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Influence of free fatty acids and water on alkaline transesterification of rapeseed oil by *n*-butanol

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The influence of free fatty acids and water on the process of alkaline transesterification of rapeseed oil by n-butyl alcohol was studied. It was shown that neutralization of free acids by additional amount of alkaline with formation of soap has not affect on the yield of main products. On the contrary, free water strongly decreasing the yield of main products and therefore it must be completely removed.

Today methyl and ethyl alcohols became traditional ones for transesterification of natural oils whereas a number of works dedicated to search of new raw alcohol for biodiesel fuel preparation. Now n-butyl alcohol is considered as the most perspective among developing bioalcohols.

However, the problems of alkali synthesis become more obvious with carbon chain in alcohol increasing because of easier saponification [1]. It is well-known that heating leads to very low yields of main products [2]. Therefore, the researchers refuse from alkali synthesis to more expensive, corrosive and power-consuming acid synthesis [3]. All these aspects turn away of the attention of biodiesel fuel producers from biodiesel manufactured from *n*-butanol. But, were shown obtained butyl esters of rapeseed oil with middle yield at room temperature process [4]. This aspect intensifies interest to *n*-butanol as raw material for biodiesel production.

The optimal temperature for rapeseed oil transesterification by *n*-butyl alcohol is below 20 °C, molar ratio alcohol/oil is 7,5/1, acid value is 2,2 g KOH/ 100 g oil.

The aim of work was to identify the influence of free fatty acids and water presence in natural oils on tranesterification by *n*-butanol. For abovementioned purpose realization both admixtures have been added to reaction medium and the process has been carried out at the same conditions.

Transesterification has been realized at ambient temperature (20 °C) and at slightly decreased temperature (10 °C) for minimization of saponification.

The preparation of free fatty acids from rapeseed oil was carried out according to described method [5]. The synthesized dried fatty acids were added to reaction medium at amounts of 1–3 wt. % of oil, that corresponding to the acid value of 200–600 mg KOH/100 g oil. The process has been carried out for 4 h at alcohol/oil molar ratio 7,5/1 and was 2,2 wt. % KOH content.

Table 1 shown that the yield of butyl esters decrease on 12,6 % from 80,6 to 68,0 % at 10 °C and on 19,1 % from 74,4 to 55,3 % at 20 °C with increase of content of free fatty acids.

Decrease of yield of butyl esters can be caused by decrease of catalyst (KOH) content, which partially involved in saponification of free fatty acids (equation 1). A number of experiments with additional amount of KOH in reaction media shown results close to results without adding fatty acids (Table 2).

$$RCOOH + KOH \leftrightarrow RCOOK + H_2O \quad (1)$$

According to the results obtained (Fig. 1), formed soaps practically have not influence on process of alkaline transesterification of oil by n-butyl alcohol.

It is well-known that water presence in ethanol cause problems with esters and glycerin dividing after transesterification reaction. Therefore, dehydrated ethanol must be used for transesterification [6].

With aim to clarify the influence of admixtures of water

Table 1. **The influence of free fatty acid content on yield of main products of butyl transesterification of rapeseed oil**

The number of experiment	Content of free fatty acids, g/100g of oil	Concentration of KOH, wt. % to oil	Yield of esters, %	Temperature, °C
1	0	2,2	80,6	10
2	3	2,2	68,0	10
3	0	2,2	74,4	20
4	1	2,2	68,8	20
5	2	2,2	64,2	20
6	3	2,2	55,3	20

Table 2. **The influence of free fatty acid on yield of main products of butyl transesterification of rapeseed oil with compensation of alkaline**

The number of experiment	Content of free fatty acids, g/100g of oil	Concentration of KOH, wt. % to oil	Yield of esters, %	Temperature, °C
1	0	2,2	80,6	10
7	1	2,4	80,3	10
8	2	2,6	78,8	10
9	3	2,8	81,3	10
3	0	2,2	74,4	20
10	1	2,4	72,2	20
11	2	2,6	73,5	20
12	3	2,8	69,5	20

in the oil on the reaction flowing, the additional amounts of water were added to reaction medium (Fig. 2). It was detected high negative effect of free water on the main process realization. The yield of main products decreases on 30,6 % to 43,8 % from 74,4 % at 2 wt. % of water content and to 20,2 % at 1 wt. % water.

The results obtained show significant influence of free water. The last can be an admixture in natural oil or arise during *in situ* preparation of alkali catalyst (potassium butoxide) in transesterification process [7]. This reaction water (equation 2) could not been ignored. It's theoretical amounts is about 0,7 %, could cause significant decrease of yield of butyl esters of fatty acids as the main products.

$$C_4H_9OH + KOH \leftrightarrow C_4H_9OK + H_2O \quad (2)$$

With the purpose to remove reaction water after KOH and butanol mixing the previous distillation using Dean-Stark trap has been carried out. As against to ethanol in butanol case the water removing could be achieved easily by distillation because of butyl alcohol and water azeotrope consists more water than butanol-water solution, and as result condensate divides in two phases. The needed amount of butyl alcohol for compensation of distilled alcohol was added to residua (dehydrated solution of KOH in butanol). Further, transesterification reaction was carried out at 20 °C with the same conditions as described in previous cases.

In result, as we expected the increase of the main products yields (to 87,2 wt. %), have been obtained.

Conclusions

Low free fatty acids content (acid value < 600 mg KOH/100 g) does not cause significant contribution in decrease of yields of rapeseed oil butyl esters. Additional catalyst amount can be used for compensation of catalyst lost on neutralization of acids.

Although, free water causes significant contribution to yield of main products and it must be removed completely from reaction media. As against ethanol, *n*-butanol dehydratation can be realized by simple distillation without dehydrated components using.

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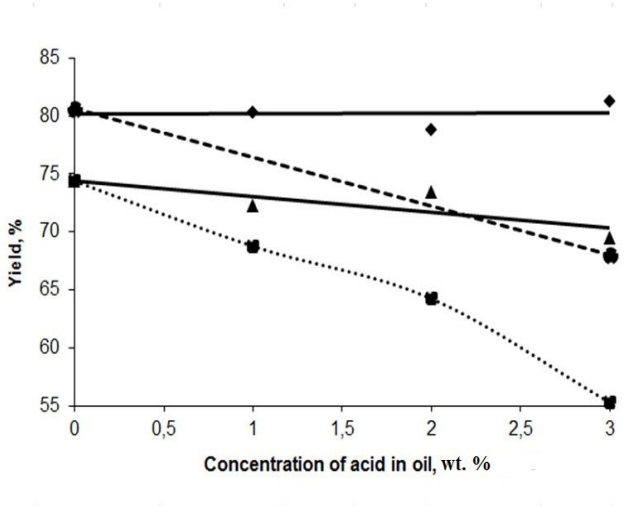

Figure 1. Dependence of yield of rapeseed oil butyl esters on concentration of added fatty acids. ◆ – With compensation (10 °C); - ▲ - – Without compensation (10 °C); ▲ – With compensation (20 °C);···■··· – Without compensation (20 °C)

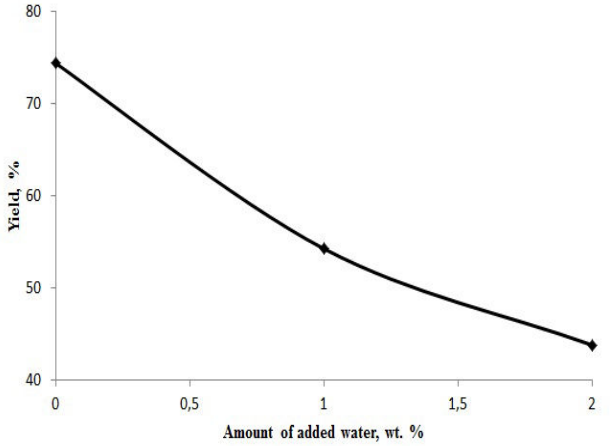

Figure 2. Dependence of yield of rapeseed oil butyl esters on amount of water

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Вплив вільних жирних кислот та води на лужну переестерифікацію ріпакової олії *н*-бутанолом

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Визначено вплив вільних жирних кислот та води на процес лужної переестерифікації ріпакової олії н-бутиловим спиртом. Показано, що при нейтралізації вільної кислоти за допомогою додаткової кількості лугу, утворені мила не впливають на вихід цільових продуктів. Вільна вода, навпаки, сильно зменшує вихід цільових продуктів і потребує повного видалення.

Влияние свободных жирных кислот и воды на щелочную переэтерификацию рапсового масла *н*-бутанолом

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Определено влияние свободных жирных кислот и воды на процесс щелочной переэтерификации рапсового масла *н*-бутиловым спиртом. Показано, что при нейтрализации свободной кислоты при помощи дополнительного количества щелочи, полученные мыла не влияют на выход целевых продуктов. Свободная вода, наоборот, сильно уменьшает выход целевых продуктов и требует полного удаления.