



VARIABILITY OF GLYCERIN FRACTIONS OBTAINED DURING BIODIESEL PRODUCTION

Mariusz SULEWSKI*, Włodzimierz URBANIAK

Faculty of Chemical Technology and Engineering
University of Technology and Life Sciences
Seminaryjna 3, 85-326 Bydgoszcz, Poland

ABSTRACT

Recently, problems concerning the necessity of increasing the contribution of renewable energy are raised very often. In the aspect of combustion engines, the most common and promoted method consists in making liquid fuels from vegetable raw materials, which are subsequently added to conventional mineral fuels. In this study, the authors' interest lies in the glycerin fraction, a side product of biodiesel production. Thus, it can be concluded that after phase separation, biofuel and glycerol are obtained and then glycerol can be utilized in the cosmetic, pharmaceutical or any other industry. However, in reality, we have to do with a three-stage equilibrium process, therefore, in the process of biodiesel production it is not glycerin that we deal with but a mixture of many substances of which glycerin is the main component. The amounts and contents of glycerin phases obtained in various technological conditions have been studied. Refined rapeseed oil, raw rapeseed oil and waste rapeseed oil were used as raw materials in biodiesel production.

Keywords: glycerin phase, biodiesel, transesterification

1. INTRODUCTION

Recently, problems concerning the necessity of increasing the contribution of renewable energy are raised very often. In the aspect of combustion engines, the most common and promoted method consists in the production of liquid fuels from vegetable raw materials which are subsequently added to conven-

* Corresponding author: Mariusz Sulewski; e-mail: m.sulewski@wp.pl

tional mineral fuels. In the case of petrol engines, dehydrated alcohols (methyl and ethyl) and their ethers can be applied. However, biofuels which are suitable for compression-ignition engines remain to be a matter under discussion. Much attention has been paid to the use of fatty acid methyl esters (FAME) [1,2], of which the viscosity and cetane number are similar to those of diesel oil [3]. The use of esters as additives to diesel oil has been proved to cause no harm to the engines [4,5,6]. It has been evidenced that the addition of esters reduces the emission of toxic combustion products to the atmosphere [7,8]. In particular, the emissions of sulfur oxides and polycyclic aromatic hydrocarbons, classified as carcinogenic, have been substantially reduced [9]. The production of FAME, their effect on the operation and use of combustion engines and the related problems of emission of pollutants have been studied rather intensely. In this study, the authors' interest lies in the glycerin fraction, which is a side product of biodiesel production. In many popular books or papers the process of biodiesel production is described by the following reaction:

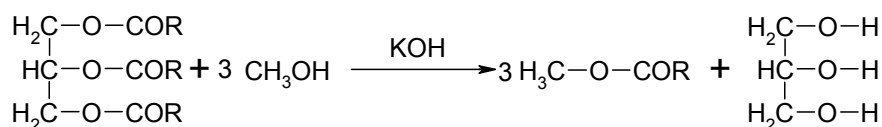


Fig. 1. Simplified scheme of triglyceride transesterification

Thus, it can be concluded that after phase separation, biofuel and glycerol are obtained and then glycerol can be utilized in the cosmetic, pharmaceutical or any other industry.

However, in reality, we have to do with a three-stage equilibrium process running as follows:

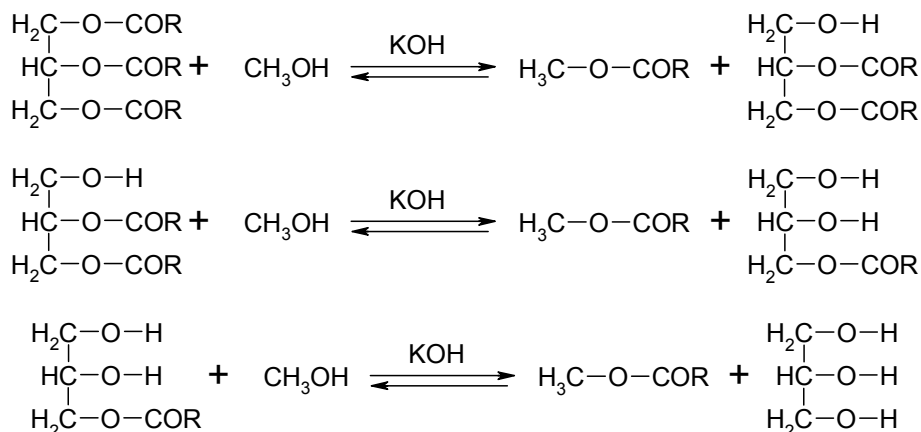


Fig. 2. Reversible reactions during the transesterification process

The transesterification of triglycerides (TG) with methanol runs through a series of reversible intermediate reactions, leading to diglycerides, monoglycerides, glycerin and esters of fatty acids [10]. Thus, in the process of biodiesel production what we deal with is not glycerin (an important substrate for the production of pharmaceuticals, cosmetics and explosives) but a mixture of many substances of which glycerin is the main component.

The glycerin phase is an off-flavour liquid, having a density in the range of 1.05-1.06 kg/dm³ and a relatively high calorific value [11]. The glycerin phase contains: free glycerol, phospholipides, proteins, polysaccharides, nitroorganic compounds, mono- and diglycerides, soaps, unreacted methyl alcohol, spent catalyst.

A typical glycerin phase after periodic transesterification contains:

- 40 to 60% of free glycerol,
- 10 to 20% of methanol,
- 20 to 50% of a mixture of compounds such as: soaps, part of non-separated FAME, acyl-glycerols, dyes, water, and many other ones, depending on the quality of the oil used, as well as some technological aspects.

The raw glycerin phase may constitute a major threat to the environment because of its high biological oxygen demand and content of toxic methanol. Besides, it is highly hygroscopic, so adding water to glycerol will decrease the mixture's freezing temperature [12].

It is generally assumed that glycerin (1,2,3-propanetriol) is a valuable raw product used in many industries and that the glycerin obtained as a side product in the process of biofuel production will be fully used. However, analysis of the use of glycerin in particular industries indicates that glycerin is expected to satisfy certain quality demands to be attractive for industry, and the glycerin fraction obtained in the process of biodiesel production does not meet such demands.

Free glycerol is widely used in many industries. Actually, glycerol is an ideal ingredient in many personal care products and pharmaceuticals. It mostly helps to prevent moisture loss and provides lubrication and smoothness to many cough syrups and elixirs. Glycerol is also commonly used in toothpaste, mouthwash and sugar-free chewing gum providing sweetness without contributing to tooth decay, as well as in cosmetics to hold moisture against the skin to prevent dryness [13].

Demand on glycerol in the food industry keeps growing. Glycerol is a source of carbohydrates and provides sweetness without causing insulin secretion during digestion. Glycerol is also used in food products, helping to preserve food and keep it fresh. Using glycerol in the food industry, especially as a sweetener and humectant has reached about 11% of the overall glycerol production [14].

The application of glycerol in the explosives industry is emerging. It is used for the production of nitroglycerin which is a powerful explosive. There-

fore, glycerol is now used as a component in the explosives production process; its consumption in the explosives industry was about 2% in the year 2006 [15].

The use of glycerol in alkyd resin formulations is also increasing. The consumption of glycerol in the alkyd resins industry is about 8% and was still increasing during last decade. These materials are used as a component of coatings, especially in paints and plastics [16].

The consumption of glycerol in the chemical industry as a polyether or alcoholic hydroxyl group polyol was raising in last decade. It provides one of the basic chemical building blocks for the construction of polyurethane foams.

Another common use of crude glycerin is to burn the substance at light temperatures (290–300°C) for heating industrial boilers [17].

Glycerol can be used for the synthesis of many products or as a raw material in the chemical industry.

There is a concept to use glycerol by transforming it into ketals. Ketals can be used as an anti-freeze additive to biodiesel [18].

Several concepts for the chemical transformation of glycerin are known [19]:

- etherification
- oxidation to carboxylic acids or dihydroxyacetone
- hydrogenolysis – obtaining propane-diols or ethylene glycol
- dehydration – obtaining acrolein [20]
- pyrolysis – mixture of alkanes, olefins and alcohols
- production of hydrogen or synthesis gas by glycerol pyrolysis, gasification and steam reforming [21]
- hydrochlorination – obtaining epichlorohydrin.

There are also several methods of biochemical transformation of glycerol, namely:

- biological conversion of glycerol to succinic acid, using *Actinobacillus succinogenes* [22],
- ethyl alcohol, using *Escherichia coli* [23]
- propionic acid, using *Propionibacterium acidipropionici*, *Propionibacterium acnes* and *Clostridium propionicum* [24]
- citric acid [25]
- Poly(3-hydroxybutyrate) using *Cupriavidus necator* [26]
- Phytase, using *Pichia pastoris* [27].

Many governments and ecological societies prefer dispersed production of biodiesel in small rural agrorefineries on farms. The idea is to use the fuel on farms to power agricultural machinery. This is based on the contention that production of biodiesel is a simple technology that does not require high capital and knowledge.

The only technology that can be used in small rural refineries due to its simplicity is the periodic cold technology. However, that simple technology should be optimized to obtain a good quality and yield of products. As regards the optimization process, biodiesel should be considered as well as the glycerin fraction, which is important due to environmental protection and process economy.

2. METHODS OF STUDY

The process of transesterification was performed in a thermostated reactor equipped with a mechanical stirrer and thermometer. Rape oil was heated to the reaction temperature and was fed into the reactor. Then a mixture of methanol and catalyst was slowly added. The contents of the reactor was vigorously stirred at a constant rate and at a constant temperature. When the reaction was complete, the contents of the reactor was transferred to the sedimentation tank to separate the phases. Every reaction was carried out three times and the results presented in this paper are the means of those samples.

Samples for chromatographic analysis were prepared by dissolving a weighed portion of the glycerin fraction in 2-propanol. The glycerin and esters were identified using a gas chromatograph model Hewlett Packard 5890 series II equipped with split injection and MS detector HP 5972. Phase separation was made on a chromatographic column HP-FFAP with internal diameter 0.53 mm, length 30 m and film thickness 3 μ m. The temperature program was: 100°C for 2 min – 10°C/min – 240°C for 5 min. Quantitative analysis of the glycerin fraction was made in a GC-FID system applying the same procedure as for qualitative analysis. The content of glycerin was estimated from the calibration curve plotted for an analytically pure glycerin as standard. The analytical problems related to the chromatographic analysis of the products of transesterification of vegetable oils have been considered [28,29].

3. DISCUSSION OF RESULTS

The amount of the glycerin fraction formed depends on many factors such as the type and amount of catalyst, the quality of vegetable oil and parameters of the process of biodiesel production. The effect of the type and amount of the catalyst on the amount of the glycerin fraction obtained was considered previously [30].

For a stoichiometric methanol-to-oil ratio with a small excess of methanol (3.5:1 molar ratio) the amount of the glycerin fraction depends on the reaction temperature. Increasing the temperature results in a few percent higher amount of the glycerin fraction, but methanol is used in excess (Fig. 3). Using a large excess of methanol (methanol-to-oil molar ratio 6:1), the amount of the glycerol fraction obtained does not, practically, depend on the reaction temperature at all (Fig. 4). The amount of the produced glycerol fraction for the ratio is 6:1 is higher on average (circa 4%). This is due to the fact that the excess of unreacted methanol (high polarity) is shifted to the glycerol fraction.

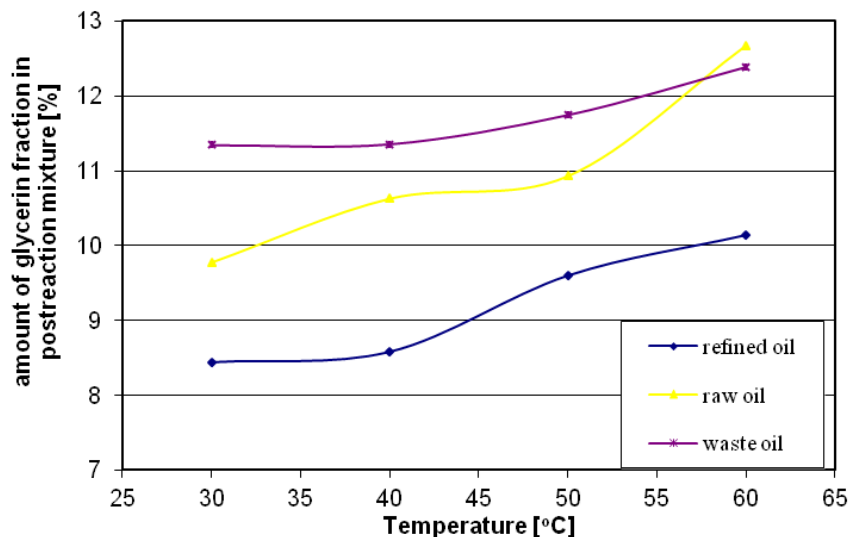


Fig. 3. The amount of glycerin fraction formed with methanol-to-oil molar ratio 3.5:1.

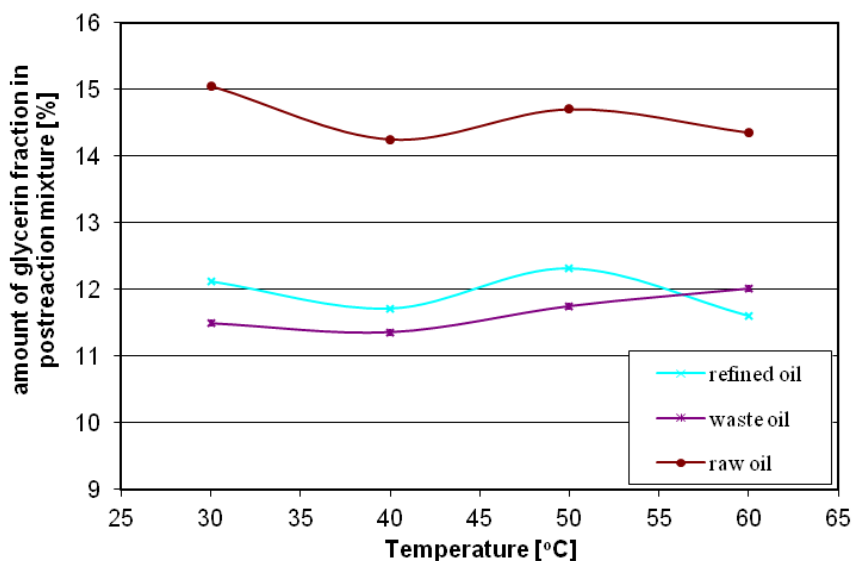


Fig. 4. The amount of glycerin fraction formed with methanol-to-oil molar ratio 6:1.

In the optimum conditions the glycerin fraction makes from 11 to 15% vol. of the post-reaction mixture. Assuming that the addition of esters in the biofuel is only 5%, production of every liter of biofuel is accompanied by the formation of 7 – 8 cm³ of the glycerin fraction. It may seem a small amount but in a large scale production, a single refill of a motor truck (about 600 liters) means the

production of 4 – 5 liters of the glycerin fraction. This amount of the side product must be utilized rather than wasted.

Just as important as the quantity of the obtained glycerol fractions is their composition.

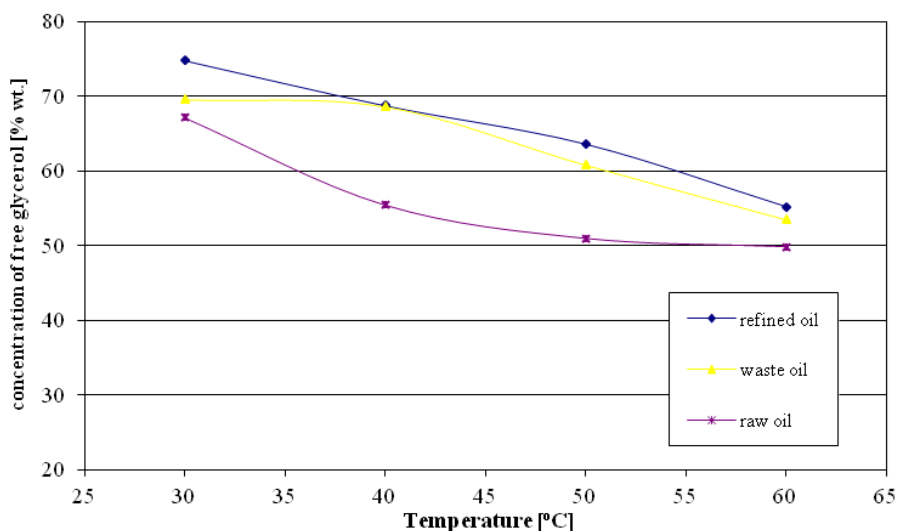


Fig. 5. The concentrations of glycerin in the glycerin fractions for methanol-to-oil ratio 3.5:1

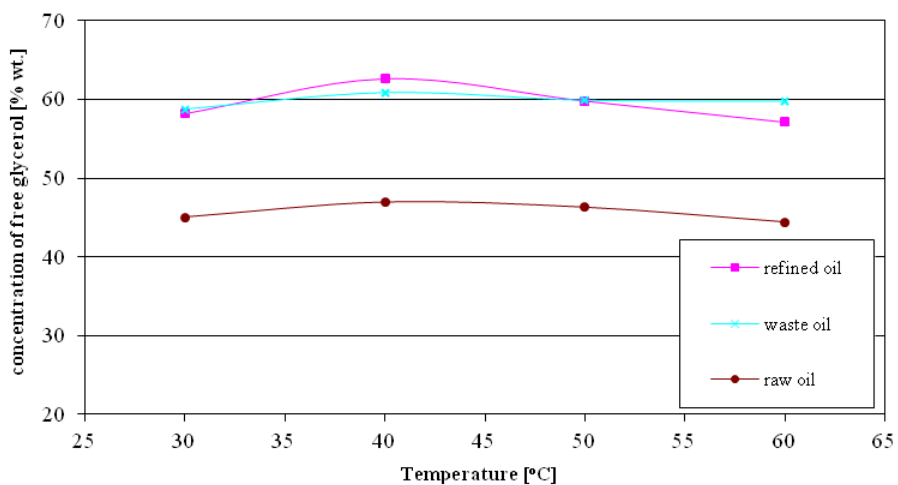


Fig. 6. The concentrations of glycerin in the glycerin fractions for methanol-to-oil ratio 6:1

The content of free glycerol in the glycerin fractions obtained when using different types of rape oil can vary in a wide range from 33 to 61% [31]. The concentration of pure glycerol in the glycerin fraction has been analyzed (Fig. 5 and 6).

According to the study, when using a considerable excess of methanol (methanol-to-oil molar ratio 6:1) the concentration of free glycerol does not depend significantly on the temperature of the transesterification process, even if the highest concentrations in all the cases have been reported for a temperature of 40°C. When using the methanol-to-oil ratio of 3.5:1 the highest concentrations of free glycerol have been reported for a temperature of 30°C, and raising the temperature leads to lower concentrations of glycerol from about 70% for 30°C to about 50% for 60°C in all the cases.

The total amounts of free glycerol obtained were calculated based on the volumes of the obtained glycerin fractions and the concentrations of free glycerol in each of them. The results have been presented in Figures 7, 8 and 9.

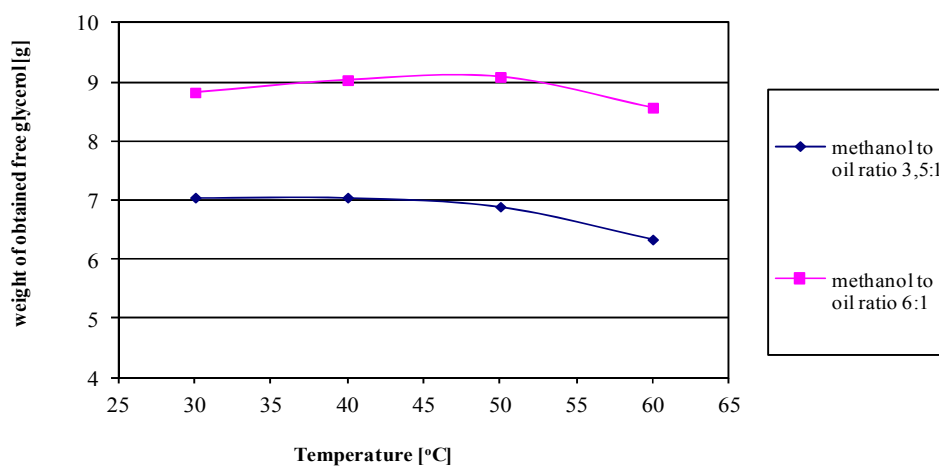


Fig. 7. The weight of obtained free glycerol for refined oil

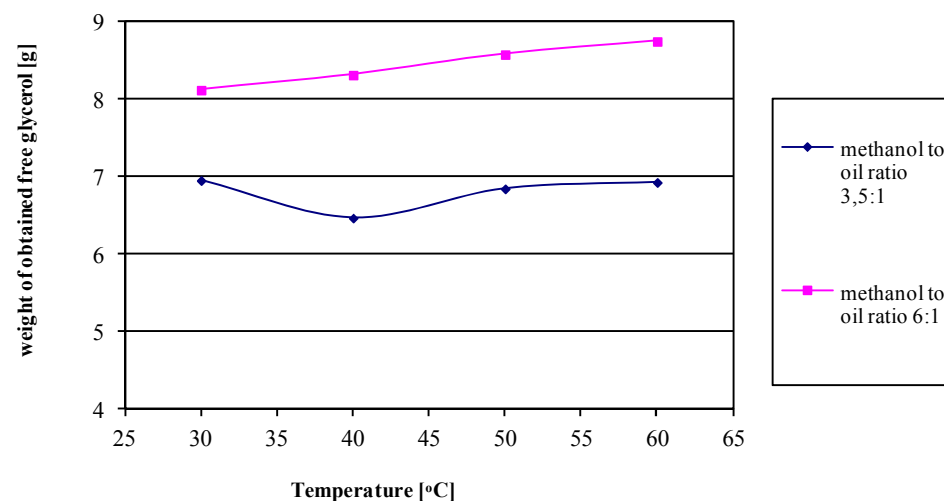


Fig. 8. The weight of obtained free glycerol for waste oil

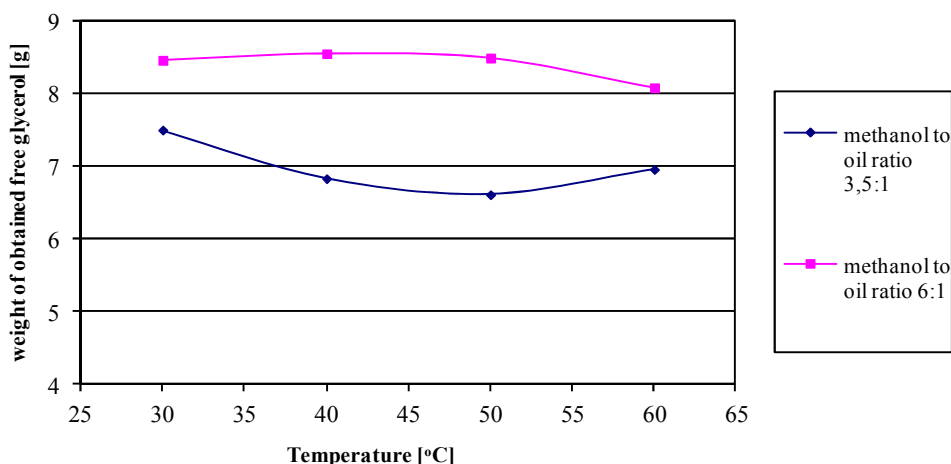


Fig. 9. The weight of obtained free glycerol for raw oil

It is common knowledge that higher amounts of the obtained free glycerol mean, in practice, a shift of the equilibrium of the transesterification process to the synthesis of the final products. In all cases, the total weight of glycerol was higher when using the higher methanol-to-oil molar ratio (6:1).

Where the 6:1 methanol-to-oil ratio was used, the amount of glycerol obtained did not depend significantly on temperature. Slightly better efficiencies were achieved at 40°C and 50°C. Only in the case of waste oil did a further increase in temperature to 60 degrees result in higher efficiencies.

Where the 3.5:1 methanol-to-oil ratio was used, the quantity of free glycerol obtained usually decreased as the process temperature was increased. Increased temperatures did not lead to lower efficiencies only where waste oil was used as a raw material.

Best efficiencies were observed for the refined rapeseed oil. This is probably due to a lower content of substances other than glyceride, that does not undergo the process of transesterification. However, it should be noted that the use of refined oil on an industrial scale might be counterproductive because of the high cost of refining.

As follows from analytical results, the glycerin fraction contains, on average, just over 50% by weight of free glycerol, so the claim that glycerol is a side product of biodiesel production is far from the truth. The glycerin fraction does not meet the requirements of a glycerol used for the production of pharmaceuticals, cosmetics or food products. Studies have shown that shortening of the separation process leads to the presence of fatty acid methyl esters in the glycerol fraction. The presence of contaminants also seriously limits the use of the crude glycerol fraction as a substitute for glycerol in industrial processes. According to our results, the glycerol fraction separated within a few hours from the completion of the transesterification process contains considerable amounts of methyl esters of fatty acids that have not been transformed into the ester phase.

4. CONCLUSIONS

The contents of free glycerin in the glycerin fraction show considerable variations, from 40 to over 70%, depending on the type of oil used and the conditions of the transesterification process. The remaining part of the fraction is made of contaminants.

According to our results, to ensure an exact separation of fatty acid esters from the glycerin fraction the post-reaction mixture should remain in the separator for a minimum of 16 hours. Reduced separation times result in lower yields of the main product (biofuel) and in contamination of the glycerin fraction, increasing the difficulty of its application.

Increased process temperatures lead to higher content of the esters in the glycerin fraction. Although the increased process temperature accelerates the reaction, in view of the increasing content of the esters in the glycerin fraction, the effect of temperature should be carefully analyzed and its optimum value should be established.

The great variation in the contents of the side product of biofuel production from vegetable oil indicates the need of a detailed analysis of the relationships between the parameters of the initial oils, the process conditions and the quantity and quality of the glycerin fraction obtained. Taking into regard the necessity of increasing the use of biofuels, the results of the analysis presented in this paper also indicate the need of developing a cost-effective and environmentally friendly process of utilization of the glycerin fraction obtained in the process of biofuel production.

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