Biodiesel Production from Waste Oil and Its Blends with Glycerol Ketals

PETRE CHIPURICI[1], ALEXANDRU VLAICU[1], CRISTIAN EUGEN RADUCANU[2], STEFANIA DANIELA BRAN[3], ADINA IONUTA GAVRILA[1]*

[1]University Politehnica of Bucharest, Faculty of Applied Chemistry and Materials Science, Bioresources and Polymer Science Department, 1-7 Gh. Polizu Str., 011061, Bucharest, Romania

[2] University Politehnica of Bucharest, Faculty of Applied Chemistry and Materials Science, Chemical and Biochemical Engineering Department, 1-7 Gh. Polizu Str., 011061, Bucharest, Romania

[3]Bucharest University of Economic Studies, Doctoral Programs in Economics and Law, 11 Tache Ionescu Str., 010352, Bucharest, Romania

In the last years, researchers, governments, and industries spent significant resources towards biofuels production. Biodiesel has attracted attention as a renewable, non-toxic, and biodegradable fuel. In this work, biodiesel production using waste oil from the margarine industry is described. Another objective of this paper is additivation of biodiesel with glycerol ketals in order to improve the physicochemical properties. Biodiesel blends with additives were further analyzed and compared with the EN biodiesel specifications. The characterization of biodiesel blends revealed the improvement of their density, viscosity, cold filter plugging point, flash point, and iodine index.

Keywords: biodiesel, waste oil, glycerol ketals, additives

In the last decades, the research regarding alternative fuels has received a lot of attention due to global warming and depleting fossil fuel resources. Biofuels are considered a sustainable alternative to fossil fuels because they are prepared from renewable materials and are friendlier to the environment [1-6]. Among biofuels, biodiesel is accepted as the *future fuel* because its low toxicity, very low sulfur content, and biodegradability [7-9]. This biofuel presents such advantages as high cetane number, high flash point, high combustion efficiency, and good lubrication [9-12]. The obstacles for biodiesel commercialization is the high production cost related to costs of the raw materials and the competition between the food and fuel industries over agricultural land and plants with high oil content. In this context, using cheaper feedstock, such as waste cooking oil (WCO), is a promising alternative, and would add to the positive environmental impact of using alternative fuels. Waste oil is a significant feedstock due to an increasing quantity being available as a result of economic development specifically in the food industry [13-16]. Due to the interest in biodiesel production, design, modeling, and simulation of production facilities were the subject of recent studies [17-21].

A problem derived from biodiesel production is the large excess of glycerol, the main byproduct generated in this process, which must be dealt with identifying new valuable products and pathways for glycerol valorization. Glycerol produced through this process contains methanol and cannot be used as an ingredient in food and pharmaceutical products. An alternative is the usage as fuel additive, but its high boiling point is undesirable in fuels. Thus, in recent years, transformation of glycerol into valuable derivatives by different catalytic process such as: esterification, etherification, dehydration, hydrogenation, and oxidation were studied by many research groups [22-25]. Glycerol derivatives present important uses such as surfactants and solvents, but in last decade a new strategy has been developed, consisting of utilizing these compounds as biofuel additives. Thus, the influence of oxygenated compounds obtained from glycerol on biodiesel quality parameters was studied and adding of these glycerol derivatives was found to improve cold flow, ignition properties, and cetane number of fuels [26-28].

Ketalization of glycerol with different ketones can be an attractive alternative for glycerol valorization, providing oxygenated compounds that can be used as biodiesel additives. These compounds possess antioxidant and good combustion properties and by additivation of biofuels they improve viscosity, cold filter plugging point (CFPP), pour point (PP), and particles emission [29-31].

The aim of this paper is to present an alternative feedstock for biodiesel synthesis and its subsequent additivation with glycerol ketals. In this study biodiesel obtained through transesterification of waste oil from the margarine industry, which has no known uses and requires being stored, was blended with glycerol ketals and the influence of these compounds on the density, viscosity, CFPP, flash point and iodine index was studied.

Experimental part

Materials and methods

Biodiesel was obtained by transesterification of waste oils from the margarine industry with methanol (J.T. Backer) in alkaline catalysis (KOH, Merck). In order to obtain glycerol ketals, acetone (Lab-Scan Analytical Sciences), 2-butanone (Reactivul) and glycerol (Reactivul) were used. Sulfuric acid (Merck) solution (5%) was used as catalyst, and ethyl alcohol (Chimreactiv SRL) and ethyl acetate (Chimactiv SRL) were used as solvents. 1,2-Isopropylideneglycerol (Solketal) used as standard for Gas Chromatography (GC) analysis was purchased from Sigma Aldrich.

Synthesis of biodiesel

Biodiesel was obtained by the transesterification of waste oils from the margarine industry with methanol, in batch homogeneous alkaline catalysis. The flow diagram of the operation for obtaining biodiesel is shown in figure 1. Initially, the raw oil was characterized by determining the acidity index, the iodine index, and the saponification index.

* email: adinagav@yahoo.com

The reaction is performed in a 250 mL three-necked round bottomed flask, equipped with mechanical stirring system, thermometer, reflux condenser, and a temperature controlled heating bath. The transesterification reaction was carried out under the following conditions: molar ratio oil / methanol = 1/6; 1/12; 1/18; catalyst (KOH) = 1.5 and 2% w/w of fed oil; temperature = 60 °C; reaction time = 2 and 3 h.

The separation of the phases resulted from the reaction was accomplished by decantation. Biodiesel was washed with water, dried on calcium chloride (anhydrous), and then characterized. For the chosen optimum conditions, a larger amount of biodiesel (800 mL) was prepared.

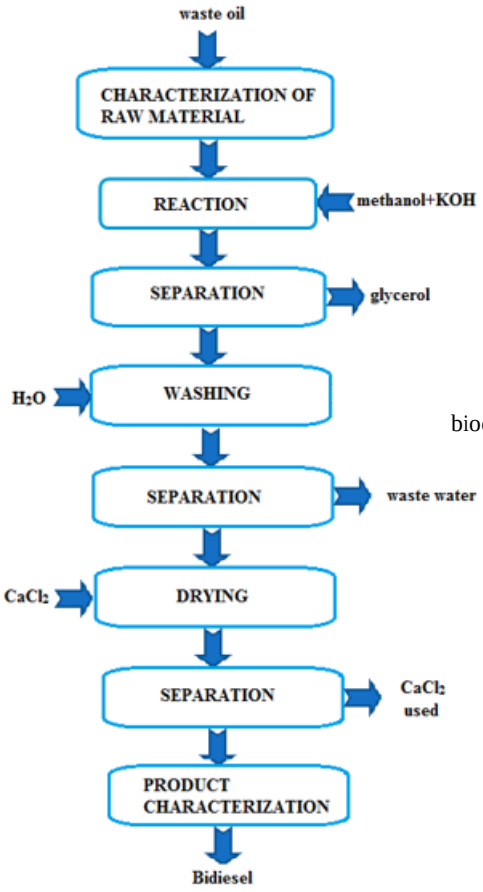

Fig. 1. Flow diagram for biodiesel producti

Analysis of biodiesel

In order to determine the glycerol, mono-, di-, and triglyceride content, the biodiesel obtained from transesterification of oil waste was analyzed by Gas Chromatography (GC) according to EN 14105. The analyses were done using a GC equipped with an injection system, adjustable temperature, and a flame ionization detector (capillary column - stationary phase - 100% dimethyl-polysiloxane, 15 m length, 0.32 mm inner diameter, 0.1µm film thickness, hydrogen carrier gas). The phosphorus content was determined by spectrophotometric method according to EN 14107.

Synthesis of glycerol ketals

The glycerol ketals used for the biodiesel - additives blends were synthesized according to the reaction scheme and flow scheme shown in figures 2 and 3, following the procedure described by Miriam de Torres et al. [26]. Thus, starting from acetone and butanone, two glycerol ketals, k_1 and k_2, were obtained.

Analysis of glycerol ketals

The synthesized ketals (k_1 and k_2) were analyzed using an HP 6890 gas chromatograph equipped with a FID

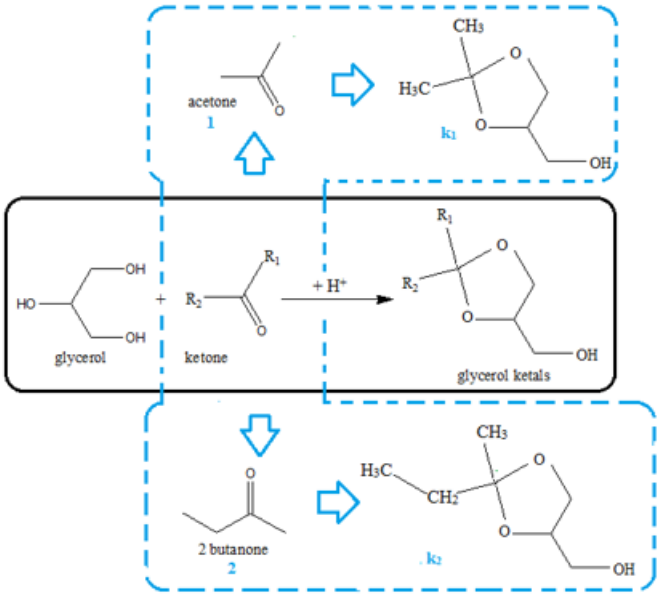

Fig. 2. Reactions used for synthesizing glycerol ketals

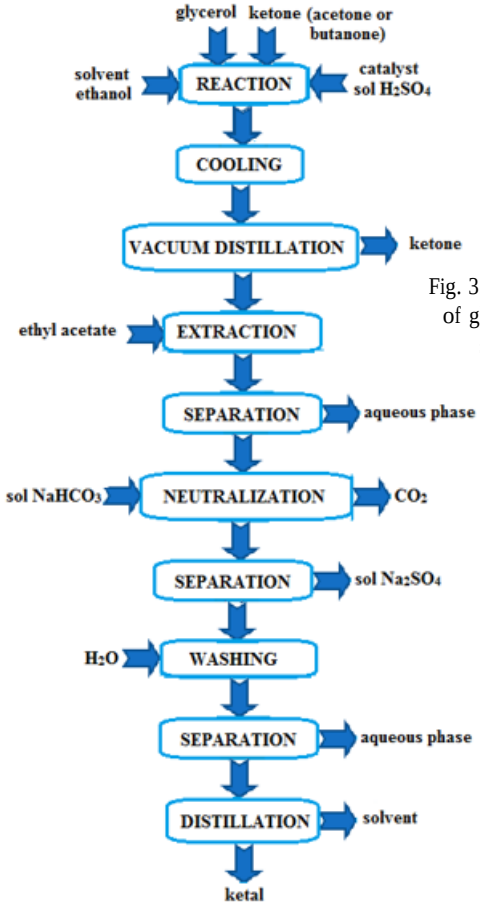

Fig. 3. Flow diagram of glycerol ketals synthesis

detector and a DB-5 capillary column (30 m length, 0.25 mm inside diameter, 0.25µm film thickness). Helium was used as a carrier gas. The temperature program used for this analysis was as follows: the initial temperature was set at 400°C; after 2.5 min the temperature was programmed to rise to 90 °C with a ramp of 10 °C per minute after which the temperature increased to 250 °C at a rate of 30 °C per min.

Preparation of biodiesel - glycerol ketals blends

Glycerol ketals (k_1 and k_2) were mixed in ratios of 1, 3, 5, 7, and 10 g/100 g biodiesel. The corresponding blends were subjected to an analysis according with EN 14214/2013 - Automotive fuels - Fatty acid methyl esters (FAME) for diesel

engines - Requirements and test methods. The results were compared to the unblended biodiesel. All experiments and analyses were repeated three times and average values were used. The methods used to determine the accordance of biodiesel - glycerol ketals to existing standards are given in SR EN 14214, namely for: density EN ISO 3675; viscosity EN ISO 3104; flash point EN ISO 3679; iodine index EN 14111; cold filter plugging point (CFPP) EN 116.

Results and discussions

Characterization of feedstock

Waste oil from the margarine industry used as raw material for biodiesel production is characterized by an acid content of 0.63% of the sample mass, which can be correlated to an acidity index of approximately 6.5 mg KOH/g sample determined by titration with potassium hydroxide in the presence of phenolphthalein. The value of the iodine index was determined by titration according to the Hanus method, having a value of 44 g I_2/100 g sample and the saponification index 221.63 mg KOH/g sample. Using the determined saponification index, we could estimate an average molecular weight of 758 g/mol, approximated to 800 g/mol, in order to assure methanol excess required for the reaction due to the lack of homogeneity in the raw material.

An important parameter of biodiesel quality regarding its accordance with European Standard EN 14214 is the phosphorus content, which must be below 4 mg P/kg in order not to affect the operation of catalytic converters used as exhaust systems in vehicles [32, 33]. Considering the origin of raw material, *i.e.*, waste oils from margarine production, it was necessary to determine the phosphorus content of this raw material. The value obtained by the spectrophotometric determination of the phosphorus content was 3.5 mg P/kg, indicating that no pretreatment of the raw material is required.

Synthesis of biodiesel

The dependence to working parameters of conversion to biodiesel and the quality of the obtained biodiesel was studied by varying the amount of catalyst used, the excess of methanol, and the reaction time. The working conditions and results obtained in the transesterification reaction are shown in table 1.

It can be seen that in all carried out experiments conversions of over 99% were obtained with no major differences between the samples. For these reasons we have chosen the following experimental conditions to obtain a higher amount of biodiesel: molar ratio oil / methanol = 1/6, 1.5% catalyst, and a reaction time of 180 min.

Characterization of glycerol ketals - biodiesel mixtures

European Standard 14214/2013 provides all relevant characteristics, requirements, and test methods for fatty acid methyl esters (FAME).

The petroleum fuel quality is correlated with the density because it affects the engine performance. A high density indicates the presence of aromatic hydrocarbons in the fuel composition which burns slower. Density in correlation with chemical composition influences certain fuel properties such as jet penetration, self-ignition resistance, Diesel index, and heating value. Influence of the ketal concentration in the biodiesel / ketal mixture on its density is presented in figure 4.

As shown in figure 4 the density of biodiesel blends with synthesized glycerol derivatives is proportional with the amount of the glycerol ketals added. The increase is justified by the additive character of density and the higher

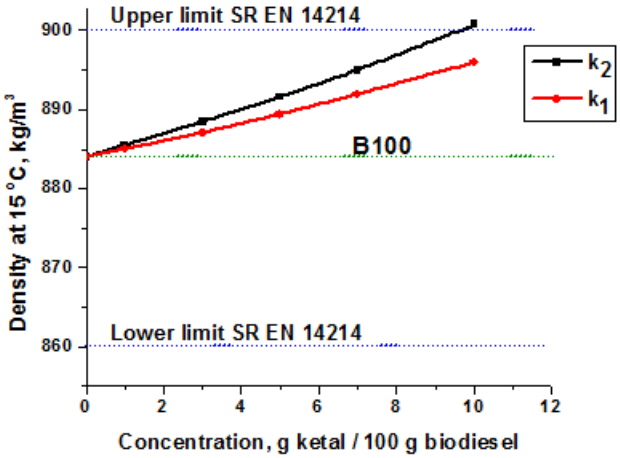

Fig. 4. Influence of ketal concentration on density

density of the ketals. The increase in density of the mixtures prepared with the increase of the ketal content can be observed, but these fall within the limits imposed by SR EN 14214/2013. The exception appears using the maximum concentrations of glycerol ketal derived from methyl ethyl ketone ketal, *i.e.*, 10 g ketal/100 g biodiesel, when the density values of the mixtures are above the limit admitted by the standard.

Viscosity is the property of fluids to produce tangential tensions that prevent the movement of molecular layers. This property is due to the internal friction forces between the molecules. The fuel combustion is directly influenced by viscosity due to the spraying process; a low viscosity favors the formation of a suitable fuel jet resulting in a homogeneous air-fuel mixture, thus ensuring optimum combustion conditions.

For the proper operation of the thermal motors, the viscosity variation must be as small as possible for the operating temperature range. For biodiesel, SR EN 14214/2013 stipulates that the viscosity at 40 °C should be in the range 3.5 - 5 mm^2/s. The lower viscosity limit is imposed by the requirement of satisfactory lubrication of the moving parts in the injection system and the upper limit by the injection characteristics and the deposits in the engine. A viscosity that falls within the limits required by quality

Molar ratio oil/methanol	1/6			1/12	1/18
Catalyst (% w/w)	1.5		2	1.5	1.5
Reaction time (min)	120	180	180	180	180
GC analysis (% w)					
Monoglyceride	0.43	0.28	0.28	0.26	0.32
Diglyceride	0.04	0.16	0.16	0.05	0.04
Triglyceride	0.04	0.06	0.05	0.03	0.07
Free glycerol	0.02	0.0003	0.03	0.0001	0.03
Conversion (%)	99.47	99.50	99.48	99.66	99.54

Table 1
WORKING CONDITIONS AND RESULTS OBTAINED IN THE TRANSESTERIFICATION OF WASTE OIL WITH METHANOL

standards ensures proper lubrication as well as proper pumping and spraying characteristics.

The presence of ketals in biodiesel leads to a slight reduction in the viscosity of the mixture. The values obtained fall within the limits imposed by standard SR EN 14214/2013, as can be seen from the data presented in figure 5.

The flash point is the lowest temperature at which, under the specified conditions and at a pressure of 760 torr, the vapor and air mixture at the surface of the product ignites

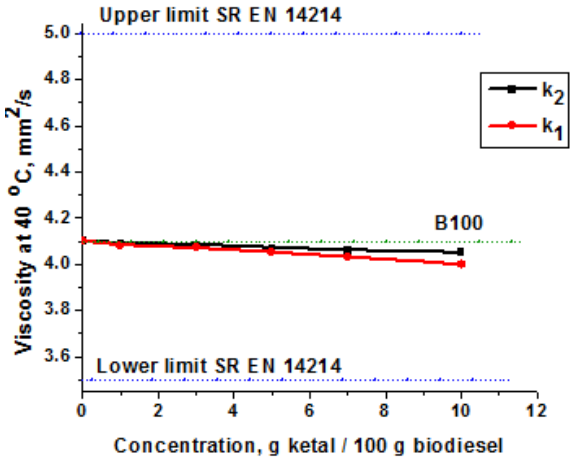

Fig. 5. Influence of ketal concentration on viscosity

for the first time in contact with an open flame. The flash point is related to the presence of volatile, light fractions that can form explosive mixtures with air without being proportional to the concentration of these fractions. The flash point characterizes the degree of fire safety during storage.

Experimental data revealed a similar behavior for the two glycerol derivatives tested. The maximum flash point of 164.5 °C is reached for pure biodiesel. Mixing ketals with

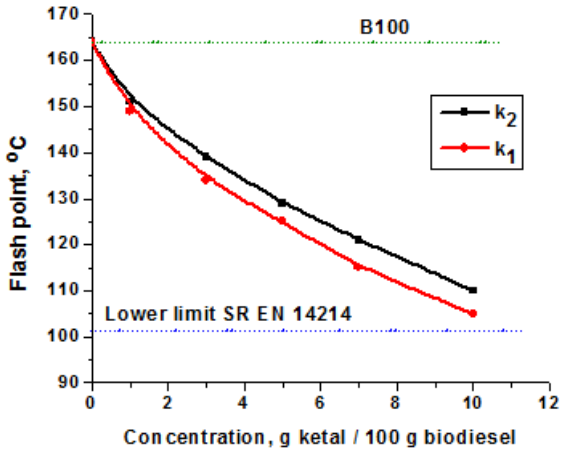

Fig. 6. Influence of ketal concentration on flash point

biodiesel leads to a reduction of the flash point which can be explained by the fact that pure glycerin derivatives have lower flash points than pure biodiesel. As shown in figure 6 even at maximum concentrations of ketals, the value of the flash point falls within the limit required by the standard.

The iodine index provides information about the degree of unsaturation of the samples. The presence of double bonds in biodiesel components has repercussions on the stability of this product, since these double bonds are susceptible to oxidation by the formation of hydroperoxides.

The introduction of ketals into the biodiesel / ketal mixture leads to a decrease in the iodine index of the mixture as shown in figure 7.

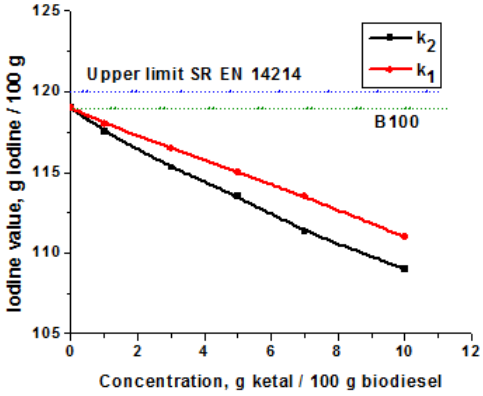

Fig. 7. Influence of ketal concentration on iodine index

Concerning the low temperature properties of diesel blends related to the FAME quality used as blending components, clear indications have emerged regarding the relationship with saturated monoglycerides and sterile glycosides. Since no test method has yet been developed to detect these components separately, an intermediate solution in establishing CFPP (limit filtrability temperature) and limitations of pour point were included in the version approved in 2013 of SR EN 14214. In the previous editions there was no such correlation.

The experimental data obtained in the CFPP determination of biodiesel / ketal mixtures (fig. 8) show that these compounds have a lowering effect on CFPP with increasing the ketal concentration in the mixture.The climate-dependent requirements for FAME used as a blending component for diesel fuel are shown in table 2.

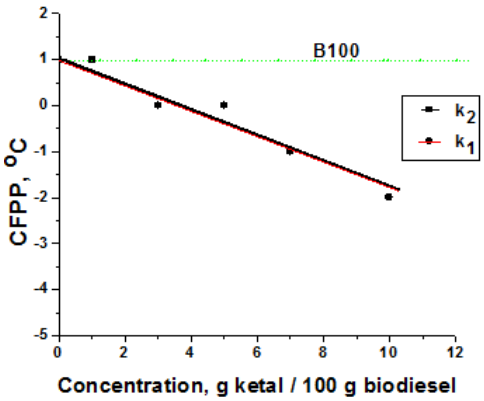

Fig. 8. Influence of ketal concentration on CFPP

Using additives in biodiesel to meet climate-dependent requirements may result in their incompatibility with diesel fuel or heating fuel. Low temperature flow additives must be specifically chosen for the quality of diesel fuel or heating

Season	Period	Cloud point °C, max.	CFPP °C, max.	Monoglycerides content % (w/w), max.
Summer	1 May – 30 September	0	-5	0.7
Winter	1 October – 30 April	-3	-10*	0.7
* Non-additivated product				

Table 2
CLIMATE-DEPENDENT REQUIREMENTS FOR FAME USED AS A COMPONENT FOR DIESEL FUEL

fuel and FAME in order to ensure performances according with the requirements of EN 590.

Conclusions

A low-cost and environmentally friendly raw material derived from margarine industry was used successfully for biodiesel production. The higher yield in biodiesel was obtained using the following conditions: molar ratio oil / methanol = 1/6, 1.5% catalyst, 60 °C temperature, and a reaction time of 180 min. Biodiesel was blended with glycerol ketals obtained by reaction of glycerol with two ketones (acetone and methyl-ethyl-ketone). The blends of biodiesel with ketal-based additives present an increased density compared to pure biodiesel, a lower viscosity at 40 °C and it decreases with increasing the percentage of tested additives in the fuel, lower CFPP, lower flash point, and lower iodine indexes than the initial biodiesel sample.

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