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Impact of residual glycerides on viscosity of biodiesel (waste and rapeseed oil blends)

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ABSTRACT

Purpose: Biodiesel, mixture of fatty acid methyl esters is a biodegradable alternative fuel that is obtained from renewable sources as a vegetable oils or animal fats. Use of waste cooking oils reduce the cost of raw materials for biodiesel production and also reduces the environment pollution. Moreover, pure edible vegetable oils for biodiesel production have an ethical significance because food is used to produce fuel. The aim of this work is a presentation of effects that residual glycerides have on kinematic viscosity values of biodiesels produced from the various waste cooking oils with crude rapeseed oil blends. Kinematic viscosity is one of the most important property of biodiesel and it directly depend on raw material composition.
Design/methodology/approach: This article includes analysis and estimation of the effect that residual mono-, di- and triglycerides which remain in the biodiesels after transesterification processes have on their kinematic viscosities. Results obtained for biodiesel produced from various percentages of waste cooking oils and crude rapeseed oil blends were presented.
Findings: Investigation during biodiesels production showed that the biggest impact on biodiesel kinematic viscosity have monoglycerides, diglycerides, and then at the end triglycerides. From these follows that kinematic viscosity of biodiesel is not a function only of the conversion (transesterification process) but also of the residual incompletely reacted glycerides which amount depend of the waste cooking oils percentage in raw material blends used for biodiesels production.
Research limitations/implications: These presented results are the closed solution considering the used raw materials. Quality and chemical composition of the used waste cooking oils are quite different from each other, which affects the quality of the produced biodiesels. Because of that these results should be an indicator for the further testing and improvements to achieve optimization of transesterification process which can reduce the amount of the residual glycerides in the biodiesel.
Practical implications: The results presented in the paper can be applied in the industry for estimation and selection of the optimal percentages of waste cooking oils and crude rapeseed oil blends for the biodiesel production.
Originality/value: This paper presents research of the influence of residual glycerides on kinematic viscosity of biodiesels produced from the various waste cooking oils and crude rapeseed oil blends. Application of these research can leads to the better kinematic viscosity value of produced biodiesel with optimization of the transesterification process.
Keywords: Biodiesel production; Waste cooking oils; Crude rapeseed oil; Residual glycerides; Kinematic viscosity

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1. Introduction

The sustainable development has become the main indicate of how to implement the principles for the protection of the environment. Progressive degradation of the natural environment has given the issue of the natural environment the world dimension [1] Problem with the waste management has become one of the biggest challenges of our times. At the beginning of XXI century, this task is still one of the most difficult municipal problems and requires a solution as soon as possible [2]. Every technological process in general way can be described to mutual account of three basic streams: stream input (raw materials and energy), stream output that is the stream of products and the stream of waste which make growing environmentally threat. Use of waste cooking oils for biodiesel production has a big impact in the environmental protection [3].

Biodiesel is alternative fuel derived from vegetable oils or animal fats and it is an renewable and biological fuel in contrast to the traditional diesel fuels derived from petroleum and it is used as a fuel for diesel engines. Biodiesel is produced from the triglyceride conversion in the oils such as those obtained from palm oil, soybean, rapeseed, sunflower and castor oil, in methyl or ethyl esters by transesterification process. In this process the three chains of fatty acids of each triglyceride molecule reacts with an alcohol in the presence of a catalyst to obtain ethyl or methyl esters - biodiesel. The reaction is carried out with a catalyst, usually a strong base such as sodium or potassium hydroxide and with alcohol, usually methanol [4].Cost of biodiesel production is high if it is produced from pure vegetable edible oils because of high price of food, whose share in the cost exceeds 80% [5] .However, the use of a food source (edible oil) to produce biodiesel have an ethical significance because of hungry people in the world. An increase in the demand for vegetable or edible oil results in an unnecessary clearing of forests for oil plantation [6]. Biodiesel production cost can be significantly lowered if the raw material or the part of it is replaced with waste edible cooking oils, used frying oils. Cheaper raw mateials have a influence on required quality of biodiesel. Because of that the production of biodesel only from waste cooking oils can not be satisfactory. Waste cooking oil can affect the final characteristics of biodiesel. For this reason biodiesel can be produced by use of blends of crude vegetable edible oil and waste cooking oil. The kinematic viscosity is the most important property of biodiesel and it directly depend on raw material composition. For achieve this property of biodiesel the optimal blend of raw material is very important. If as a raw material for biodiesel production is used half-refined or nonrefined vegetable oil then the problem create gum formation which are polymeric products of oxidation of unsaturated bonds in triglycerides. In that case oil must first undergo a pre-treatment process that consists of degumming and neutralization. The aim of neutralization is to remove free fatty acids which would neutralize alkaline catalyst in the process of transesterification. This results in an decrease in conversion of oil to biodiesel, and the resulting products would make the separation of the ester (biodiesel) and glycerol phase difficult. After degumming and neutralization oil is ready for the transesterification process and post reaction processing. Since vegetable oils are food they have undergone the process of refining. Because waste cooking oils are formed by frying of refined vegetable oils and fats no gummy substances are formed, and thus oil degumming is not required. Use of waste cooking oils, used frying oils for biodiesel production have also the ecological aspect. Waste cooking oil causes severe environmental problems, "a liter of oil poured into a water course can pollute up to 1000 tanks of 500 liters”. It’s feasible to demonstrate the contamination with the dumping of these oils to the main water sources. The oil which reaches the water sources increases its organic pollution load, to form layers on the water surface to prevent the oxygen exchange and alters the ecosystem. The dumping of the oil also causes problems in the pipes drain obstructing them and creating odors and increasing the cost of wastewater treatment [7]. As a environmental pollutant a great role have the waste oils and fats that originate from petroleum if they have not been properly disposed of. Unfortunately, these waste oils and fats can not be used to produce biodiesel [8]. Generally, if waste cooking oils are used for biodiesel production then the value of kinematic viscosity is differ between biodiesel fuels because of different fatty acids present in raw material. However, it may be expected that the properties of biodiesel derived from waste cooking oils or fats can differ widely. One reason is that different vegetable edible oils are used by different facilities. Another reason is that the oils or fats are likely exposed to varying degrees of use such as temperature and time, thus increasing the variability of composition and resulting properties even more [9]. The most widely used oil for biodiesel production in Europe is rapeseed oil.

The purpose of this paper is to present how biodiesel viscosity depend on raw material composition. The particularly attention was done to investigate the influence of residual glycerides on kinematic viscosity characteristics of biodiesel produced from waste cooking oils and crude rapeseed oil blends.

2. Biodiesel production process

Biodiesel production is performed with the use of the transesterification process with alcohol which converts vegetable oil or animal fat in biodiesel (Fig. 1) [9]. If the alcohol used in this transesterification is the methanol then the mixture o fatty acid methyl esters represent the produced biodiesel.

The presence of a catalyst (a strong acid or base) accelerates the conversion and a little excess of alcohol is used to shift the equilibrium towards the formation of esters (biodiesel) [10].

This process consists of three consecutive and reversible reactions. The first step is the conversion of triglycerides to diglycerides, which is followed by the conversion of diglycerides to monoglycerides and of monoglycerides to glycerol, yielding one methyl ester molecule from each glyceride at each step. In each reaction one mole of methyl ester is released as shown in Fig. 2 [11]. In produced biodiesel, crude methyl esters may consist of excess methanol, residue of the unreacted oil products as glycerides, catalyst residue, soap, and glycerol [12].

The waste cooking oil is generated from the fried food, which need large amounts of oil because it requires the full immersion of food at temperatures greater than 180°C. Waste cooking oils, frying oils contain products of oil decomposition, water and other impurities that reduce oil quality. This causes an reduction in conversion of oil into biodiesel in the transesterification process and may also generate undesirable by-products which affect on the quality of final product. A comparison of the refine, crude and waste jathropa based oils showed that much impurity the oil has the higher is the viscosity: This could be due to the different impurities as well as traces of particulate matter in the waste oil [13].

For these reason the purification of waste cooking oil is very important and two steps must be done: 1) Filtration, 2) Neutralization. Filtration is operation for removing solids, inorganic material, and other contaminants in the oil. It can be carried out at temperatures higher than 60°C, where substances carbonaceous produced from burnt organic material, pieces of paper, waste food and other solids are removed or occur at low temperatures which depend on the physical condition of the oil. In addition, we can delete solid fats or products of low melting points from the frying process. Neutralization is purification process for removal of free fatty acids and it is the most difficult step of the oil purification process, mainly because it has the maximum economic impact on oil production and can be performed by chemical, physical or miscellaneous methods [7].

3. Materials and methods

3.1. Materials

The experimental laboratory productions of biodiesels were carried out with transesterification process from various waste cooking oils and rapeseed oil blends. The laboratory reactor used for the implementation of the refining and transesterification process is shown in Fig. 3. The low cost and ecological impacts of waste cooking oils led to the use of these materials as raw materials for biodiesel fuel production. Normally, for waste cooking oil to be used in a transesterification procedure, a pre-treatment by filtration, neutralization, washing and drying is needed. In this work, the waste cooking oils were only filtered to remove solid impurities, turning it suitable to be converted into biodiesel with satisfactory yield and quality. No other pre-treatment was necessary.

$$\begin{array}{l} CH_2-OOC-R_1 \\ | \\ CH-OOC-R_2 \\ | \\ CH_2-OOC-R_3 \end{array} \quad + \quad 3\ R'OH \quad \xrightleftharpoons{\text{Catalyst}} \quad \begin{array}{l} R_1-COO-R' \\ R_2-COO-R' \\ R_3-COO-R' \end{array} \quad + \quad \begin{array}{l} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array}$$

Triglyceride (Oil or fat) — Alcohol — Fatty acid esters (Biodiesel) — Glycerol

Fig. 1. The general equation for the transesterification of trglycerides

1. $\text{Triglyceride} + R'OH \xrightleftharpoons{\text{Catalyst}} \text{Diglyceride} + R'COOR_1$
2. $\text{Diglyceride} + R'OH \xrightleftharpoons{\text{Catalyst}} \text{Monoglyceride} + R'COOR_2$
3. $\text{Monoglyceride} + R'OH \xrightleftharpoons{\text{Catalyst}} \text{Glycerol} + R'COOR_3$

Fig. 2. The three consecutive and reversible reactions in the transesterification process; R_1, R_2 R_3 and R' represent alkyl groups

Fig. 3. The laboratory reactor used for the transesterification process

3.2. Analytical methods

The monoglyceride, diglyceride, triglyceride content was determined by a method in accordance with the CSN EN 14105 standard with use of the gas chromatograph Varian 3800. Kinematic viscosity was determined in accordance with the EN ISO 3104 standard with use of Ostwald viscometer.

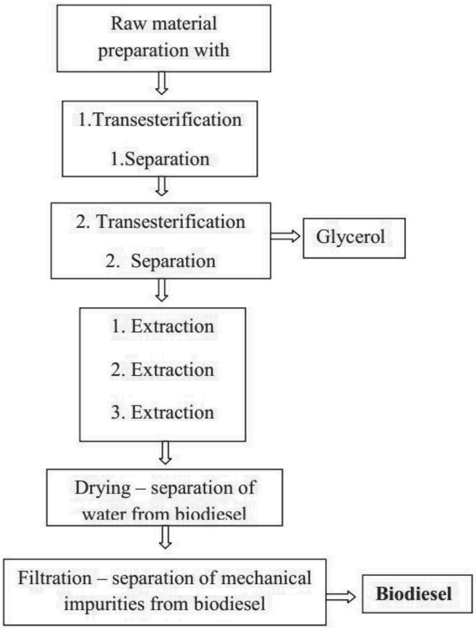

Fig. 4. Simplified process flow chart of alkali-catalyzed biodiesel production

3.3. Test procedure

Crude rapeseed oil and waste cooking oils have much higher kinematic viscosity value at 40°C than the diesel fuel derived from petroleum.

In order to achieve better yield of biodiesel the two transesterification processes are performed one after the other. The simplified process flow chart of alkali-catalyzed experimental laboratory production of biodiesel is shown in Fig. 4. Catalyst for these reactions was sodium hydroxide.

A certain amount of mono-, di-, and triglycerides can remain unreacted after transesterification process in the mixture of biodiesel with glycerol and other by-products.These residual glycerides are undesirable in biodiesel fuel because they can cause various problems in diesel engines as a filter plugging, especially at cold temperatures, and injector and engine deposits. Residual glycerides present in biodiesel can also limit the vehicle operability over a wide range of conditions. Monoglycerides can lead to an increase of the injector deposits. Diglycerides can lead to a filter plugging. The triglyceride content is a good indicator of unreacted oils or fats in the biodiesel. Glycerol, which is a by-product of the chemical reaction that produces biodiesel, may remain in the fuel if the biodiesel is inadequately separated or washed. Also this glycerol can cause trouble in diesel motor [13].

4. Results

The measured kinematic viscosities at 40°C of crude rapeseed oil and waste cooking oils WCO1 and WCO2 showed it's more than 10 times greater kinematic viscosity than the viscosity of diesel fuel derived from petroleum (petrodiesel) [14] as showed in Table 1. Very high kinematic viscosities of crude rapeseed oil and waste cooking oils do not fulfil the requirements for its direct use as fuel in diesel engines. With use of transesterification process, which converts these oils into biodiesel, its kinematic viscosity decreases at approximately twice that of diesel derived from petroleum.

Table 1.
The kinematic viscosity values measured at 40°C for the crude rapeseed oil, waste cooking oils WCO1 and WCO2

Parameter	Oil type			Petrodiesel
	Crude rapeseed	WCO1	WCO2	[14]
Kinematic viscosity, mm^2s^{-1}	38.56	44.55	55.13	2.0 - 4.5

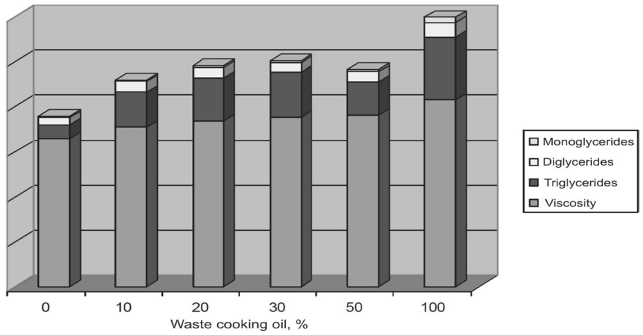

Fig. 5. The influence of amounts of the residual mono-, di- and triglycerides on the kinematic viscosities at 40°C for the biodiesels produced from various percentages of waste cooking oil WCO1 and crude rapeseed oil blends

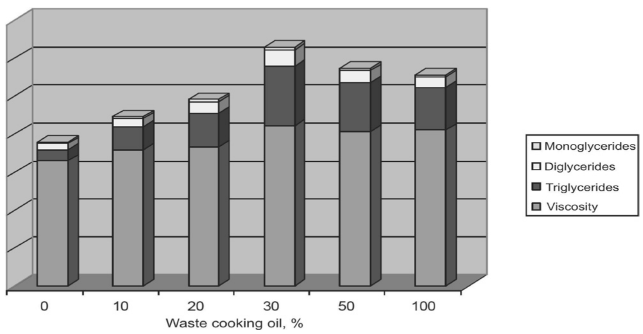

Fig. 6. The influence of amounts of the residual mono-, di- and triglycerides on the kinematic viscosities at 40°C for the biodiesels produced from various percentages of waste cooking oil WCO2 and crude rapeseed oil blends

The influence of amounts of the residual mono-, di- and triglycerides which its have on the kinematic viscosities at 40°C for the biodiesels produced from various percentages of waste cooking oil WCO1, WCO2 and crude rapeseed oil blends is shown in Figs. 5 and 6.

5. Conclusion

The results of analysed biodiesels produced from various waste cooking oils and crude rapeseed oil blends showed that kinematic viscosities of biodiesels are in big correlation with degree of triglyceride conversion.

The obtained results of investigation during biodiesels production from various percentages of waste cooking oils WCO1, WCO2 and crude rapeseed oil blends showed that incompletely reacted triglycerides residual in the biodiesel significantly affect the viscosity increase**.** Better results are obtained with use of 10% and 20% WCO2 waste cooking oil blends. This is because waste cooking oils WCO1 and WCO2 are oils from different sources.

The biggest impact on the biodiesel kinematic viscosity have monoglycerides, diglycerides, and then at the end triglycerides. From these results follows that viscosity of biodiesel is not a function only of the oils conversion (transesterification process) but also of the residual incompletely reacted glycerides and of the raw material blends.

The composition and quality of the raw materials have a direct impact on the quality of the final product. Since cheaper raw materials are often of lower quality, it is necessary to make mixture of raw materials which will achieve the required quality of the final product, and by the same time lower the production costs to the minimum. WCO is a cheap, convenient alternative raw material which, if added in a satisfactory ratio, significantly reduces production costs and gives a satisfactory final product quality [15].

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