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Alkaline synthesis of fatty acids *iso*-propyl esters

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Fatty acid alkyl esters are widely used products. Most of them are used as renewable transport fuel named "biodiesel". Production of fatty acid *iso*-propyl esters mainly based on acid process but using of alkaline catalysts may give good yields also. Alkaline catalysts have some advantageous such as low corrosivity and higher reaction rate. In current work the effectivity of potassium hydroxide and treated potassium hydroxide solution as catalyst for transesterification was compared. It was shown that using of KOH solution in *iso*-propyl alcohol after special treatment gives almost twice higher yields (95-96 %) from refined sunflower oil triglycerides than over KOH under the same conditions. Yield of fatty acids *iso*-propyl esters from wasted frying oil stabilized after 1-1.5 hours of reaction over both catalysts. Using 1.8 and 2.0 % treated catalyst at 90 °C leads to yield of about 86-88 % at 9:1 alcohol-to-oil ratio. Reaction temperature has significant impact on a yield which decreases with temperature reduce in the range from 30 to 90 °C. During reaction proceeding the alkali saponification and thus loss the catalytic activity, which displayed in stopping the yield rising. The lower yield of esters from wasted oil comparing to the refined oil may be caused by presence of heavy polymerized triglycerides components formed during frying. Such components cannot be fully converted into monoalkylesters and gives also the oligomerized esters, which is not visible in standard gas chromatographic analysis of biodiesel. Indirect confirmation of the presence of such compounds in wasted frying oil sample is the sufficiently larger mass of the cube residue in vacuum distillation. For refined oil amount of such residue was only 5.4%, while for wasted oil it was three time higher (14.9%). In case of wasted frying oil as raw stuff, even after full conversion and effective self-separation conventional purification methods (like water washing or dry washing with adsorbents) may not provide the necessary purity of resulted biodiesel due to the presence of heavy oligomeric admixtures. In such cases vacuum distillation should be included as necessary final purification stage.

Keywords: *iso*-propyl alcohol, alkaline catalyst, wasted frying oil, transesterification

Introduction

Fatty acid alkyl esters are widely used products. Most of them are used as renewable transport fuel named "biodiesel". Biodiesel manufacturing is mainly based on methanol, utilizing as reagent both in the triglycerides transesterification and fatty acids esterification processes. This is due to its lowest price among the monohydric alcohols, as well as its high efficiency in this reaction. But methanol using has also some disadvantageous. First of all, these are high methanol toxicity and impossibility of "winter biodiesel" obtaining without using of specific additives, enhancing methyl esters cold flow properties. All another aliphatic monohydric alcohols have much lower toxicity and better low temperature properties of their fatty acid esters.

iso-propyl alcohol has good perspectives as transesterification reagent. First of all, it is widely used large-scale product of basic organic synthesis, having relatively low price. It is also known from literature sources, that fatty acid *iso*-propyl esters are characterized by better cold flow properties than methyl and ethyl esters, obtained from the same raw materials [1-7].

Effective transesterification of triglycerides by *iso*-propyl alcohol, resulting in high conversion of raw stuff and high yield of *iso*-propyl esters, is possible in case of reaction catalysis by strong mineral acids [2, 3, 8]. Alkaline-catalyzed transesterification by *iso*-propyl alcohol is strongly influenced by reaction parameters: temperature, catalyst concentration, molar ratio of alcohol-to-oil (R_{AO}) and time of reaction. Because of this, different authors reported different results even at the same catalyst – KOH. So, authors [9] did not obtain *iso*-propyl esters at 25 °C, 1% of catalyst load, $R_{AO} = 6$ after 1 hour of reaction. Carrying out transesterification at higher temperature (45 °C, 0.5% KOH, $R_{AO} = 6$, 0.5 hour) resulted in 43 % yield of *iso*-propyl esters, while further increasing the temperature to 60 °C enhanced the yield to about 80% both at 0.5% and 1.0% KOH and unchanged another reaction conditions [10]. Under close reaction conditions (50 °C, 0.5% KOH, $R_{AO} = 6:1$, 0.5 hour) another authors achieved 86% yield of *iso*-propyl esters [11], however it was not observed any separation of glycerol layer. Authors [8] failed in preparing *iso*-propanol-based biodiesel via alkaline catalysis over KOH even under unacceptable harsh reaction conditions (77 °C,

1.5% KOH, $R_{AO} = 70$, 48 h) and preferred to carry out acid-catalyzed process over H_2SO_4 . Low reactivity of *iso*-propyl alcohol was attributed to its branched structure. As generally known, the branched monohydric alcohols are characterized by far lower acid strength, than linear once. Namely *iso*-propanol has almost two-magnitude weaker acid strength, than methanol [12]. When catalyzing transesterification with hydroxides, weaker acidity of the alcohol strongly suppresses the formation of alkoxide-anion, which acts as real catalyst in this process. In case of *iso*-propanol, its concentration would be very low comparing with methanol-based process. Another difference from methanolysis consists in better miscibility of triglycerides with *iso*-propanol, which is favorable for saponification, resulting in catalyst loss. From our point of view, the difference in results with KOH as catalyst is first of all due to the inequality of the hydroxide reagents used in terms of water content. It is widely known, that KOH reagents may contain about 15% of water. For example, in work [13] 16% moisture content was revealed in high-pure KOH. Higher water content during transesterification both decrease the alkoxide concentration and increase the saponification rate. Direct utilization of alkoxides reagents is able to provide the very high concentration of *iso*-propoxide anions in reaction media, which is necessary for the effective transesterification. Earlier it was described the using of potassium and sodium *iso*-propoxides [7]. The former was the commercially purchased substance, while the later was obtained by reaction of *iso*-propanol with metallic Na, which is non-option on the large production scale. The fullness of feed-stock conversion was controlled by measuring total glycerol content in reaction products after washing. Best results (0.04% total glycerol content) were obtained in reflux condition at $R_{AO} = 20:1$ over potassium *iso*-propoxide (1.34% in terms of K, or 1.9% in terms of KOH relative to oil mass) after 8 hours of reaction. Utilization of 1-1.5% Na under the same conditions provided higher total glycerol content – 0.18-0.34%. Decreasing the alcohol-to-oil ratio ($R_{AO} = 10$ or $R_{AO} = 6$) provided closer result at 1.25% Na load, but in case of potassium *iso*-propoxide conversion was substantially lower (total glycerol content 0.64-0.70%). However, no phase separation was observed under any reaction conditions over both catalysts.

Regardless of relatively lower yields of *iso*-propyl esters, than in case of acid catalysis, alkaline-catalyzed route has some advantageous such as low corrosivity and high reaction rate. So, we decide to develop the method of preparing the alkaline catalyst, which will be free from some disadvantageous, having alkaline metal hydroxides. Also, we used the really valuable from practical point of view source of

triglycerides such as wasted frying oil, instead of high-expensive fresh vegetable oils.

Materials and methods

Chemicals

Oil raw stuff included commercial refined sunflower oil (Ukraine; acid value 0.07 mg KOH/g and 0.03% of water and fatty acids composition: C16:0 – 6.7%, C18:0 – 2.8%, C18:1 – 33.0%, C18:2 – 54.6%, others – 2.9%) and wasted frying sunflower oil (Ukraine: 0.86 mg KOH/g and 0.03% of water and fatty acids composition: C16:0 – 8.8%, C18:0 – 4.1%, C18:1 – 35.1%, C18:2 – 47.6%, others – 4.4%). Another chemicals, used in current study, were the following: analytical grade KOH (China, 83% KOH; as catalyst of refined oil transesterification); technical grade KOH (China, 84% KOH; as catalyst of wasted oil transesterification); chemical grade *iso*-propyl alcohol (Russian Federation); 0.1 N HCl water solution (prepared from fixanales); indicators bromophenol blue and phenolphthalein; reagent-grade methyl palmitate (>97%); reagent-grade *n*-hexane; synthetic molecular sieves KA-Y/3A (Russian Federation, dynamic water vapor capacity – 150 mg/cm³); technical grade anhydrous calcium chloride.

Experimental

Preparation of catalytic solution

Solution of alkaline catalyst based on KOH and *iso*-propyl alcohol (SMC – self-made catalyst) was prepared by analogous to the method of the hydroxide/ethanol based alkaline catalyst preparation, described in patent [14]. Procedure consisted in boiling of the KOH solution in *iso*-propanol and selective dehydration of alcohol water azeotrope, condensed over the bed of KA-Y/3A molecular sieves in Soxhlet extractor. Dried *iso*-propanol was returned into the alkali solution. The boiling-condensation-drying sequence was repeated for several times.

Comparison of hydroxide and prepared alkaline solution

In these series of experiments KOH, previously dissolved in dried with molecular sieves *iso*-propyl alcohol, was used as catalyst. Also, SMC, obtained as above mentioned from KOH *iso*-propanol solution, was utilized. Investigations were carried out using refined sunflower oil with specified content of triglycerides about 99.9%. For each synthesis 2% KOH load (hereinafter catalyst load expressed relative to mass of oil) was used. Contents of alkali in reagent (KOH), measured by titration, was about 83%, catalyst amount is expressed in terms of 100-% KOH. In each synthesis 100 g of oil was used. In order to compare the efficiency of the catalysts, the same load of SMC in equivalent of reagent KOH was used (1.66 %_{eq. KOH}). R_{AO} ratio was in range of 6-15 mol/mol. Syntheses were carried out in 500 cm³ round-bottom flask,

equipped with reflux condenser and water trap tube (filled with CaCl_2) in reflux conditions (bath temperature 120-125 °C) for 2 hours. Heating of the mixture was provided with oil bath, placed on electric stove.

Influence of catalyst concentration and reaction temperature

In this series of experiments only SMC alkaline catalytic solution was used. It was prepared from KOH and *iso*-propyl alcohol. Investigations were carried out utilizing used frying sunflower oil. Marked concentration of alkaline catalyst was calculated in equivalent of KOH (%_{eq. KOH}). Syntheses were carried out in 250 cm³ two-neck heart-like flask, equipped with thermometer, reflux condenser and water trap tube (filled with CaCl_2), reaction mixture was stirred by magnetic stirrer. In each synthesis 70 g of oil was used. Heating of mixture was provided with oil bath, placed on the magnetic stirrer. Sampling was carried out each 0.5 hour, beginning sample was taken immediately after immersion of the flask into hot oil bath.

Enlarged synthesis of fatty acid iso-propyl esters

In this process was used SMC alkaline catalytic solution and wasted frying oil sample. Synthesis was carried out under next conditions: 2%_{eq.} KOH to oil, $R_{AO} = 9$, reaction time – 2 hours, loading of oil – 250 g, bath temperature – water trap tube (filled with CaCl_2) under reflux conditions. Heating of mixture was provided with oil bath, placed on electric stove.

Analysis

Determination of iso-propyl esters yield

The yield of the *iso*-propyl esters during and after syntheses was estimated from the decrease of the *iso*-propyl alcohol content in reaction products, measured by the mass loss of the sample due to evaporation at room temperature. The sample (5-10 g) was placed into the open Petri dish and periodically weighted until the stable mass achievement. All the mass losses were regarded as evaporated alcohol due to high boiling temperature of all another reaction components. Then the theoretically possible mass of *iso*-propyl esters, which can be formed from the alcohol consumed in reaction, was calculated.

In particular case (enlarged synthesis after chose the reaction parameters), yield of the *iso*-propyl esters after finishing synthesis was also calculated from their known concentrations in reaction products. The latter was measured by gas chromatographic analysis, using modified method based on European standard method of determination of methyl esters in biodiesel EN14103. When analyzing fatty acid *iso*-propyl esters far more affordable methyl palmitate may be used as internal standard instead of expensive methyl heptadecanoate. Samples and standard were dissolved in *n*-hexane. Analyses were performed on the gas

chromatograph Agilent 7890A Series, equipped with split/splitless inlet, flame-ionization detector and Agilent J&W HP-5 capillary column ((5% phenyl)-methyl polysiloxane, 30 m length, 0.32 mm internal diameter, 0.25 μm film thickness); high-purity helium was used as carrier gas. Conditions of analyses were the following: inlet temperature 250 °C, inlet excess pressure 82.7 kPa, split ratio 36:1, chromatographic column oven temperature program 210 °C/27 min – 5 °C/min up to 320 °C, detector temperature 250 °C. The yield of fatty acid *iso*-propyl esters was calculated as the ratio of their total mass in reaction products to mass, which could be formed when triglycerides fully convert to esters. After subtraction of free fatty acids, oil was regarded as pure triglycerides having average molar mass, calculated from known oil fatty acid composition.

Estimation of heavy residue in samples of oil

Residue of heavy polymerized compounds in oils samples, which could not be converted into compounds, visible in gas chromatographic analyses was determined by complicated method of successive treatment of oil samples. It included saponification of the oil, acid hydrolysis of formed soaps, washing, drying and vacuum distillation of obtained fatty acids as described in detail in earlier work [15].

Titration of the reaction products

Alkaline catalyst and soap content in the reaction products were determined by two-step acid-base titration method as described in [16]. Alkali was determined in a first titration step, using HCl 0.1 N solution as reactant, *iso*-propanol as solvent and phenolphthalein as indicator. In a second titration step, the soap content was determined using the same titrant and bromophenol blue as indicator.

Results and Discussions

After transesterification of refined sunflower oil both over KOH and SMC solutions one-phase clear mixtures of reaction products, showing no tends for phase separation, were formed. Yield of fatty acids *iso*-propyl esters over KOH appeared to be not higher, than 53% at highest excess of alcohol used (Fig. 1, yield values, estimated from the alcohol content decrease, are given). Using of SMC was remarkably more efficient and resulted in yield of about 92% at $R_{AO} = 6$ and about 95-96% at higher excess of *iso*-propanol.

For further investigation of transesterification of wasted oil sample over SMC reagents ratio $R_{AO} = 9$, which was the lowest among that providing enough high fullness of refined oil transformation (see Fig. 1), was chosen. Yield of *iso*-propyl esters stabilized after 1-1.5 hours of reaction at 90 °C (Fig. 2, yield values, estimated from the alcohol content decrease, are given).

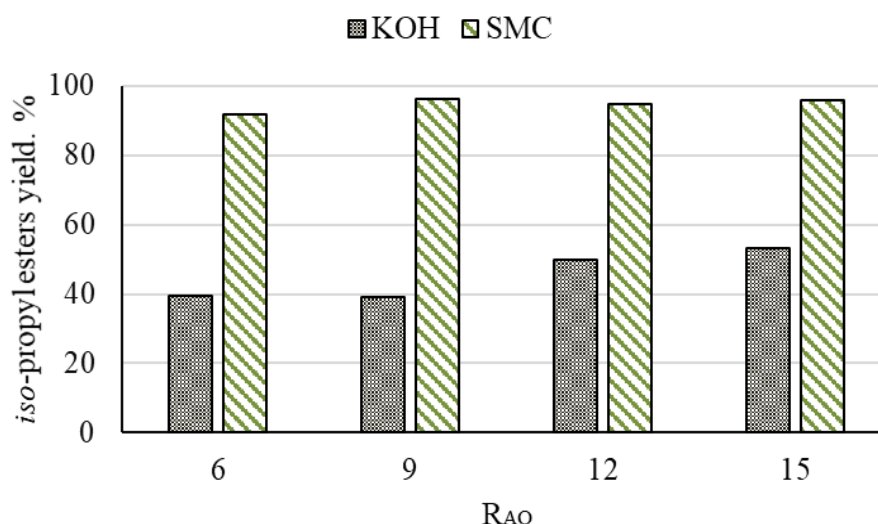


Fig. 1. Yield of *iso*-propyl esters in refined sunflower oil transesterification over KOH and SMC (reflux – 90 °C, 2 h, 2% KOH or 1.66%_{eq. KOH} SMC).

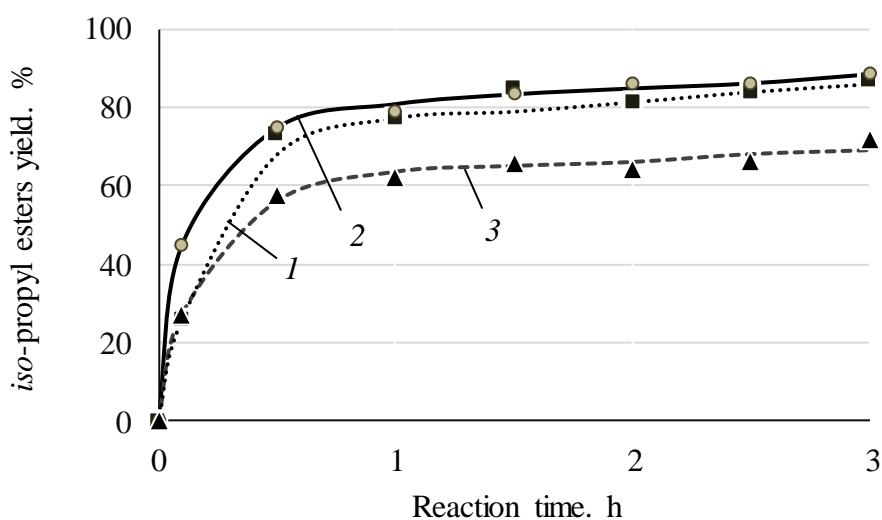


Fig. 2. Changing of *iso*-propyl esters yield in course of wasted sunflower oil transesterification using different load (1 – 2.0, 2 – 1.8, 3 – 1.6%_{eq. KOH}) of SMC (90 °C, R_{AO} = 9).

Using of 1.8 and 2.0%_{eq. KOH} catalyst load provided almost the same yield of esters about 86–88%, while decreasing of the catalyst load to 1.6%_{eq. KOH} resulted in reducing the yield by about 15%.

Further attempts to gradually decrease the reaction temperature under the unchanged other conditions (SMC load – 2%_{eq. KOH}, R_{AO} = 9) in order to provide more environmental friendly energy-saving process resulted in regular decreasing of the *iso*-propyl esters yield (Fig. 3, yield values, estimated from the alcohol content decrease, are given). It is interesting to mentioned, that the temperature impact on the alkaline *iso*-propanolysis appeared to be totally different from that observed in our previous studies for butanolysis using the similar approaches for the alkaline catalytic solution preparing [17, 18]. Namely, alkaline-synthesis

of *n*-butyl esters proceeds very fast even at 15 °C and, moreover, carrying out reaction without heating provides the effective phase self-separation. Another synthesis with larger mass of oil loaded was carried out under reaction conditions, which was chosen as most efficient on the base of discussed results (2%_{eq. KOH} SMC, reflux, 2 hours, R_{AO} – 9:1). In these cases *iso*-propyl esters yield was determined both from the alcohol losses due to evaporation and from the results of gas chromatographic analysis.

Both values were enough close – 72 and 74% respectively. However, these values are some lower, than achieved in smaller synthesis (see Fig. 2 and Fig. 3). Probably, this is due to faster saponification under reflux conditions than during mechanical stirring at close temperature.

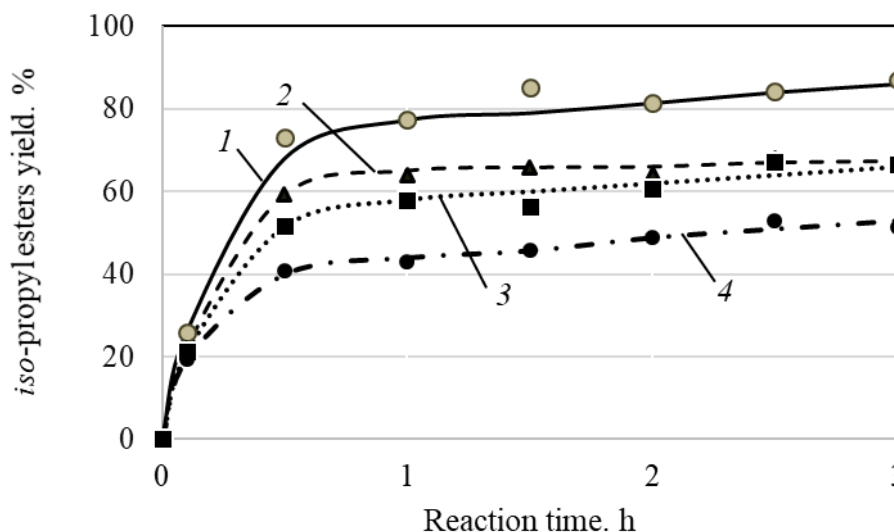
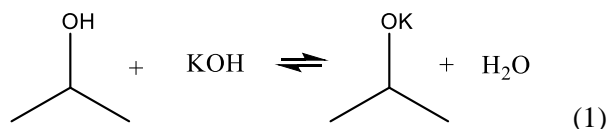


Fig. 3. Changing of *iso*-propyl esters yield in course of wasted sunflower oil transesterification over SMC at different reaction temperatures: 1 – 90, 2 – 70, 3 – 50, 4 – 30 °C (2%_{eq.} KOH, R_{AO} = 9).

It should be emphasized, that titration of reaction mixture after 2 hours of synthesis revealed the absence of the alkaline catalyst due its full saponification. Only saponified alkali was determined via titration with bromophenol blue (concentration of soaps – more than 10% in whole mixture). This may explain stopping rising of esters yield at some stable level before reaching full conversion of the oil or reaction equilibrium (see Fig. 2 and Fig. 3).

There arise the question concerning the reasons of the higher catalytic efficiency of SMC comparing with ordinary KOH, dissolved in *iso*-propyl alcohol. The answer is first of all the difference in water content in the alkaline catalytic solution, and thus in reaction medium during the process. In homogeneous alkaline catalysis of transesterification water content is known to be a critical factor [19-22]. Water leads to secondary hydrolysis and saponification reactions which cause a drop in yield and consume part of the catalyst. Although there are no official specifications, one can be met information about maximum water content in the reaction medium about 0.1% for biodiesel applications [19]. In case of transesterification with branched alcohols, such as *iso*-propanol, the water content influence may be even more critical.

The preparing procedure of SMC consisted in selective water removal from initial KOH alcohol solution. The main source of the water was the potassium hydroxide reagents, containing only 83-84% of KOH (water was the main admixture). Some water also where present in the *iso*-propanol. The removing of this water leads to the shift of the equilibrium of alcohol reaction with alkali towards the alkoxide formation:



Also, additional water, formed in reaction (1) may be removed as process goes on. This may result in further growth of the alkoxide content. As was already mentioned, the alkoxide is the real active catalytic specie in alkaline transesterification. As generally known, alkoxide-anions play a role of nucleophile particles attacked the carbonyl groups of glycerides on each of three successive stages of triglycerides transesterification [23]. The water impact on the equilibrium (1) should be far more pronounced, than in case of methanol with alkali reaction due to difference in acid strength between branched and linear alcohols.

Thus, it may be assumed, that in case ordinary KOH solution the alkali was consumed in saponification reactions before the target transesterification had time to pass sufficiently. In case of SMC both higher saponification reaction rate in presence of water and lower transesterification reaction rate (during to the lower alkoxide-anions content) may be assumed. As result, the higher yield of *iso*-propyl esters may be achieved before the moment of total loss of alkaline catalyst due to soaps formation.

As for the lower yield of esters from wasted oil comparing to the refined oil, this is may be due to presence of heavy polymerized triglycerides components formed during frying [24, 25]. Such components cannot be fully converted into monoalkyl esters and gives also the oligomerized esters, which is not visible in standard gas chromatographic analysis of biodiesel. Indirect confirmation of the presence of such compounds in wasted frying oil sample, used in current study, is the sufficiently larger mass of the cube residue in vacuum distillation of fatty acids,

obtained from oil samples. In case of refined oil amount of such residue was only 5.4%, while in case of wasted oil it was three times higher (14.9%).

Cleaning of reaction products to obtain biodiesel-grade *iso*-propyl esters from resulting mixture will be complicated problem till glycerol self-separation achieved. However, in case of wasted frying oil as raw-stuff, even after full conversion and effective self-separation conventional purification methods (like water washing or dry washing with adsorbents) may not provide the necessary purity of resulted biodiesel due to the presence of heavy oligomeric admixtures. In such cases vacuum distillation should be included as necessary final purification stage.

Conclusions

Obtained results showed that KOH solution in *iso*-propyl alcohol after special treatment (SMC) gives almost twice higher yield of esters from refined sunflower oil triglycerides than at KOH under same conditions. Using both 1.8 and 2.0%_{eq.} KOH amount of SMC gives same highest yield (about 86-88%) of *iso*-propyl esters from wasted frying oil. Enough high yields *iso*-propyl esters yield is achieved only at maximum reaction temperature (90 °C), which is possible to maintain in unpressurized conditions. It was also shown, that stopping of yield rising during *iso*-propanolysis is due to full alkali saponification, but not due to achievement of reaction equilibrium.

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Алкілестери жирних кислот є широко використовуваними продуктами. Більшість із них застосовують як відновлюване паливо для транспорту, яке називають «біодизелем». Виробництво ізопропілових естерів жирних кислот в основному базується на кислотному процесі, але з використанням лужних каталізаторів також можна отримати хороші виходи. Лужні каталізатори мають деякі переваги, такі як низька корозійна активність та вища швидкість реакції. У даній роботі було порівняно ефективність гідроксиду калію та додатково обробленого розчину гідроксиду калію як каталізаторів переестерифікації. Показано, що розчин КОН в ізопропіловому спирті після спеціальної обробки сприяє одержанню майже вдвічі вищого виходу (95-96%) естерів з тригліцеридів рафінованої соняшникової олії, ніж на КОН за тих же умов. Вихід ізопропілових естерів жирних кислот з відпрацьованої олії після фритюру стабілізується через 1-1,5 години реакції на обох каталізаторах. З використанням 1,8 і 2,0% обробленого каталізатора за 90°C було одержано виходи близько 86-88 % за співвідношення спирту до олії 9:1. Встановлено, що температура реакції має суттєвий вплив на вихід, який спадає із пониженням температури від 30 до 90 °C. Впродовж реакції луг омилюється і втрачає каталітичну активність, що проявляється у зупинці зростання виходу. Нижчий вихід естерів з відпрацьованої олії порівняно з рафінованою олією може бути спричинений присутністю важких полімеризованих компонентів тригліцеридів, які формуються впродовж смаження. Такі компоненти не можуть бути повністю перетворені в моноалкілестери та утворюють олігомеризовані естери, які не фіксуються при стандартному газохроматографічному аналізі біодизелю. Непрямим підтвердженням присутності таких сполук у зразку відпрацьованої олії після фритюру є значно більша маса кубового залишку, одержаного при вакуумній перегонці. Для рафінованої олії кількість такого залишку становила лише 5,4%, а для фритюрної втричі більше – 14,9%. У разі використання як сировини фритюрної олії навіть за повного перетворення та ефективного саморозділення загальноприйняті методи очищення (промивання водою або сухе очищення із застосуванням адсорбентів) можуть не забезпечити необхідної чистоти отриманого біодизеля через наявність важких олігомерних домішок. У таких випадках необхідною кінцевою стадією очищення має бути вакуумна перегонка.

Ключові слова: ізопропіловий спирт, лужний каталізатор, використана олія після смаження, переестерифікація