BIODIESEL PRODUCTION FROM WASTE COOKING OIL

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Abstract

The study theme constitutes a global interest challenge in terms of decreasing the fossil fuel reserves, and ensuring environmental protection in the context of sustainable development, which has created favourable preconditions for approaching the manufacture of alternative fuels.

The main objective of this study was to manufacture biodiesel by transesterification of fatty acids from vegetable oils made of sunflower or palm tree with basic catalysts methanol, and compare the optimum condition of fatty acid methyl ester(biodiesel production) from waste sunflower cooking oil and waste palm cooking oil through transesterification in the presence of NaOH respectively, KOH.

It was found that the highest efficiency of the transesterification process of waste sunflower and palm cooking oil, under the same operating conditions was obtained when we used the raw waste vegetable oil and sodium hydroxide as a catalyst (92.8%). Homogeneous catalysis in the presence of KOH resulted in yields of 68% in case of transesterification of waste palm cooking oil and 76% respectively for waste sunflower cooking oil.

Keywords: biodiesel, waste cooking oil, transesterification

INTRODUCTION

Due to the increase of primary energy consumption and according to European standards, Romania, along with all European countries should take measures to replace fossil fuels used in transport with biofuels, which would represent min. 5.75% until 31 December 2010 and 20% by 2020 (EU Directive 2003/30 / EC).

Due to the interest shown by man to replace fossil fuels and the need to reduce greenhouse emissions, the focus is on the use of biofuels.

Thus biodiesel is an environmentally friendly fuel equivalent of diesel fuel, a promising source of energy, it is a biodegradable fuel processed from renewable biological sources with less harmful emissions than diesel fuel, for all types of diesel engines (Klass, L.D, 1998; Arjun B.Chhetri, s.a, 2008). It can be used directly or in admixture with the oil in internal combustion engines, having similar properties to that of diesel fuel. Abbreviations are used according to the percentage of biodiesel in the blend: B100 when using 100% biodiesel, or notations such as B5, B15 or B30 (the number indicates the percentage of biodiesel in the blend volume).

It is a renewable energy source whose burning does not release sulphur compounds, does not increase the level of CO_2 in the atmosphere, and the only negative is higher NO_x emissions which can be reduced by the

use of catalytic convectors. Studies show that by biodiesel combustion the carbon monoxide emissions decrease by 46.7%, material particles by 66.7%, unburned hydrocarbons by 45.2% and CO_2 by 68% compared to diesel fuel (Canakci, M. 2007). Biodiesel is a fuel derived from renewable sources with a high fat content such as oils from agricultural crops such as soybean, cotton, sunflower, canola, recycled vegetable oils or animal fats (Vicente et al, 2007).

The method for producing biodiesel is known for a long time, but it has become practical in recent years. Obtaining biodiesel can be carried out by homogeneous catalysis in acidic or basic environment and is found in the specialty literature as the acid homogeneous catalysis or basic homogeneous catalysis.

Biodiesel production by transesterification

The transesterification is the reaction of an ester with an alcohol (also known as alcoholysis) or an acid (acidolysis), which leads to the formation of another ester and another alcohol, respectively acid. For biodiesel production, the molecule of the natural triglyceride (fat or vegetable oil) reacts with a lower alcohol to form three molecules of fatty acid esters and glycerol.

Basic homogeneous catalysis represents the process of alkaline transesterification is carried out in the presence of an alkaline catalyst. The most used catalysts are potassium hydroxide (KOH), sodium hydroxide (NaOH), sodium methoxide (CH_3ONa), as well as sodium and potassium carbonate (N_2CO_3 and K_2CO_3).

Alkaline catalysts such as sodium hydroxide and potassium hydroxide are most commonly used catalysts in the transesterification because they are more efficient than acid catalysts. The alcohols used in the transesterification are those with a short carbon chain. The methanol used is mainly due to the lower price and higher reactivity (http://www.infomate.ro/revista/indexrev.html).

The transesterification with methanol (methanolysis) is the most widely used method for the production of biodiesel. The reaction proceeds by heating a mixture of 80-90% oil, 10-20% methanol and a small amount of catalyst. Figure 1 shows the general scheme of the process of transesterification of organic oils into biodiesel using methanol.

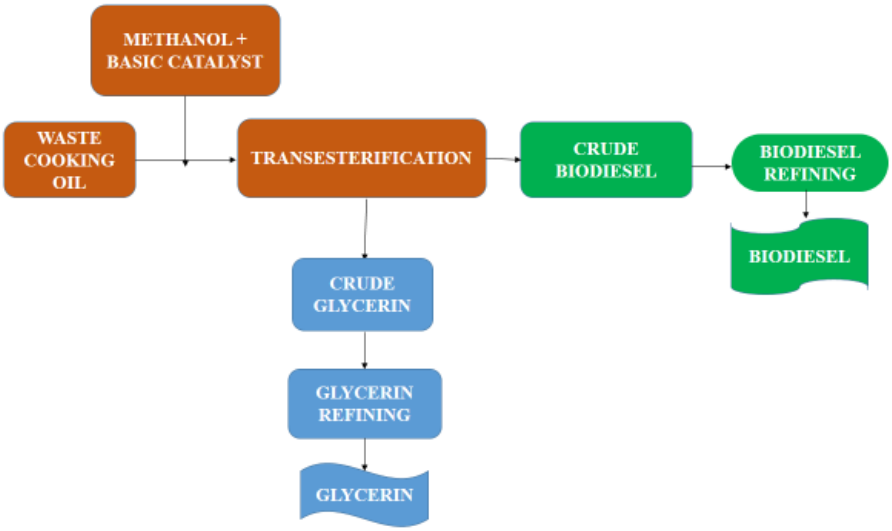

Fig. 1. General scheme of the process of transesterification of organic oils into biodiesel by using methanol

Transesterification of oils with an alcohol takes place in different phases. The first step is the conversion of triglycerides to diglycerides, followed by subsequent conversion of the monoglycerides and diglycerides, ultimately, the release of the glycerin from monoglycerides in each stage to form a ester molecule of alcohol with fatty acid from triglycerides (A.B.M.S. Hossain, A.N. Boyce, 2009). The transesterification reaction is moderately exothermic and reversible.

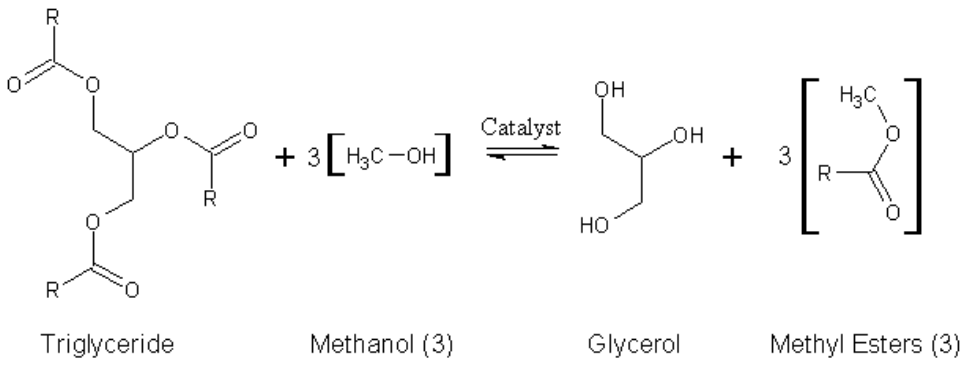

Fig.2. Biodiesel production using alkaline catalysts (http://biofuels.dbioro.eu/biodiesel.php)

MATERIAL AND METHODS

The material which is necessary to obtain the biodiesel process in the laboratory consisting of waste sunflower oil and waste palm oil from local restaurant (Oradea city), potassium hydroxide, sodium hydroxide, methanol and ethanol. The optimum reaction time for a batch process for obtaining biodiesel was 45 minutes.

Catalyst type and concentration, alcohol:oil ratio,type of alcohol reaction, temperature of transesterification play a significant role in bioediesel production. Waste cooking oil have higher acidity, requiring increased amounts of catalyst, because part of it is consumed for neutralization.

The biodiesel was separated from glycerol using separating funnel and washed with 5% water followed by magnesium sulphate anhydrous to remove water (A.B.M.S. Hossain, A.N. Boyce, 2009).

Sample Analysis

The biodiesel samples produced were analysed for diesel quality characteristics using standard methods of analysis. Some parameters (density, viscosity, acid value) have been analysed by specific method to verify whether the products fulfil the specification of standard methods (SR EN 14214).

1. Biodiesel production in the laboratory by homogeneous catalysis using methanol and sodium hydroxide catalyst

A. Waste palm cooking oil

In a volume of 500 ml liquid waste oil palm, heated to a temperature of 70° C was added 200 ml methanol and 2.8 g NaOH. The mixture, stirred by magnetic stirrer equipped with thermostat was subjected to transesterification.

Fig 3. Mixture of biodiesel – glycerine *obtained from* used palm oil

B. Waste sunflower cooking oil

Waste sunflower cooking oil used after filtration was subjected to a heating process of 70° C temperature. When reaching that temperature were introduced 200 ml of methanol 2.8 g of sodium hydroxide. The mixture was stirred by a magnetic stirrer equipped with thermostat.The mixture was subjected to transesterification maintained at rest for 24 hours. The complete transesterification has lead to the production of biodiesel, glycerol, respectively.

In figure 4 is seen the waste sunflower cooking oil in the reaction with the mixture of methanol-sodium hydroxide.

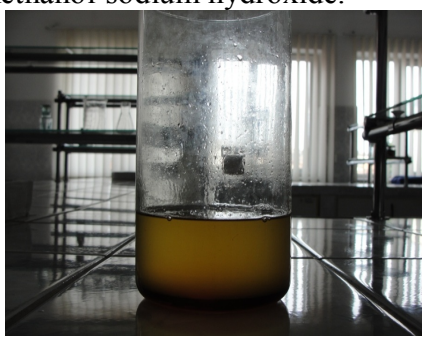

Fig.4. Biodiesel mixture – glycerine derived from used sunflower seeds oil

2. Biodiesel production by homogeneous catalysis with methanol and potassium hydroxide catalyst

A. *Waste palm cooking oil*

Waste palm cooking oil (500 ml) has been subjected to a heating process at a temperature of 70°C. On reaching the optimum temperature (70° C) we introduced 200 ml of methanol and 3.5 g of potassium hydroxide over the used oil. The mixture was stirred by a magnetic stirrer equipped with thermostat.

B. Waste sunflower cooking oil

In order to remove coarse dirt we filtered 500 ml waste sunflower cooking oil was subjected to a heating process at a temperature of 70^{o}C. Upon reaching that temperature, we introduced 200 ml of methanol and 3.5 g of potassium hydroxide. The mixture was stirred by a magnetic stirrer equipped with thermostat. The mixture subjected to transesterification was maintained for 24 hours.

RESULTS AND DISCUSSION

Following the transesterification process we obtained biodiesel and glycerine. In each case, we used the same amount of alcohol and the same quantity of catalyst using the proportions of 500 ml oil / 200 ml methanol / 2.8 g NaOH / 3.5 g KOH. The operating conditions in the laboratory were the same in each case.

Fig.5. Biodiesel from waste sunflower cooking oil

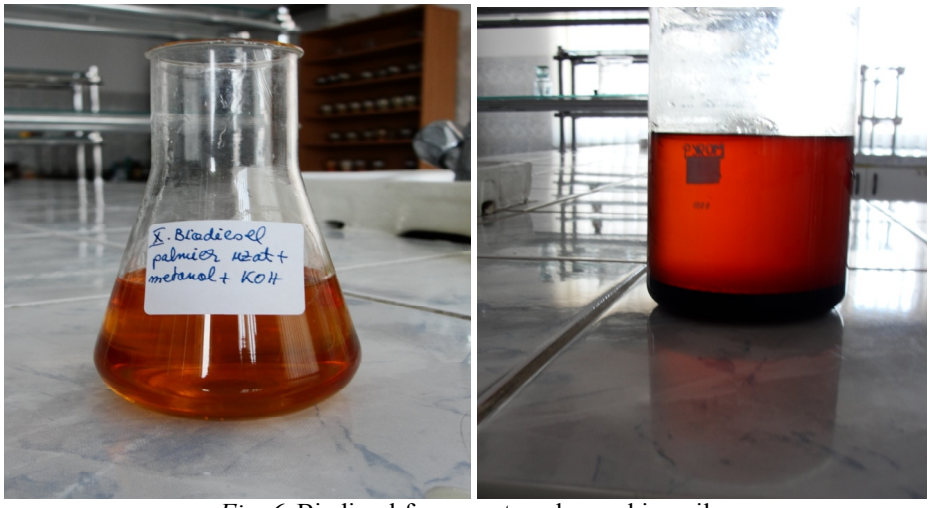

Fig. 6. Biodiesel from waste palm cooking oil

The results obtained in the case of biodiesel by homogeneous catalysis using sodium hydroxide as catalyst and the reaction medium methanol, are shown in table 1.

Table 1.

The mean values obtained by basic homogeneous catalysis with catalyst NaOH

Type of oil	**Quantity of waste cooking oil (ml)**	**Quantity of biodiesel obtained (ml)**	**Production yields (%)**
Waste palm cooking oil	500	458	91,6b n
Waste sunflower cooking oil	500	464	92,8

The data in the case of biodiesel production by homogeneous catalysis using potassium hydroxide as a catalyst, and the reaction medium methanol, are shown in table 2.

Table 2.

The mean values obtained by basic homogeneous catalysis with catalyst KOH

Type of oil	**Quantity of waste cooking oil (ml)**	**Quantity of biodiesel obtained (ml)**	**Production yields (%)**
Waste palm cooking oil	500	340	68
Waste sunflower cooking oil	500	380	76

Similar results for alkali-catalyzed transesterification (with NaOH and KOH) of sunflower oil also obtained Gemma et al (biodiesel yields 86.71% NaOH, 91.67% KOH respectively). According to the same authors production yields obtained are smaller compared to the case of using sodium or potassium methoxide (99.33% and 98.46%), because they contain

hydroxyl drags that produce the saponification of oil, in a small proportion (as an impurity). Higher production yields (up to 92%) were obtained by Dias et al for oils used for frying. Leung and Gau (2006) reported approximately 86% ethyl ester conversion of waste cooking oil using sodium hydroxide catalysts.

Analyzing biodiesel

The physico -chemical properties of biodiesel derived from waste palm oil and waste sunflower oil were evaluated in laboratory using specific gravity, kinematic viscosity, phosphorus content, acid value. The results are shown in table 3 and table 4.

Table 3

The main parameters of biodiesel production by homogeneous catalysis with methanol and sodium hydroxide catalyst

Properties	**Biodiesel**		**EN 14214**	
	Waste palm oil	*Waste sunflower oil*	*Lower limit*	*Higher limit*
Viscosity mm^2/s at 40^oC	5,1	4,8	3,5	5,0
Density g/cm^3 at 15^oC	0,869	0,87	0,86	0,90
Acid value mgKOH/g	0,27	0,1	-	0,5

Table 4

The main parameters of biodiesel production by homogeneous catalysis with methanol and potasium hydroxide catalyst

Properties	**Biodiesel**		**EN 14214**	
	Waste palm oil	*Waste sunflower oil*	*Lower limit*	*Higher limit*
Viscosity mm^2/s at 40^oC	4,98	4,76	3,5	5,0
Density g/cm^3 at 15^oC	0,864	0,867	0,86	0,90
Acid value mgKOH/g	0,25	0,1	-	0,5

Properties fulfill the restrictions of biodiesel standard (SR EN 14214). The SR EN 14214 standard for pure biodiesel sets the maximum acid value (acid number) at 0.5 mg KOH/g. The evaluated acid value of biodiesel from waste palm oil and waste sunflower oil fulfill the recommended range. The lowest value was found in the case of biodiesel from waste sunflower cooking oil (0.1 mg KOH/g)

From the results, it could be observed that the viscosity of biodiesel, (5.1 mm^2/s at 40^oC; 4.98, mm^2/s at 40^oC, from waste palm oil or 4,8 mm^2/s at 40^oC and 4.76 mm^2/s at 40^oC, from waste sunflower oil) was in agreement with SR EN 14214 (3.5 – 5.0 mm^2/s at 40^oC). The viscosity of biodiesel is higher compared to that of fossil diesel the implication is that biodiesel will have lubricating effect in engines which will be an added advantage to the users, since it will reduce wear and tear in the engine

The density obtained for the biodiesel from waste palm oil (0.869 g/cm^3: 0.864 g/cm^3) and waste sunflower oil oil (0.87 g/cm^3: 0.867 g/cm^3) was in agreement with the specified value, which range from 0.860 to 0.90 for biodiesel, and also in agreement with 0.868 reported by Belewu et al, (2010). than the specified standard of 0.860- 0.900 g/cm^3.

CONCLUSIONS

Biodiesel fuels are an environmentally friendly alternative to diesel fuel being much cleaner, but offers the advantage that it can be produced from many renewable sources are the main technique being vegetable oils. Catalyst type and concentration, alcohol:oil ratio,type of alcohol reaction, temperature of transesterification play a significant role in bioediesel production. Biodiesel quality is influenced not only by the type of catalysis used, and the type of fatty acids in the raw material.

As shown in tables 1 and 2 the most effective combination was that when we employed used palm oil as a raw material of and sodium hydroxide as a catalyst solution. We can note that the most efficient catalyst proved to be sodium hydroxide, as compared to potassium hydroxide, but but biodiesel obtained in both cases has similar properties and in accordance with legal limits.

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