



## Transesterification of triglycerides with ethyl acetate

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### HIGHLIGHTS

- ▶ We investigated the transesterification of rapeseed oil and ethyl acetate.
- ▶ We compared the efficiency of acid and alkaline catalysts for transesterification.
- ▶ The efficiency of the reactive distillation process was researched.

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### ABSTRACT

Transesterification of triglycerides with ethyl acetate instead of methanol seems to be advantageous in respect to glycerin waste elimination. Sodium methanolate and metal sodium dispersion (0.4%) were used as a catalyst. The reaction occurred very quickly (5–30 min) at the temperature of 22–78 °C in a similar way as the common methanolysis but reached an equilibrium with a high content of acetylated monoglycerides (9–13%) and diglycerides (3–6%) in addition to fatty acid ethyl esters (72–81%) and glycerol acetates (4.5–6.2%). A similar product yield could be obtained while using 5% *p*-toluenesulfonic acid as a catalyst but after 40 h of reaction time.

During reactive distillation (RD) it was possible to evaporate the light volatile glycerol acetates and fatty acid ethyl esters and to shift the equilibrium towards the desired products. Reactive distillation was performed at the temperature of 200–230 °C by bubbling ethyl acetate vapor through rapeseed oil layer. Dodecylbenzene sulfonic acid (1%) was used as a catalyst. The product yield attained 8 g/h and was composed mainly of fatty acid ethyl esters (90%) and only little amounts of glycerol acetates. During the reaction a rapid decrease in catalyst activity was observed. The use of alkaline catalyst, like sodium methanolate, gave lower product yield of 2.6 g/h with higher content of glycerol acetates (7.7%) besides ethyl esters (90%). Using 2% zinc oxide as a catalyst contributed to obtaining only negligible yield of transesterification products (0.2 g/h).

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### 1. Introduction

Biodiesel is a renewable fuel that can be manufactured from different vegetable oils (Table 1), animal fats or recycled greases from food industry. As a green fuel it has many advantages over conventional diesel fuel, such as non-toxicity and biodegradability [1–3], a high flash point (>130 °C), insignificant sulfur content and increased lubricity that extends the life of diesel engines [4,5].

Biodiesel is a mixture of fatty acids methyl esters currently manufactured by transesterification of triglycerides with methanol using NaOH or KOH as a catalysts [7]. However, the main drawback of the process is the instability of the base catalyst owing to its rapid saponification, which leads to a loss of their activity and consequently to an incomplete conversion of triglycerides [7,8].

Soap formation is unavoidable even by using sodium or potassium methanlates because of water traces still present in the reaction mixture [3,8].

Since the beginning of the 1990s of the XXth century, the alkaline catalyst technology for the production of fatty acid methyl esters has been well established. It consists of the reaction of vegetable oils or animal fats with methanol at the temperature of 60–70 °C, at the molar ratio of methanol to triglycerides equal to 6:1 and using 1% NaOH or KOH as a catalyst. By use of good quality raw materials, especially with an acid number below 1, it is possible to obtain over 98% conversion of triglycerides in 20–60 min of reaction time [9]. The obtained products meet the principal quality parameters according to EN-14214, in particular with the content of di- and triglycerides below 0.2% and monoglycerides below 0.8%.

However, when the acid number of raw material exceeds 3, an acidic catalyst should be used in order to provide simultaneous esterification of free fatty acids and transesterification of triglycerides with methanol. Mineral or Lewis acids are well known as

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**Table 1**  
Oil-Producing Crops [6].

Plant	Latin name	Oil/hectare (kg)
Cashew nut	<i>Anacardium occidentale</i>	148
Soybean	<i>Glycine max</i>	375
Coffee	<i>Coffea arabica</i>	386
Sunflower	<i>Helianthus annuus</i>	800
Peanut	<i>Arachis hypogaea</i>	890
Rapeseed	<i>Brassica napus</i>	1000
Jajoba	<i>Simmondsia chinensis</i>	1528
Brazil nut	<i>Bertholletia excelsa</i>	2010
Coconut	<i>Cocos nucifera</i>	2260
Palm oil	<i>Elaeis guineensis</i>	5000

effective esterification catalysts. Unfortunately, the acid catalyzed transesterification is slower than the alkaline one by 3 orders of magnitude [5,10]. The process requires a much higher temperature, in the range of 100–200 °C, and appropriate pressure of 1–3 MPa to retain methanol in the liquid state [5]. In supercritical condition both the esterification and transesterification reactions proceed fast and effectively even without catalyst [11,12].

By use of heterogeneous alkaline catalyst (14%) at temperature of 200 °C, pressure of 50 bar and 9:1 reagent molar ratio it was possible to obtain over 99% yield of fatty acid methyl esters exceeding EU 14212 quality specification. The advantage of heterogeneous catalysis was the lack of waste soaps and the easy separation of glycerin phase. However, the disadvantageous effect of polyunsaturated fatty acids on the catalyst activity was pointed out [13].

The main by-product in common methanolysis is the glycerin fraction in the amounts of 15–25% of total reaction volume. This amount exceeds twice the stoichiometric content of glycerol in vegetable oils (about 10 wt.%) because of methanol excess together with dissolved soaps and emulsified methyl esters [14]. In the past, the glycerin fraction was a lucrative source of pure glycerol with many industrial applications. Nowadays the glycerol market collapsed dramatically and the supply of glycerol exceeds about 10 times its demand. Thus, the glycerin fraction remains spent liquor sometimes oppressive for the environment [15].

Spent glycerin fraction is less attractive as a fuel because of only moderate combustion value and rentability estimated as low as 100–300 USD/t. Bioconversion of glycerol to more valuable derivatives like 1,3-propanediol, succinic or fumaric acids does not exceed pilot plant stage [15]. Glycerol can be also used as a raw material to produce ketals or acetals in reaction with acetone or formaldehyde as well as t-butyl ethers in reaction with isobutene [16]. The obtained compounds with partially blocked hydroxyl groups are soluble in hydrocarbons and can be used as octane number improving agents. The anti-knock enhancement of petrol compositions is also assigned to glycerol triacetate which is normally hard to obtain.

An elegant and effective method to overcome the glycerin surplus seems to be the transesterification of triglycerides with methyl acetate instead of methanol. In principle, the process should give only two main products: fatty acid methyl esters and glycerol triacetate. According to patent description [2] the novel transesterification process proceeds at the temperature of 60–80 °C with the molar ratio of methyl acetate to triglycerides of 6:1 and the use of 2–5% sulfuric acid or p-toluenesulfonic acid as a catalyst. After 2 h of reaction the product contains 80% of methyl esters, 17–19% of glycerol triacetate and 1–3% of intermediates (mono- and diglycerides). Noteworthy was the surprisingly high effectiveness of acid catalysis and high yield of obtained products. No difference in reaction yield occurs while replacing methyl acetate by ethyl acetate as reagent.

The reaction product consisting of a mixture of fatty acid methyl(ethyl) esters and glycerol triacetate was directly suitable for use as

a diesel fuel. From the mass balance it was evident that 10 weight parts of oil raw material can give 12 parts of the mixture of fatty acid methyl(ethyl) esters and glycerol triacetate. In reality, the high yield of reaction products should be decreased because of the chemical equilibrium occurring in the reaction mixture. In contrast to methanolysis, where the high reaction yield is a result of glycerol settling, glycerol triacetate is soluble in the reaction mixture. Thus, the main side component remains in equilibrium with other esters and inhibits the full conversion of triglycerides. As a result, the reaction mixture may contain significant amounts of acetylated mono- and diglycerides as well as unreacted triglycerides. The shift of chemical equilibrium into the product side requires high molar excess of methyl acetate in the range of 30:1. Recently, stoichiometric yield of methyl esters was obtained using high excess of supercritical methyl acetate at temperature of 399 °C, at reaction time of 59 min, and without any catalyst added [17].

In some cases it is possible to overcome the slow kinetics of acid catalysis by off-distillation of fatty acid methyl esters from unreacted components [8]. A methanolysis process using a heterogeneous catalyst  $ZrO_2/SO_4$  at 200 °C and the pressure of 4 MPa gave 90% yield of methyl esters. The product was then separated by fraction distillation in vacuum and the unreacted components were recycled in the next methanolysis step. Additionally, the costs of product with the use of distillation did not exceed 10% of total production costs [18]. It was possible to use an alternative  $ZrO_2/WO_x$  catalyst, which was easier to prepare and shows better stability under both oxidizing and reducing conditions. A process of transesterification at 200 °C and the methanol-oil molar ratio of 15:1 yielded 97% of methyl esters [19].

By combining the reaction and separation steps into a single unit (reactive distillation) the reaction equilibrium can be shifted towards the key products (esters) by continuous removal of by-products (water) instead of using an excess of reactants. In case of fatty acids esterification with methanol, the secondary reactions (etherification or dehydration) can be avoided by using a selective solid catalyst such as sulfated metal oxides. The process based on RD does not produce waste salt streams [8]. The appropriate temperature is in the range of 130–150 °C, which corresponds to a pressure of 6–10 bars to retain methanol in its liquid form. The residence time in the column is below 10 min, much less than the reaction time of 60–90 min in the conventional process. Depending on the reflux ratio and total production rate of FAME, the energy requirements are in the range of 150 kcal/kg. At a catalyst loading of 15%, the production of fatty acid esters as high as 3250 kg/(h m<sup>3</sup>) was reported [6].

A reactive distillation process is also proposed for the esterification of dodecanoic acid with 2-ethylhexanol and methanol [20]. At the temperature of 453 K and with molar ratio acid:alcohol of 1:1 mol/mol the ester conversion reached 70% after 25 min. The same reaction at a lower temperature of 353 K with a large excess of alcohol (25:1 mol/mol) needed about 25 h to achieve the same conversion rate.

## 2. Experimental

The reactive distillation was carried out in a glass column (25 mm inner diameter, 1 m height), filled with glass Raschig rings and equipped with an electric heat mantle (Fig. 1). The temperature of the column was controlled at the bottom, in the middle part and at the distillate outlet using Fe/FeNi thermocouples connected with a scanning thermometer (DT16, Metrol). The vapors of ethyl acetate were produced in an evaporator heated to 160 °C and introduced continuously to the bottom of the column, together with a nitrogen stream (20–30 l/h). The amounts of light reagent dosed to evaporator were controlled using a Micro-Dose syringe pump (type 335A, UNIPAN). The reaction products were collected using a distillation

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