

Thermal investigation of biodiesel blends derived from rapeseed oil

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Abstract Over the last few years, the production of biodiesel from vegetable oil has significantly increased in Romania due to its obligatory use in the composition of diesel fuel. In this study, biodiesel from rapeseed oil was produced using methanol and a base catalyst. Four samples of biodiesel/diesel blends were prepared for analysis to determine the main thermal decomposition processes and calorimetric events. The thermal profiles were compared to reference diesel. The data obtained on the Thermogravimetry/Differential thermogravimetry and DTA curves show the quality of biodiesel/diesel blends and the possibility that the fuel be used in diesel engines. It was found that biodiesel blends with higher percentage of biodiesel in their compositions were more thermally stable than diesel fuel.

Keywords Thermogravimetry · Biodiesel · Rapeseed oil · Petrodiesel · TG–DTG–DTA

Introduction

Discovery of biodiesel and its peculiarities similar to conventional fuel is older than the diesel engine invention itself. However, until a few decades ago, there was no research about biodiesel, because of the large amount of fossil fuels available, the ease of obtaining them, and the degree of global pollution, whose consequences have been studied only in recent years. An important characteristic of

Romania is represented by the large areas of unused land, chemically free, ideal for cultivating rapeseed and sunflower crops. This asset, which many of the EU states don't have, could make Romania an exporter of biodiesel [1]. According to the US Standard Specification for Biodiesel (ASTM 6751-02), this is defined as a fuel consisting of mono-alkyl esters of long-chain fatty acids originating in vegetable oils or animal fats. The definition is also accepted by the European Union specification concerning biodiesel (EN 14214). But the very strict regulations define biodiesel as fatty acid methyl esters (FAME) [2–4]. As for diesel fuel renewable substitutes, FAME biodiesel, appear to be the most popular, since their properties are similar to mineral diesel and can be used in conventional diesel engines without significant modifications. The substitution of conventional diesel fuels with rapeseed oil methyl esters already represents a commercial activity in many countries of central Europe [5]. Several vegetable oils obtained from soybean, castor, sunflower, cotton, corn, palm, and others, are widely applied for biodiesel production [6]. The biodiesel quality obtained from several oil sources is associated to different parameters, which can be divided in two groups: the physico-chemical parameters (cetane index, flash point, viscosity, distillation, etc.) and the chemical composition (free and total glycerin, iodine index, mono-, di-, and triacylglycerides, etc.) [7]. In the EU the majority of biodiesel is made from rapeseed oil with sunflower oil as second. Diesel substitutes made from rapeseed oil are either rapeseed methyl ester (RME) or rapeseed ethyl ester [8]. Biodiesel is typically produced by the reaction of vegetable oils or animal fats with alcohol, methanol or ethanol, in the presence of catalysts, to produce monoalkylesters and glycerin, which is removed from the ester [9]. Combustibility and application of a substance as fuel depends on how easily it undertakes combustion, and on

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how much mechanical energy is gained during this process [10, 11]. Biodiesel shows improved volatility characteristics approaching those of petroleum diesel fuel [12]. Thermal analysis characterizes some physical and chemical properties of substances depending on the temperature at a defined heating rate, or on the time at a constant temperature. These techniques are settled to continuously monitor the physical or chemical changes of a sample which occur as the temperature of a sample is increased or decreased. Thermogravimetry (TG), Differential thermogravimetry (DTG), and differential scanning calorimetry are the principal thermoanalytical methods [13]. The purpose of this study is to investigate four different biodiesel blends by TG and derivative DTG, and to compare them with the thermogravimetric profile of diesel fuel.

Materials and methods

Seeds collection

The seeds were obtained from the society Cerealcon Dolj SA produced at Segarcea field, located in Dolj County, in Romania.

Oil extraction

Crude rapeseed oil was obtained through the cold extraction process using a press PU-200 from IPROCON SRL Craiova, with a capacity of 152–168 kg/h with a productivity of 67 l/h. After pressing, the oil was filtered in a filter with plates; model FU-01, to remove the residue.

Methyl ester production

The rapeseed oil was converted to biodiesel by transesterification to modify the parameters of the vegetable oil to make it closer to the parameters of diesel fuel. In the experiments a base catalyst was used, NaOH with a purity of 99% purchased from S.C. Laborex Romania. The quantity of catalyst used was measured with a precision balance model PGW 153e. The sample was prepared with a molar ratio 6:1 of methyl alcohol and rapeseed vegetable oil, using NaOH as catalyst (4%), under constant agitation at 60 °C. In the first phase, methanol and sodium hydroxide were placed to react under stirring until achieving a complete homogenization of the base catalyst, resulting in sodium methoxide. After reaction, the glycerin was separated by decantation and the biodiesel was washed with warm distilled water. The washing was followed by a heating process at 100 °C for 3 h.

Physico-chemical analyses

The physico-chemical tests on biodiesel were performed according to standardized methods ASTM and EN. Tests for flash point, kinematic viscosity, cetane number, and density determinations were done according to the standards adopted by Romanian Standards Association.

Diesel fuel

Diesel fuel was purchased from a local gas station from Craiova, Romania on November 5th 2011. Euro L Diesel is a diesel fuel from LuKoil Company obtained at Petrotel Ploiesti Refinery.

Thermal analysis

In this study, the thermal degradation characteristics of biodiesel blends were studied using a Diamond TG/DTG Analyzer from PerkinElmer Instruments. Thermogravimetric analysis provides a measurement of weight loss of the samples as a function of temperature and time. The apparatus consists of a microbalance within a furnace, allowing the weight of the sample to be continuously monitored while the temperature is controlled. Samples can be run either in a dynamic (temperature ramp) or in an isothermal mode [14]. The experimental procedure involves the placing of the sample in an aluminum crucible, setting the heating rate and the flow rate of the purge gas (air) and then starting the experiment. The samples were heated at room temperature with 10 °C per minute with an air flux of 150 ml/min. All thermal conversion data were recorded in a computer coupled to the thermoanalytical equipment and evaluated by Pyris software.

Results and discussion

The quality of the raw material influences the transesterification reaction. The results of the physico-chemical analyses for biodiesel of rapeseed oil and diesel fuel are displayed in Table 1. The biodiesel obtained by the methanol route is in accordance with the specifications established by ASTM and EN standards.

Biodiesel presents a higher value of flash point compared to diesel fuel. This value suggests that the rapeseed biodiesel can be transported or stored safely. For the kinematic viscosity of biodiesel, an increase was observed which suggests a reduced atomization and incomplete combustion in the engine. A higher cetane number for biodiesel provides more time for the fuel combustion process to be completed with shorter ignition delays. Biodiesel has a higher density than mineral diesel which

Table 1 Physical chemical properties of biodiesel of rapeseed and Euro L Diesel

Parameters	Methods	Biodiesel of rapeseed	Limits B100	Euro L diesel
Flashpoint/°C	ASTM D93	169	>130	77
Kinematic viscosity 40 °C/mm ² /s	ASTM D445	4.1	1.9–6.0	2.8
Cetane number	ASTM D613	53	≥47	51
Density at 15 °C/kg/m ³	EN ISO 3675	879	860–900	844

suggests an impact on fuel consumption. The fuel is determined volumetrically when it is introduced in the combustion chamber. The properties of diesel fuel are according to the standard SR EN 590/2010 [15].

Fuels for diesel engines are characterized by different properties from the gasoline, respectively hydrocarbon components must oxidize easily with the formation of peroxides and other products of incomplete oxidation, so that the autoignition start easily. Chemically there are some important differences between diesel and these biodiesel samples. Methyl esters have oxygen in their composition while diesel fuel does not. Diesel is composed of an average of 75% saturated hydrocarbons and 25% aromatics. Furthermore diesel is composed of saturated non-branched

molecules with carbon atoms ranging from C₁₂ to C₁₈ and aromatics. Biodiesel is a mixture of fatty acid methyl esters with a composition according to the oil source [15]. Thermal profile TG of diesel fuel presented one mass loss step. In diesel this occurs between 16.59 and 253.31 °C with a weight loss of 99.613% (Fig. 1) due to the decomposition of its compounds. Diesel fuel is thermally stable in air up to 40–50 °C. The mass loss step was attributed to the volatilization of the shorter carbon chains identified by the endothermic transition in the DTA curve between 50 and 160 °C. At 240 °C an exothermic peak is observed assigned to the hydrocarbons combustion. The maximum speed of the weight loss of the sample according to the DTG curve was observed at 210 °C. The TG curve of B10 in Fig. 2 shows a

Fig. 1 TG, DTG, and DTA curves of diesel fuel in air 150 ml/min at a heating rate of 10 °C/min

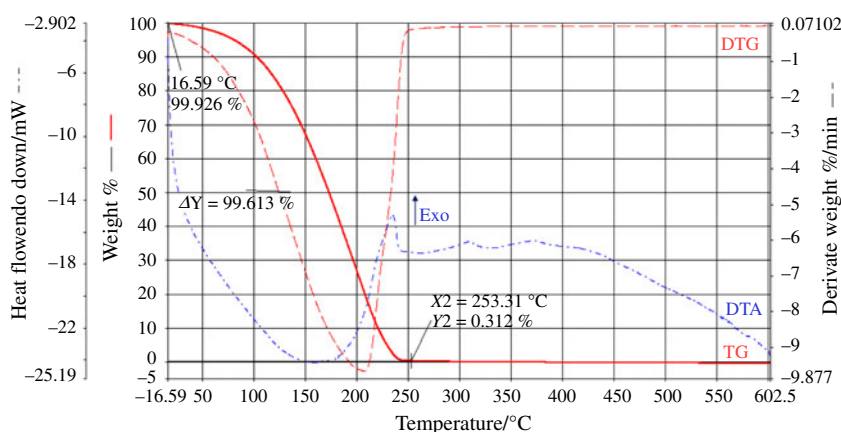
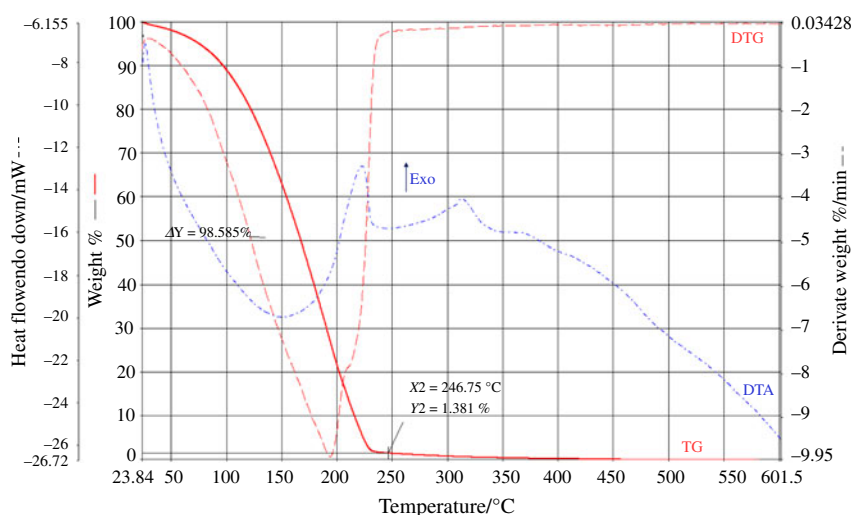


Fig. 2 TG, DTG, and DTA curves of B10 in air 150 ml/min at a heating rate of 10 °C/min



level of thermal stability higher than the diesel fuel with two mass loss stages. The first takes place in the 23.84–246.75 °C with a weight loss of about 98.585% assigned to the decomposition of hydrocarbons of diesel fuel. The second is easier to 246.75 °C up to 450 °C with a weight loss of about 1.381% assigned to the decomposition of the methyl esters. The calorimetric analysis of the DTA curve of B10 showed an endothermic transition in the range 25–170 °C in TG corresponding to a mass loss of 98% primarily related to the volatilization of saturated hydrocarbons. After this endothermic transition occurred, there were two exothermic transitions: one between 200 and 250 °C with a peak at 230 °C assigned to the combustion of diesel fuel and the second between 300 and 350 °C with a peak at 315 °C assigned to the combustion of methyl oleate, the most abundant component in the rapeseed biodiesel. The maximum speed of the weight loss of the sample according to the DTG curve was observed at 190 °C.

The TG curve of B20 in Fig. 3 presents two main mass loss stages. The first one is between 32.03 and 257.70 °C with a weight loss of 97.518% assigned to the decomposition of hydrocarbons of diesel fuel. The second stage is between 257.70 and 500 °C with a weight loss of 2.475% assigned to the decomposition of the methyl esters. As it can be seen in Fig. 3, practically there is no significant residue after 500 °C for the sample in the oxidative ambient of the air flow. On the DTA curve different processes were observed: an endothermic transition between 32.05 and 200 °C assigned to the volatilization of hydrocarbons, and two exothermic transitions, one between 200 and 250 °C with a peak at 240 °C assigned to the combustion of diesel fuel and the second between 300 and 350 °C assigned to the combustion of RME. The maximum speed of the weight loss of the sample according to the DTG curve was observed at 220 °C. The TG curve of B40 in Fig. 4 presents two mass loss stages. The first one is between 14.57 and 280.54 °C with a weight

Fig. 3 TG, DTG, and DTA curves of B20 in air 150 ml/min at a heating rate of 10 °C/min

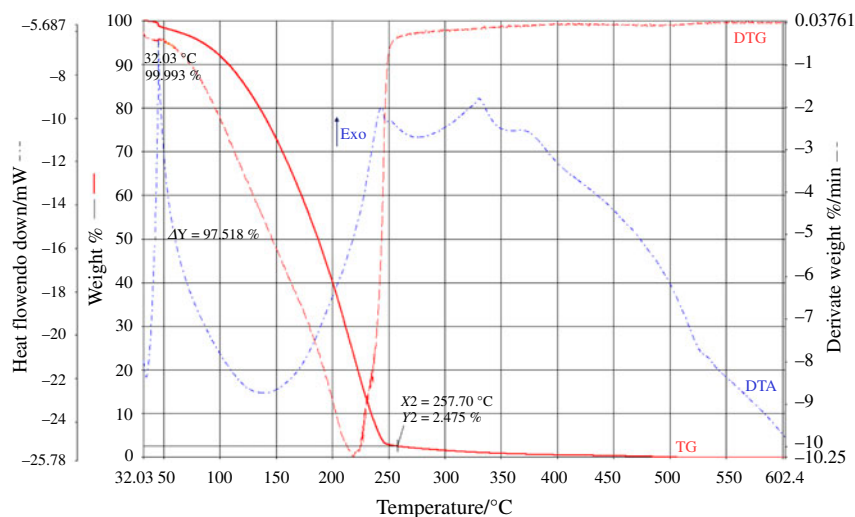
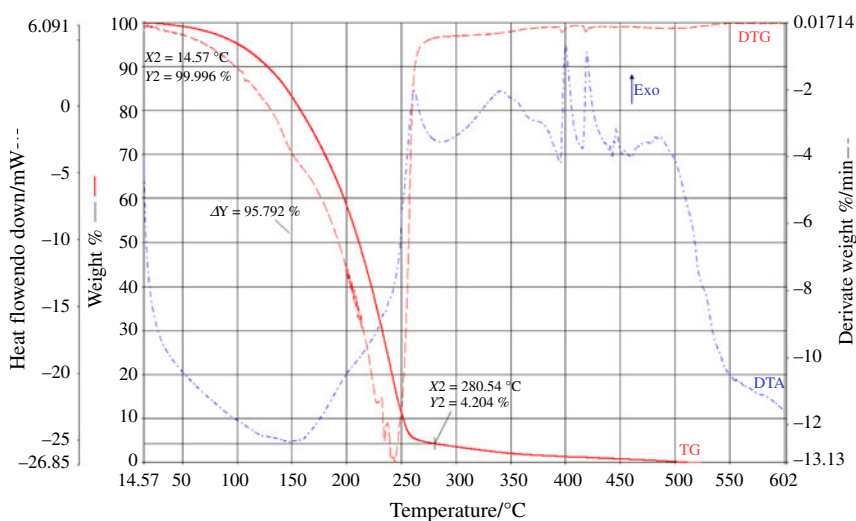


Fig. 4 TG, DTG, and DTA curves of B40 in air 150 ml/min at a heating rate of 10 °C/min



loss of 95.792% assigned to the decomposition of hydrocarbons and methyl esters with short carbon chain lengths ranging from C₁₂ to C₁₈. The second stage is between 280.54 and 510 °C with a weight loss of 4.204% assigned to the decomposition of methyl esters with long carbon chain lengths ranging from C₁₈ to C₂₂. The DTA curve presents an endothermic transition between 14.57 and 200 °C assigned to the volatilization of hydrocarbons, and six exothermic transitions attributed to the combustion of the methyl esters (methyl myristate, methyl palmitate, methyl stearate, methyl oleate, methyl linoleate and methyl linolenate), one between 250 and 300 °C with a peak at 260 °C, the second between 300 and 350 °C with a peak at 335 °C, the third between 350 and 400 °C with a peak at 400 °C, the fourth between 410 and 435 °C with a peak at 430 °C, the fifth between 435 and 450 °C with a peak at 445 °C, and the sixth between 450 and 500 °C with a peak at 480 °C. The maximum speed of the weight loss of the sample according to the DTG curve was observed at 240 °C.

The TG curve of B50 in Fig. 5 presents two mass loss stages. The first one is between 35.84 and 285.35 °C with a weight loss of 95.058% assigned to the decomposition of hydrocarbons and methyl esters with short carbon chain lengths ranging from C₁₂ to C₁₈. The second step is between 285.35 and 510 °C with a weight loss of 4.942% assigned to the decomposition of methyl esters with long carbon chain lengths ranging from C₁₈ to C₂₂. As it can be seen in Fig. 5, practically there is no significant residue after 550 °C. The DTA curve presents an endothermic process between 50 and 200 °C attributed to the volatilization of hydrocarbons and four exothermic processes with peaks at 260, 335, 420, and 480 °C assigned to the combustion of methyl stearate, methyl oleate, methyl linoleate, and methyl linolenate. The maximum speed of the weight loss of the sample according to the DTG curve was observed at 240 °C.

Methyl ester of rapeseed is a methyl ester mixture made up of saturated and unsaturated C₁₆ to C₂₂ fatty acids. As

Fig. 5 TG, DTG, and DTA curves of B50 in air 150 ml/min at a heating rate of 10 °C/min

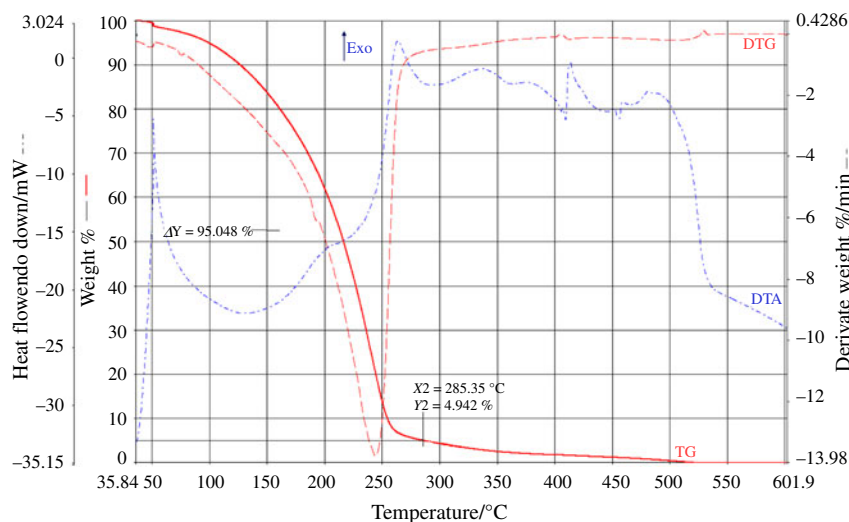
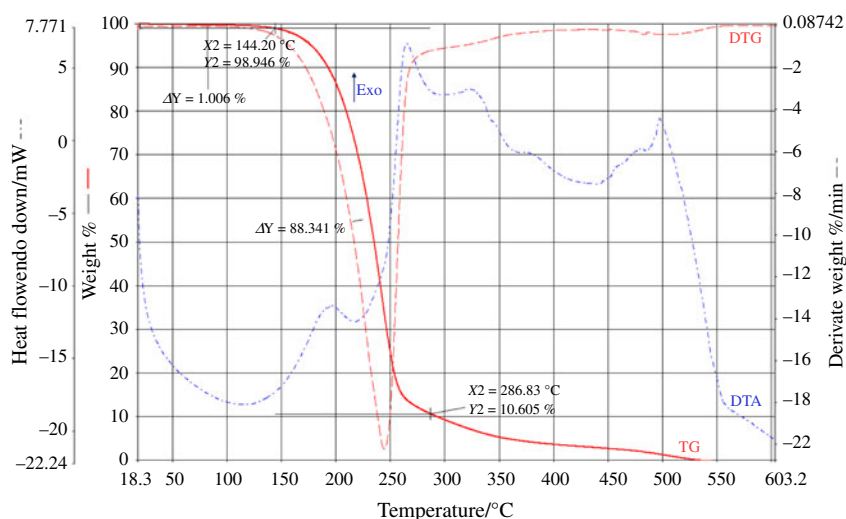


Fig. 6 TG, DTG, and DTA curves of rapeseed biodiesel in air 150 ml/min at a heating rate of 10 °C/min



the fatty acid methyl esters carbon chains lengths increases, the boiling point increases. The main constituents of methyl ester of rapeseed are the oleic, linoleic, linolenic, palmitic, and myristic acids. The TG curve of rapeseed biodiesel in Fig. 6 presents a level of thermal stability up to 144.20 °C with three mass loss stages. The first one is between 18.13 and 144.20 °C with a small mass loss of weight of 1.006% corresponding to the burning of moisture and volatile fractions which released a small amount of heat. The second is between 144.20 and 286.83 °C with a weight loss of about 88.341% corresponding to the thermal-oxidative decomposition of methyl esters with short carbon chains lengths. The third stage is between 286.83 and 530 °C with a total weight loss of 10.605% attributed to the decomposition of methyl esters with long carbon chains lengths. The DTA curve presents an endothermic transition between 18.13 and 150 °C assigned to the volatilization of the methyl esters, and four exothermic transitions, one between 150 and 200 °C with a peak at 195 °C, the second between 250 and 300 °C with a peak at 270 °C, third between 300 and 350 °C with a peak at 330 °C and the fourth between 470 and 530 °C with a peak at 495 °C attributed to the combustion of methyl esters. The maximum speed of the weight loss of the sample according to the DTG curve was observed at 240 °C.

A thermal comparison between the fuels is shown in Fig. 7, showing substantial differences between diesel and biodiesel blends. Through the same process, it was observed that the decomposition occurred in a single stage in the case of petrodiesel fuel, in two stages for biodiesel blends and in three stages for biodiesel. These mass losses are attributed to the decomposition of the methyl esters, mainly of the methyl oleate, methyl lineolate, and methyl linolenate, the most abundant components in the biodiesel, given the high concentration of these acids in rapeseed oil. The decomposition and volatilization process of the biodiesel and biodiesel blends initiates and finishes at higher temperatures than the diesel fuel. The lower stability of diesel can be due

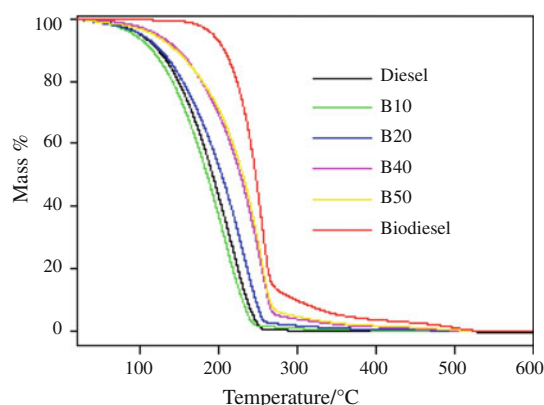


Fig. 7 TG curves of diesel, biodiesel blends, and rapeseed biodiesel

to its content of aromatic compounds and some organic volatile compounds that are not present in biodiesel [16]; this difference can also be explained by the chain size as diesel samples contain shorter molecules in relation with the biodiesel blends, making volatilization easier.

Conclusions

The thermal behaviors of diesel fuel and biodiesel blends were evaluated using TG, DTA, and DTA techniques. From the TG curves it was observed that rapeseed biodiesel has a higher thermal stability than the others fuels; this could be attributed to the high content of methyl oleate and methyl lineolate in their composition. Volatilization was observed at different temperatures according to the chemical composition of the methyl esters and hydrocarbons from diesel fuel. Except for the diesel fuel, which has a significantly different thermal decomposition behavior, the biodiesel blends presents more decomposition stages with higher decomposition temperatures indicating the formation of more stable compounds.

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References

1. Robu T, Robu AD, Chiran A, Gindu E. Studies regarding the potential of biodiesel production in the north-east development region of Romania. *Environ Eng Manag J*. 2009;8(5):1035–8.
2. Leca M, Tcanceco L, Micutzi M, Staicu T. Optimization of biodiesel production by transesterification of vegetable oils using lipases. *Rom Biotechnol Lett*. 2010;15(5):5618–30.
3. Lois E. Definition of biodiesel. *Fuel*. 2007;86:1212–3.
4. Adamczak M, Bornscheuer UT, Bednarski W. Review: the application of biotechnological methods for the synthesis of biodiesel. *Eur J Lipid Sci Technol*. 2009;111:808–13.
5. Austrian Biofuels Institute. Biodiesel documentation of the world-wide status. Austria: ABI; 1997.
6. Freire LMS, Bicudo TC, Rosenhaim R, Sinfronio FSM, Botelho JR, Carvalho Filho JR, Santos IMG, Fernandes VJ Jr, Antoniosi Filho NR, Souza AG. Thermal investigation of oil and biodiesel from *Jatropha curcas* L. *J Therm Anal Calorim*. 2009;96:1029–33.
7. Mittelbach M. Diesel fuel derived from vegetable oils, VI: specifications and quality control of biodiesel. *Bioresour Technol*. 1996;56:7–11.
8. Kavalov, B. Biofuel potentials in the EU. Report EUR 21012 EN. Institute for prospective technological studies. Joint research centre; 2004.
9. ASTM American society for testing and materials. ASTM D6751-02 specification for biodiesel fuel blend stock (B100) for middle distillate fuels; 2002.
10. Stournas S, Lois E, Serdari A. Effect of fatty acid derivatives on the ignition quality and cold flow of diesel fuel. *J Am Oil Chem Soc*. 1995;72:436.

11. Conceicao MM, Candeia RA, Dantas HJ, Soledade LEB, Fernandes VJ, Souza AG. Rheological behavior of castor oil biodiesel. *Energy Fuel*. 2005;19:2185.
12. Lujaji F, Berezky A, Janosi L, Novak C, Mbarawa M. Cetane number and thermal properties of vegetable oil, biodiesel, 1-butanol and diesel blends. *J Therm Anal Calorim*. 2010;102: 1175–81.
13. Kok MV. Recent developments in the application of thermal analysis techniques in fossil fuels. *J Therm Anal Calorim*. 2008;91(3):763–73.
14. Rodriguez RP, Perez L, Alfonso M, Duarte M, Caro R, Galle J, Sierens R, Verhelst S. Thermal behavior of *Jatropha curcas* oils and their derived fatty acid ethyl esters as potential feedstocks for energy production in Cuba. *J Therm Anal Calorim*. 2011;. doi: [10.1007/s10973-011-1827-8](https://doi.org/10.1007/s10973-011-1827-8).
15. Fuel for Diesel Engines. <http://www.lukoil.ro/pdf/EuroLDiesel.pdf>. Accessed Nov 2011 (in Rumanian).
16. Rodriguez RP, Sierens R, Verhelst S. Thermal and kinetic evaluation of biodiesel derived from soybean oil and higereta oil. *J Therm Anal Calorim*. 2009;96:897–901. doi:[10.1007/s10973-009-0043-2](https://doi.org/10.1007/s10973-009-0043-2).