

## PURIFICATION STEPS FOR BIODIESEL SYNTHESIZED FROM WASTE OILS

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**Abstract:** The aim of this study was to monitor the transesterification reaction of the neat sunflower oil and of two different waste cooking oils and to compare two purification steps of biodiesel obtained: purification with hot distilled water and purification with HCl 0.5% solution. The comparison was made through physical and chemical characteristics of biodiesel before and after purifications steps: acid value, density and viscosity. The results obtained showed that purification step had significant influence on biodiesel characteristics. Lower values of density, viscosity and acid index for washed biodiesel were registered, in comparison with biodiesel without purification step, while saponification values increased. Generally, biodiesel washed with hot distilled water had better characteristics over biodiesel washed with HCl solution 0.5%.

**Key words:** Biodiesel, Oils, Transesterification, Purification

### 1. INTRODUCTION

Biodiesel can be considered a good substitute for petroleum-based fuel due to its environmental benefits: it can be biodegraded (more than 90%) within 21 days, used in any compression ignition engine without the need of modification (Leung & Guo, 2006) and also it reduces the exhaust emissions like CO, SO<sub>2</sub>, hydrocarbons, particulate matter (Demirbas, 2008; Leung & Guo, 2006). However, the price of biodiesel is the biggest issue in its commercialization due to the high cost of the edible vegetable oils (Phan & Phan, 2008). In order to reduce the price of biodiesel, attention has been focused on other raw materials, especially non-edible oils, like waste cooking oils. On the other hand, using waste cooking oils in transesterification reaction can affect the biodiesel synthesis. Because of the frying process, waste oils have different physical and chemical properties in comparison with neat vegetable oils. Waste cooking oils can contain important amounts of free fatty acids and water which are responsible of soaps formation, biodiesel yield reduction, difficulties in biodiesel separation. Therefore, pre-treatment step of oils and purification step for biodiesel are necessary.

In this paper, biodiesel synthesis from two waste cooking oils was monitored by saponification value and compared with transesterification of neat sunflower oil, in order to find out the differences between feedstock. Biodiesel was characterised by acid index, density and viscosity, which are the most correlated properties with triglycerides decomposition and methyl esters formation. Also two purification steps for biodiesel have been investigated: (a) washing with hot distilled water and (b) washing with HCl solution 0.5%, in order to establish the best purification step that can be applied.

### 2. EXPERIMENTAL

#### 2.1 Materials and Methods

The samples used in this research were: Sample S0 – neat sunflower oil; Sample S1 – waste cooking oil from a local restaurant; Sample S2 – waste cooking oil from households.

Materials: methanol and NaOH were used for transesterification reaction, while ethanol, ethyl ether, KOH, HCl and phenolphthalein were used for acid and saponification values determinations. The viscosity was determined with Ubbelohde glass capillary viscometer and density with a pycnometer. Biodiesel synthesis was carried out in a 500 ml three-neck reactor, equipped with condenser and thermometer, placed on a hotplate with magnetic stirrer. First, methanol (molar ratio methanol:oil - 6:1) and 1 wt% NaOH catalyst were mixed for 30 min. On the second step, 120 ml oil were added in the reactor, heated at 60 °C and stirred for 60 min. From 10 to 10 min, 2 g of sample were taken from the reactor to monitor the saponification number during transesterification reaction. After 60 min, the reaction was complete and the products resulted were left to settle in a separating funnel. Biodiesel, the upper layer was separated from glycerol and soaps.

Biodiesel samples obtained were purified by two methods:

(a) equal volumes of biodiesel and hot distilled water (at 50 °C) were mixed with a mechanical stirrer several minutes; after stirring, water was left to settle at the bottom of a separating funnel and in the end separated; biodiesel was washed until the pH of the washing water became neutral; 5 washing steps were necessary to reduce the alkaline pH.

(b) first, 50% (v/v) of biodiesel and acid solution (0.5% HCl) were mixed in the same manner as in the step (a) and after that biodiesel was repeatedly washed with distilled water until neutral pH; in this case there were necessary 6 washing steps.

After each purification step, biodiesel samples were dried with anhydrous sodium sulphate in order to remove residual water and then filtered.

### 3. RESULTS AND DISCUSSIONS

#### 3.1 Monitoring biodiesel synthesis

The monitoring of the saponification value (an indicator of the content of fatty acids from oils and the solubility of their soaps) was made in order to observe the differences between sunflower oil and waste cooking oils during transesterification reaction. The variation of saponification number of oils is illustrated in Fig. 1. It can be observed that for each oil sample the saponification value decreased in the first 30 min of transesterification reaction and then remained constant (in case of samples S0 and S2) or slightly increased (in case of sample S1), being a proof of biodiesel synthesis. Also, saponification value gives information about the chemical composition of the lipids: the higher the molecular weight of lipids (due to the content of superior fatty acids), lower the saponification value will be. At the beginning of the reaction, sample S0 had the lowest saponification number in comparison with waste cooking oils. During frying process, oil is continuously or repeatedly subjected to high temperatures in the presence of air and moisture. Under these conditions a variety of degradation reactions can occur, such as autoxidation, thermal polymerization, thermal oxidation, isomerization, cyclization and hydrolysis (Predojevic, 2008), leading to less molecular

weight compounds and therefore to a higher saponification value.

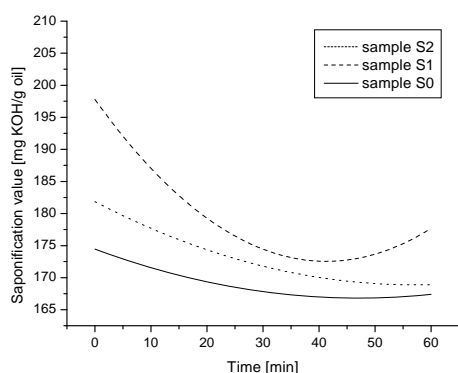


Fig. 1. Variation of saponification value during biodiesel synthesis

### 3.2 Effect of purification step

The effect of the two purification steps could be demonstrated by biodiesel characteristics before and after the purification. The characteristics determined: acid value, density and viscosity (Tab. 1-3) defined the completeness of the transesterification reaction and the quality of biodiesel, conforming the EN 14214 standard.

Substrate analyzed	Sample S0	Sample S1	Sample S2
oil	1.105	2.736	1.116
biodiesel before purification	0.837	0.833	0.82
biodiesel purification (step a)	0.56	0.78	0.544
biodiesel purification (step b)	0.41	0.27	0.41

Tab. 1. Acid value of the oil and biodiesel, [mg KOH/g oil]

Substrate analyzed	Sample S0	Sample S1	Sample S2
oil	0.916	0.9156	0.9224
biodiesel before purification	0.8792	0.871	0.8794
biodiesel purification (step a)	0.809	0.808	0.8
biodiesel purification (step b)	0.833	0.811	0.845

Tab. 2. Density of the oil and biodiesel, [g/ml]

Substrate analyzed	Sample S0	Sample S1	Sample S2
oil	23.21	27.46	28.28
biodiesel before purification	2.1077	2.41	2.2173
biodiesel purification (step a)	2.14	2.498	2.182
biodiesel purification (step b)	2.196	2.4	2.23

Tab. 3. Viscosity of the oil and biodiesel, [cP]

Acid value indicates the free fatty acids content in the sample and the proper ageing of the fuel (Enweremadu & Mbarawa, 2009). EN 14214 standard limits the acid value to 0.5 mg KOH/g oil. It can be observed that waste cooking oils had much higher acid values due to the degradation reactions during frying which lead to a high content of free fatty acids. It also can be seen that purification steps provided lower values of acid index for biodiesel samples. Washing with acid solution was more efficient, all acid values being within the standard limit. This it can be explained by the fact that HCl was more reactive for the free fatty acids than distilled water.

Density is a very important parameter of biodiesel because it influences the injection performance of the fuel (Dias et al., 2008). Density depends on methyl esters content and the remained quantity of catalyst and methanol (Enweremadu & Mbarawa, 2009; Predojevic, 2008). Comparative with oils, all biodiesel samples had lower values of density, confirming the biodiesel synthesis. Also they were in the range of 0.86-0.9

g/ml specified by EN 14214 standard. In this case, biodiesel purified with hot distilled water registered the lowest values, probably because the heat of distilled water helped dissolving the catalyst and soaps.

Viscosity is the major characteristic which affects the fuel atomization and the performance of the injectors. High viscosity leads to incomplete combustion of fuel and carbon deposition. Waste vegetable oils had higher viscosity values because of the oxidation and polymerization of triglycerides during cooking. Both washing methods caused similar viscosity reduction, in the same way like the biodiesel samples before purification.

## 4. CONCLUSION

The following conclusions can be drawn from the study:

- biodiesel synthesis monitoring showed different properties of waste cooking oils comparative with neat sunflower oil;
- purification steps have positively affected the characteristics of biodiesel;
- all the characteristics were of biodiesel in the limits of EN 14214 standard;
- the results could not conclude which was the best purification step - purification method (b) was more efficient for acid value decreasing, while purification method (a) for density; similar results were obtained for viscosity;
- large amount of water was needed in the purification steps.

Because the results could not conclude which purification step is the most suitable for improving the quality of biodiesel, it will be necessary to determine other characteristics of biodiesel, like saponification, iodine, peroxide values, cetane index, water content, fatty acids methyl ester composition, product yield. Also, to avoid using large quantities of washing water, the next step of the research will be to test dry purification steps of biodiesel, using silica gel or magnesol.

## 5. ACKNOWLEDGEMENTS

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