sheep fat	37.016

Raw animal fats and vegetable oils have high viscosity. High viscosity leads to poorer atomization of the fuel spray and less accurate operation of the fuel

injectors. Additionally, the average viscosity of raw animal fats and vegetable oils increases more rapidly as temperature is decreased. Regarding the said above one of the main tasks of the practical application of fats and oils in the exploitation is improving their characteristics at a low temperature. Consequently, fats and oils are better to be converted into other forms of liquids (methyl esters or various blends of oils with diesel). Table 3 & 4 present gross calorific values of animal fat and vegetable oil methyl esters (biodiesel/B100), and blends with diesel under proportion 80/20% (calorific value of used diesel was measured 45.784 J/g). Gross calorific values of methyl esters and blends are higher than raw fats and oils.

Table 3. Gross calorific values of methyl ester (B100) samples

Sample	H _{Oan} [J/g]
Cottonseed oil methyl ester	40.146
Corn oil methyl ester	40.124
Cardoon oil methyl ester	39.785
Olive oil methyl ester	40.415
Rapeseed oil methyl ester	40.378
Sesame oil methyl ester	40.117
Soybean oil methyl ester	40.180
Sunflower oil methyl ester	39.928
Beef fat methyl ester	40.454
Pork fat methyl ester	40.449
Sheep fat methyl ester	40.643

Table 4. Gross calorific values of blends of animal fat and vegetable oil with diesel (80/20%) samples

Sample	H _{Oan} [J/g]
Cottonseed oil blend	40.581
Corn oil blend	40.414
Cardoon oil blend	40.427
Olive oil blend	40.736
Rapeseed oil blend	40.601
Sesame oil blend	40.622
Soybean oil blend	40.755
Sunflower oil blend	40.285
Beef fat blend	40.661
Pork fat blend	40.640
Sheep fat blend	41.054

Agents that are added to fuels in a concentration of < 1% described as "additives". They are

sometimes added to the fuel at the refinery but more usually at a marketing terminal. Fuel additives perform a variety of functions and are now indispensable components of fuels. Some of these additives enhance the properties of the base fuel (e.g. corrosion inhibitors); some help to maintain them (e.g. antioxidants, stabilizers); others aid the movement of fuel through the distribution chain (e.g. pipeline drag reducers, demulsifiers, antifoams). On some occasion's additives improve "performance" features as cetane number and cold filter plugging point (malan-styrene esters, polymethacrylate and ethylene vinyl acetate additives). Cetane improvers are alkyl nitrates of which 2-ethyl hexyl nitrate is most commonly used. In order to improve performance and flow characteristics at low temperature, we have used a fuel optimizer in animal fats and vegetable samples. Gross calorific values of fats and oils with additives samples are reported in table 5.

Table 5. Gross calorific values of animal fats and vegetable oils with additives samples

Sample	H _{Oan} [J/g]
Cottonseed oil + additives	39.569
Corn oil + additives	39.612
Cardoon oil + additives	39.289
Olive oil + additives	39.785
Rapeseed oil + additives	39.606
Sesame oil + additives	39.551
Soybean oil + additives	39.560
Sunflower oil + additives	39.553
Beef fat + additives	39.642
Pork fat + additives	39.613
Sheep fat + additives	39.681

Figure 1 shows a comparison between calorific values of rapeseed oil and its conversion into other forms of liquids (methyl ester or various blends of oil with diesel and additives). Rapeseed oil methyl ester and rapeseed oil blend have gross calorific values above 40.378 J/g which are higher than that of raw rapeseed oil (39.638 J/g). Also, methyl esters and blends of the others fats and oils have higher gross calorific values than raw fats and oils. This clearly indicates that fats and oils are better to be converted in other forms of liquid fuels.

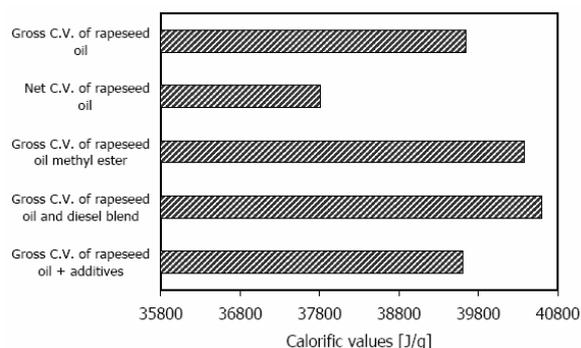


Figure 1. A comparison between different calorific values of rapeseed oil and its conversion into other forms of liquids (methyl ester or various blends of oil with diesel and additives).

CONCLUSIONS

Calorific value is the quantity of heat energy, which is emitted by fuel at the time of combustion. Although the diesel combustion chamber system can accept wide variations in heating value, practical systems are only suitable when calorific value of the fuel is high. In this work, the calorific values of various animal fats and vegetable oils were investigated in raw form or with some minor modifications. From the results and discussion, it is obvious that:

- Calorific values of fat and oil samples obtained in the present work are in agreement with results in the international literature.
- Calorific values of fat and oil samples were approximately 12-14% lower than those of diesel.
- In order to minimize fats and oils "cold-plugging" problems due to high viscosity, they can be converted in oil methyl esters or various blends with diesel. Additionally, oil methyl esters and various blends with diesel gave higher calorific values. Calorific values of blending fats and oils with diesel (80/20%) range from 40.285 to 41.054 J/g.
- Calorific values of oil blends with fuel optimizer were no different than raw fats and oils. The effect of fuel optimizer on fats and oils performance should be investigated in much more detail.

It is hoped that continuing research on this project may provide more information about this in the future.

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