

A COMPARISON BETWEEN OF SODIUM METHOXIDE AND SODIUM HYDROXIDE CATALYSTS FOR ETHYL ESTERS PRODUCTION

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EXTENDED ABSTRACT

This paper investigates the transesterification reaction of refined vegetable oils (soy bean oil) by means of ethanol, using sodium methoxide and sodium hydroxide as catalysts. Particularly, the objective of this work was to prepare ethyl esters with the two different homogeneous catalysts, while the reaction had been carried out in one step. Afterwards, the resulting products were evaluated regarding the physicochemical properties, specifically, if the derived ethyl esters are compliant to the specifications as established in European Norm EN14214, indicating if the produced ethyl esters are correctly termed as “biodiesel”, more renewable due to the replacement of harmful methanol and as well as, regarding its utilization if ethyl esters could be used as an effective substitute of regular petroleum diesel along with the european standard EN590. During the set of experiments, two variables were investigated: the molar ratio of ethanol to oil (9:1-15:1) and the catalyst concentration (% m/m of the oil, with the before-mentioned homogeneous catalysts. The other parameters during the course of reaction such as temperature, stirring speed and the reaction time of each experiment were fixed. The optimized biodiesel, with respect to the European requirements, was obtained by a molar ratio of 12:1 with sodium methoxide (0,7% m/m) at 80 °C. Conversely, the utilization of sodium hydroxide revealed inferior behavior, in the already-mentioned analogy of 0,7% m/m, the sodium hydroxide made difficult the phase separation and formed soaps and emulsions during purification stages. Additionally, in a attempt to limit the saponification a lower concentration of sodium hydroxide (0,4% m/m) was used, revealing a sufficient improvement of triglycerides conversion, showing, as said before for methoxide catalyst, the better yield at 12:1, but in hydroxide case a lower catalyst amount was demanded. Moreover, it is worth of noticing that the use of sodium hydroxide, due to the intensive soap formation, influenced negatively the final yield of purified biodiesel (on a mass basis) compared to the initial weighted oil, that was considerably lower in opposition to sodium methoxide for both concentrations. Therefore, the ethyl esters by sodium methoxide showed better results, high conversion in an only one-step reaction with an optimum yield, although, the use of ethyl esters needs further examination since they should be completely compatible with all the specifications as has been set in EN 14214. Their future use would be beneficial as a substitute of mineral diesel because ethyl esters liberate from fossil fuel dependency, with a more renewable fuel, and simultaneously, it is of considerable interest their contribution to reduced emissions of regulated and unregulated pollutants, driving to an improvement of air quality.

Keywords: biodiesel, ethyl esters, homogeneous catalysis

1. INTRODUCTION

The current awareness about the dreadful consequences from environmental degradation and concerns about conservation of non-renewable natural sources have

given rise to the development of alternative energy sources with an intent to substitute the fossil fuels in the close future. Vegetable oils and animal fats are used; their composition contains mainly triglycerides that can simply be transesterified, producing an alternative biofuel, biodiesel, and glycerol as by-product. With regard to the biofuels production, there are options relating the type of alcohol that would be used, such as methanol giving methylesters [1,2,3] and ethanol producing ethyl esters [4,5]. Biodiesel by nature is biodegradable and non-toxic, and its polar surrogates contribute to a better lubricity of diesel, that is beneficial to improve the poor lubricity of ULSD [6,7]. Moreover, biodiesel contributes to lower emissions through a reduction of regulated and unregulated pollutants such as particulate matter, carbon monoxide, and unburned hydrocarbons, making its use beneficial either in pure form, or in blends with regular diesel [6,7,8]. On the other hand, there are controversial issues relating biodiesel production, like the high cost of the raw material used, and issues relating with the conversion of forest lands and pastures to crop lands, dedicated to biodiesel production, instead of being cultivated for people nourishment. [9].

Currently, the biodiesel investigation strives to production from non-edible oils or from cellulosic origin fuels (second generation biofuels). Used cooking oils are an interesting alternative feedstock, as the use of used oils relieves from the burden of disposition of that waste [10]. These used oils are low grade oils, since they suffer from high acidity, high water content, high viscosity, due to the chemical modifications occurred in the oil composition during cooking. Therefore, these oils necessitate more pretreatment steps in order to be effectively utilized and produce an acceptable quality biodiesel [11,12].

Biodiesel is environmentally friendly, but the use of methanol underestimates its valuation, since it is derived mainly from non-renewable sources. An alternative solution is ethanol, totally renewable, as it comes from agricultural resources [4,13]. The replacement of methanol with ethanol has led also to reduced emissions, less smoke density, CO and unburned HC, as well as, marginal decrease in the case of NO_x, a pollutant with debatable results. Furthermore, the biological decomposition of rapeseed ethyl esters in aqua environment showed better behavior than rapeseed methylesters and excellent biodegradability compared to petroleum diesel [4,14]. Conversely to those positive estimations of ethanol, the drawbacks should be stressed; production of ethyl esters demands more reaction time than methyl esters, due to lower reactivity during transesterification, due to the longer carbon chain. Additionally, ethanol is better solvent, and the separation of soaps and emulsions is more difficult, complicating mass transfer during reaction. Emulsions break up in ethanolysis is more difficult compared to methanolysis, hence, the limiting stage of FAEE production is the separation and purification stage [4,16]. Another limiting factor of ethanol use is the presence of water inducing secondary hydrolysis reactions, dropping the yield, complicating the purification. The solubility of ethanol in ester and glycerol phase leads to a reduced final ester yield, as part of glycerol may be enclosed in ester-phase and part of esters may be entrained into the glycerol-phase [5,16]. Moreover, soaps and emulsions present on the reaction mixture provoke the transport of ethyl esters into glycerol phase; as it is facilitated by their polarity [15,16].

In the present work a set of experiments was carried out for producing ethyl esters under homogeneous catalysts, in line with european requirements. Refined soybean oil was intentionally utilized to avoid the side reaction of neutralization of free fatty acids. All tests were performed with sodium methoxide (CH₃ONa) and sodium hydroxide (NaOH) as homogeneous catalysts. The purity of biodiesel was assessed by ester content, compared to the european requirement in EN14214. The mass yield was determined as an indicator of the recuperation and purification of biodiesel, showing that the less soaps and emulsions led to less loss. Assessment of soybean ethyl esters needs further consideration because the reaction system is very sensitive to minor changes in the experimental conditions degrading the FAEE quality.

2. EXPERIMENTAL SECTION

The soybean oil, refined with acidity less than 0,1g oleic acid/ 100g sample was supplied by a local grocery. The fatty acid profile of soybean oil is given in Table 1, along with the fatty acid composition of sunflower oil (refined too), since there are references in the present paper as regards a previous one.

Table 1. Fatty acid composition of soybean oil and sunflower oil.

Fatty Acids	Soybean Oil	Sunflower Oil
C16:0	8,77%	5,62%
C18:0	3,71%	4,25%
C18;1	32,10%	29,71%
C18:2	53,63%	58,90%
C18:3	0,26%	0,12%

The catalysts used were CH_3ONa (30% m/m in methanol solution), and NaOH (99% m/m purity), obtained from Panreac. Ethanol was of 99,9% purity (water content: 1000 mg/kg), and it was used as the transesterification alcohol. Pure glycerol was also used in order to accelerate the separation of ester-phase and glycerol-phase. The transesterification reaction was carried out in a flat-bottomed spherical reactor, provided with mechanical stirring, sampling outlet, and vapor refluxing system. The agitation speed was chosen at 300 rpm so as to avoid the mass transfer limitations, and the reaction time was prolonged for 3 hours [16]. Catalyst concentrations examined were 0,7% m/m for CH_3ONa , as an optimal concentration for refined oils [17], and for NaOH initially the same concentration of 0,7% m/m but afterwards, 0,4% m/m was tested further. Subsequently, the raw reaction mixture was cooled down to laboratory temperature and then, it was transferred to a separating funnel. Glycerol was added in amount 10% of the reaction volume into the funnel and it was stirred vigorously for 3 minutes. Thereafter, the settlement lasted for four hours. After the separation of the two layers by gravity, the co-product glycerol was carefully withdrawn; the ethyl esters were washed several times with warm distilled water (60 °C), in order to extract the residues of catalyst [4]. The main design of recuperation and purification was similar for molar ratios of ethanol to oil 6:1 – 12:1, but at higher molar ratio of 15:1 was different, where ethanol removal from raw reaction mixture was required, in order to facilitate the separation. Eventually, the non-reacted alcohol and water were removed by rotary evaporator at reduced pressure. The clear ester phase was analyzed regarding the ester content according to EN 14103 test method, using gas chromatograph.

3. RESULTS AND DISCUSSION

3.1. Reaction Conditions

All the experiments were carried out in steady environmental conditions, at ambient pressure, at 80 °C and in one-stage transesterification process, by ethanol refluxing. The experimental variables were the two catalysts (NaOH and CH_3ONa), and the ratio of ethanol to oil, that was in the range of 6:1 – 15:1. The concentration of CH_3ONa catalyst was stable of 0,7% m/m. In a previous work, when 1% m/m CH_3ONa had been examined in soybean and sunflower oil, but the ester content was low, caused by the saponification of the oil [17]. The first tests of 0,7% m/m CH_3ONa in sunflower showed satisfactory conversion at molar ratios of 9:1 – 12:1 as shown in Table 2. A downside from processing had appeared as reduced recovery, brought about by a complicated purification process owing to the formed emulsions thus, a further tryout was carried out with soybean oil

having a different free fatty acids composition, showing an acceptable triglycerides conversion and favorably lower mass losses (Table 2).

Table 2. Ester content (%) and yield (g) of FAEE from sunflower and soybean oil with 0,7% m/m CH₃ONa catalyst.

Ethanol/Oil	Sunflower Oil FAEE		Soybean Oil FAEE	
	Ester Content (%)	Yield (g)	Ester Content (%)	Yield (g)
6:1	90,95%	85	91,70%	92
9:1	97,38%	86	93,20%	93
12:1	98,06%	83	94,16%	91
15:1	90,47%	81	91,15%	89

The concentration of 0,7% m/m CH₃ONa gave good results for both oils, with the best ethanol to oil ratio being at 12:1 for one-stage process. The same analogy (12:1) was verified as optimum for ethanolysis in soybean oil and sunflower oil, yielding ethyl esters with excellent physicochemical properties, comparable to methyl esters or better values regarding cold flow properties, lubricity, oxidation stability, and for the conversion of used frying oils, by two stages transesterification reaction [13,16]. The present work includes the evaluation of another homogeneous catalyst, NaOH, and initial concentration of 0,7% m/m NaOH was examined in soybean oil in the range of 9:1-12:1 of molar ratios. This work is aimed at estimating the differences during processing for soybean ethyl esters production, in the presence of two homogeneous catalysts in the same concentration. The purity of soybean ethyl esters was denoted by means of ester content. Also, an indicator of acceptable FAEE production was the mass yield. As revealed, throughout the processing the losses were significant for 0,7% NaOH, inhibiting its use. Consequently, the results compelled the prolongation of experiments with a lower concentration (0,4%) of NaOH. Hence, the use of hydroxides compared to methoxides should be under consideration. The system is strongly dependent on the raw oil quality and it is more sensitive to changes of experimental conditions.

3.2. Effects of NaOH and CH₃ONa

Transesterification by ethanol is a three-stage reversible reaction. Each step can easily be described as an attack on the carbonyl carbon atom of the tri, di, mono-glycerides molecules by the ethoxide anion (CH₃CH₂O⁻). The impact of each catalyst is different. The dissolution of NaOH, a strong base that dissociates extensively in the short-chain ethanol, leads to the formation of the alkoxide and water, the alkoxide, as already mentioned, acts as a catalyst. Therefore the amount of ethoxide anion depends on the catalyst concentration. During the reaction of NaOH with ethanol water is formed [5]. The presence of water in reaction mixture may cause saponification. The impact of NaOH and KOH on the transesterification reaction and soaps formation has been examined. The results revealed that when hydroxides are used, the low conversion is due to the direct transformation of these catalysts into organic alkali salts, due to the side-reaction of saponification that occurs due to the presence of water in reaction system [5]. The presence of an alcohol – water mixture induces soap formation, and the existence of water in reaction medium leads to the dissociation of either the ethyl ester product or of the triglyceride raw material. Soaps from saponification of oil are formed parallel to the soaps of neutralization of the free fatty acids content in raw oil, resulting in a turbid image of raw reaction mixture [15]. During the present experiments, the purification stages of ester phase revealed soaps presence. The coexistence of soaps, residues of reaction intermediates and glycerol in ester phase undoubtedly drove to the formation of emulsions in the first contact with water. These difficult occasions were extensively faced

for FAEE production under hydroxides, driving to lower triglycerides conversion and to a loss of ethyl esters in glycerol phase, leading to an inferior recovery. The impact of catalyst concentration in NaOH case was also studied. A low amount of NaOH (less than 0,4% m/m) did not drive to the established conversion of 96,5% according to the european norms. The amount of produced glycerol was much smaller than the expected, because the amount of the catalyst was insufficient to promote the reaction completely, giving glycerides (mono, di, tri-glycerides) in the final product. Conversely, an excessive amount of NaOH led to the formation of soaps, increasing the viscosity of reactants, inhibiting their contact. The mass transfer limitation decreased the reaction rate, accompanied by catalyst consumption for oil saponification, accelerated by the water presence in reaction medium, resulting in the formation of a white opaque ester phase during the purification stage. Increasing the ethanol:oil molar ratio has clearly a positive effect in ethanolysis, and inversely, the increasing of catalyst mass ratio has ambiguous effects, since the glycerides are converted faster and with a higher extent not only to biodiesel but also, a greater amount of soaps is formed. Also the increasing of temperature causes a higher forming of soaps [18], since the saponification reaction precedes the transesterification reaction, consuming the major amount of catalyst. Throughout all experiments the protocol of reaction temperature was intensively chosen at (80 °C) for accelerating the reaction rate whereas the saponification reaction was limited at that value. With respect to the literature, an effective way to reduce the reaction time of is undoubtedly the implementation of experiments to the boiling point of alcohol not at higher values, hindering the saponification either for ethyl ester [19,20] or methylester production [1,23,24]. As a conclusion of such circumstances there is the need for an optimized catalyst concentration, when NaOH is being used for ethyl esters production.

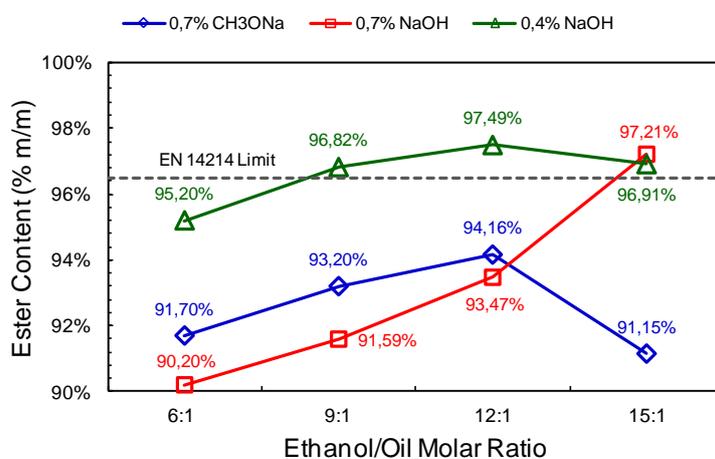


Figure 1. FAEE ester content for CH₃ONa and NaOH catalysts with ethanol to oil

A set of experiments was carried out with CH₃ONa as ethanolysis catalyst. Throughout a previous examination, a concentration of 0,7% m/m in soybean oil was sufficient for the conversion to ethyl esters [17]. In contrast to hydroxides, the reaction of CH₃ONa with ethanol doesn't liberate water but methanol, so, the absence of water prevents from hydrolysis reactions in the system. As evidenced, the ester content was satisfactory (>93%) at molar ratios 9:1 – 12:1, with an exception at the higher analogy 15:1, in opposition to the fact that the higher molar ratios of ethanol to oil are more beneficial for complete conversion. Additionally, the reverse behavior of catalysts at higher ratio of ethanol to oil was noticed.

Catalyst consumption and soaps formation as a function of reaction time in the presence of CH₃ONa and CH₃OK has been examined in sunflower oil [5]. When NaOH was used, the catalyst consumption was severe, approximating 100%, at the initial time for the

reaction, and as well, the soap formation was rapid. In contrast, CH_3ONa was consumed in a slower rate and in a smaller extent, amounting to 28% [5]. Phase separation after reaction, in case of methoxides, was fast and no soapy interfaces or emulsions were formed. During the current work, soaps and emulsions were observed for both catalysts, but in a different extent. Moreover, it is reminded that throughout the present work, the same concentration of catalysts was examined. The two catalysts have different molecular masses, hence, the final mass amount assigned to CH_3ONa and NaOH was different, and lower for CH_3ONa , explaining the less soaps and emulsions formed along processing. Also, as depicted in Figure 1, the better conversion in the presence of NaOH at (15:1) confirmed the large catalyst quantity as regards alkaline metal hydroxides.

3.3. Ethanol to Oil Molar Ratio

Another important parameter examined in this work is the molar ratio of ethanol to oil. The results shown in Figure 1 confirmed the need for the optimum molar ratio. The previous results and the literature data [1,17] showed that the best ethanol:oil ratio for FAEE production was 12:1. The results of the present work with 0,4% NaOH as catalyst showed that the molar ratios 9:1 – 12:1 were satisfactory meeting the set value of 96,5% m/m by one-step process (table 4). It was also observed that the best analogies for ethanolysis should not be higher than 12:1. In the range of 6:1 – 12:1, two distinct phases were formed spontaneously by gravitation. Conversely, at high molar ratio 15:1, one phase was formed, since the phases were perturbed and their separation was impossible to be done, even in a prolonged separation time. To overcome this problem, ethanol removal was carried out to ease the separation. Ethanol removal from raw reaction mixture always hides the danger of reversion since the mixture has none raw material, so the reaction equilibrium turns to the left side, resulting in the recombination of ester and glycerol to mono-glycerides. Reaction reversion has been examined in the presence of NaOH and KOH catalysts, with reversion losses being higher at higher temperatures. Esters loss could be recovered by heating of the separated glycerol [23]. In the presence of 0,7% m/m NaOH at 15:1 the phenomenon of catalyst dilution was observed. With regard to Figure 1, a satisfactory yield was achieved at 15:1, showing that the dilution of catalyst positively dominates over the effect of excess ethanol, giving much better ester yield. The results in Figure 1 verified the following: the ester content under 0,4% NaOH at 6:1 was significantly higher to 0,7% NaOH , for 9:1 the yield was in line with European norm (96,82%). The optimized molar ratio of ethanol to soybean oil was again 12:1, compared to 0,7% m/m of CH_3ONa . As shown in Figure 1, the molar ratio of 15:1 led to a decrease of ester yield, owing to the dilution of catalyst amount, confirming that 0,4% NaOH was the appropriate for sodium hydroxide.

3.4. Mass Basis Yield

According to the stoichiometry of ethanolysis reaction, 3 moles of ethanol and 1 mole of tri-glycerides are required to give 3 moles of fatty acid ethyl esters and 1 mole of by-product glycerol. On a mass basis, for 100 g of oil, the maximum theoretical yield for ethyl esters conversion is of 105,2%, whereas the maximum theoretical yield for fatty acid methyl esters is 100,45% [3,5], due to the higher molecular mass of ethanol. Taking into account of the mass yield results (Figure 2), the transesterification reaction with CH_3ONa was significantly better than with NaOH on a mass basis of recovered ethyl esters. The mass difference between the function of the two catalysts was caused by the higher amount of soaps formed with NaOH [5].

The soaps formed with NaOH catalyst hinder glycerol separation and part of the esters is removed with the glycerol phase. The mass losses in case of NaOH were high, even in the appropriate concentration of 0,4% (as shown in Figure 2), preventing its widespread industrial utilization. In the literature bad separation of ethyl esters from reaction mixture

due to the presence of both soaps and mono-glycerides in the reaction medium has been reported with KOH and NaOH catalysts that led to more losses in comparison with methyl esters [24]. For comparison, a design of two-stages process in the presence of 0,7% m/m CH_3ONa was further tested. The results revealed that there was an improvement in ester content, although its value is satisfactory at 12:1 molar ratio, but the major gain of the multistage process were: easier separation and purification stages, less emulsions and soaps formation, resulting to higher ethyl esters mass yield because the losses were reduced. The resultant values showed that a mass improvement was achieved even in a lower ethanol ratio of 6:1. As it was observed the formation of emulsions was significantly less in two-stage process. As referred by Olivera et.al [13], the ester yield in two-stages transesterification process was significantly improved, exceeding in cases 16% compared to one-stage process. Another examination for FAEE production showed that the yield was significantly improved by two-stages transesterification of used frying oils, from 74,2% to 94,5%, positively influencing the other properties of produced biodiesel from low-grade oils [16]. Taking the behavior of sodium methoxide in two-stages process as a challenge, a set of experiment was performed in the presence of 0,4% NaOH. The results revealed a significant improvement of mass yield, approximating 30% (80 g) for all the ethanol ratios. Besides the mass advantages for both catalysts in multistage process, the reaction time in two-stages process was less (2 h) than the one-stage process (3 h).

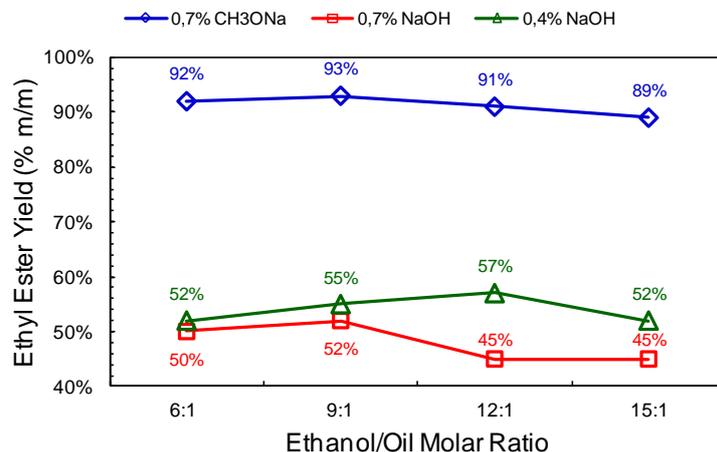


Figure 2. FAEE mass basis yield for CH_3ONa and NaOH catalysts with ethanol to oil

5. CONCLUSIONS

In an attempt to produce biodiesel with more sustainable characteristics, ethanol was used as transesterification alcohol. Ethanolysis would be of interest for direct application, but the process includes some downsides. It is a sensitive process, so any minor change in the experimental conditions could affect the final conversion, forming intensive soaps and subsequently emulsions, complicating the recuperation and purification of biodiesel. Two homogeneous catalysts were used for the conversion of soybean oil. The results showed that for both catalysts the esters yields were satisfactory, under the optimized transesterification parameters. NaOH yielded reduced mass product yield, due to soaps and emulsions formation, a drawback for utilization of sodium hydroxide as a catalyst for industrial purposes, even though it is the lower cost catalyst. When two-stage transesterification process was performed, an increase by 30% on mass basis yield was achieved. Conversely, CH_3ONa revealed satisfactory ester yield and better recovery, since the methanol solution supplied did not contain the hydroxide group to hydroxides, hindering the triglycerides saponification and ethyl esters decomposition. Hence, the ethanolysis of refined soybean oil was efficiently carried out under 0,7% m/m CH_3ONa at ambient pressure and 80 °C.

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