

## Peculiarities of potassium butylate preparation as a catalyst for the transesterification process

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Potassium butylate was synthesized based on *n*-butyl alcohol and potassium hydroxide with the use of Dean-Stark method. A twofold role of *n*-butyl alcohol was shown in the process butylate obtaining both as a synthesis reagent and as a azeotrope-forming agent for removal of water from the reaction media. Its high activity as a catalyst for sunflower oil transesterification at ambient temperature was confirmed.

The solutions of alkali-metal hydroxides in alcohol are commonly used as catalysts for base catalyzed reactions. One of such processes is a widely spread transesterification for preparation of fatty acids alkyl esters, the so-called "biodiesel fuel".

The most commonly used alcohol for biodiesel production is methanol. It has a number of advantages in comparison with other alcohols. The first advantage is its price, which is relatively lower than prices for other alcohols. Another advantage of methanol is its specific acidity. Methanol acidity ( $pK_a=15.5$ ) is higher than acidity of water ( $pK_a=15.7$ ). Therefore, methanol can remove alkali metal ion from an aqueous solution with methylate formation in alkali-metal hydroxide/methanol solution [1]. Other alcohols lead to a lower production of alkoxide.

For example, transesterification of triglycerides with the methanol/alkali-metal hydroxide solution gives high yields even in the presence of 5 wt. % of water in the reaction media [2]. But in order to achieve successful transesterification with ethyl alcohol, it is necessary to use absolute alcohol [3]. This is, first of all, due to the fact, that acidity of water is higher as compared to acidity of ethanol ( $pK_a=15.9$ ) and potassium (sodium) ethylate is formed worse. As a result, the transesterification is catalyzed by a less active hydroxide. Therefore, to increase the reaction rate it is necessary to rise the temperature. The temperature rise leads to saponification of raw materials and, as a result, to reduction in the main products yield. The saponified components stabilize the system and prevent separation into ester and glycerol layers. Whereas the use of dehydrated reagents enables to reach fast separation of the products into ester and glycerol layers [4] as it occurs in methanol transesterification.

Use of alcohols with a longer carbon chain than that of methanol in transesterification of glycerides makes their saponification easier [5] and thereby lowers the main products yield. Thus, in our previous research work, it was shown that potassium hydroxide catalyzed transesterification of triglycerides with *n*-butanol led to decrease in yield of fatty acids butyl esters at high temperatures as compared

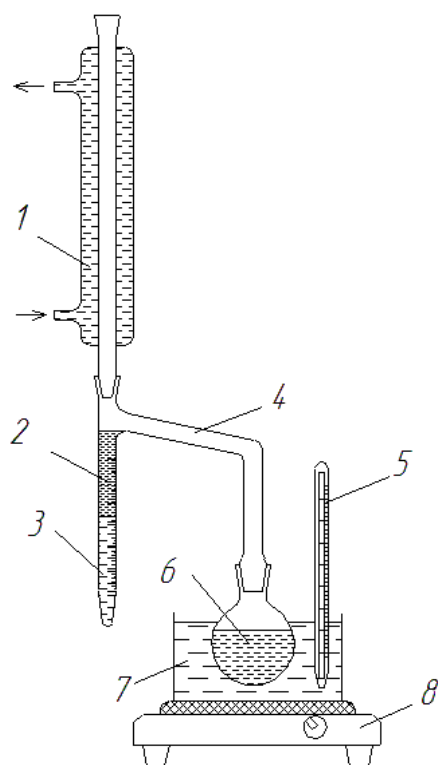
to their yields at room temperature [6]. And therefore, it is better to carry out the potassium hydroxide catalyzed transesterification with *n*-butanol at ambient or lower temperatures [7].

The paper [8] investigates the influence of water on the alkaline transesterification with *n*-butyl alcohol. It was shown that presence of insignificant water quantity can notably decrease the main products yield. Moreover, use of potassium hydroxide/alcohol solution cannot lead to a free self-separation of glycerol layer without butanol distillation [9]. To remove the whole amount of alcohol, it is necessary to heat the products media [10]. But butyl alcohol distillation with dissolved catalyst leads to products saponification. In order to prevent saponification, it is necessary to carry out catalyst neutralization by an acid. Use of additional acid makes the process more expensive and more environmentally hazardous. Therefore, there is a need to make transesterification of glycerides with all alcohols technologically easier. First of all, this includes transesterification with *n*-butyl alcohol. The problem of products separation in fatty acid butyl esters synthesis has been discussed in [9, 11–13].

Therefore, the main purpose of this paper was to synthesize potassium butylate as an active catalyst for low temperature transesterification process, which allowed to achieve high yields of the main products simultaneously with spontaneous products separation.

The following reagents were used in this study: *n*-butyl alcohol (chemical grade), *n*-butyl alcohol (technical grade), potassium hydroxide (reagent grade), and two samples of potassium hydroxide that had been stored longer than the shelf life period, for more than 10 years (reagent grade).

Having conducted a detailed analysis of water sources in the reaction of potassium butylate synthesis, we determined that potassium hydroxide of high purity contains up to 15 wt. % of water. Although presence of water in potassium hydroxide had not been regulated by domestic regulatory documents for this product [14], this parameter was specified in foreign documents published at a later time [15]. Besides, presence of 16 wt. % of water in KOH, de-



**Figure.** Scheme of laboratory water removal apparatus from KOH/butanol solution. 1 – water cooler, 2 – butanol layer, 3 – water layer, 4 – Dean-Stark trap, 5 – thermometer, 6 – KOH in butanol solution without water, 7 – oil bath, 8 – hotplate

terminated by Fisher's method, was shown in the research work [16]. Taking into account high hygroscopicity of KOH, storage of the mentioned reagent led to its quality deterioration, therefore the use of the reagent that had been stored for a long period of time led to reduction in yields of the transesterification products.

Therefore we had two sources of water – its formation in reaction of KOH with butanol and its initial content in the starting KOH. In order to level negative impact of water on the transesterification reaction, we tried to take advantage of specific features of butyl alcohol. To tackle the problem, we exploited property of *n*-butanol and higher alcohols to dissolve only sparingly in water and, like other alcohols, to form water-containing azeotrope with a lower boiling point than alcohol as it is, without water [17]. For example, *n*-butanol–water azeotrope with content of water in mixture 42.4 wt. % boiled at 93 °C, when *n*-butanol alone boiled at 117 °C [17]. This property is used as a basis for the industrial *n*-butanol dehydration process, which was implemented at the beginning of the last century [18]. Thus, the *n*-butanol dehydration process is much simpler than methanol dehydration, and especially ethanol dehydration.

The method for removal of water formed in the reaction medium of butanol and alkali, which used xylene as an additional component, had already been developed [19]. The question emerged, whether it was possible to remove water from KOH using water–butanol azeotrope. In our

research papers, we showed that alkali solutions dehydrated by distillation produced higher yields of the main products in the transesterification reaction and ensured formation of a system, in which products could be separated to ester and glycerin layers as a result of a spontaneous process [20–23].

A number of solutions of KOH in butanol were prepared. Alkali concentration in solutions was determined by titration with 0.1 N hydrochloric acid in the presence of 0.5 % phenolphthalein ethyl alcohol solution.

Titration of KOH showed 85.5 wt. % of KOH in the fresh sample (KOH sample (I)) and the rest was accepted as free water. The result of titration of the other stored samples showed that amounts of KOH equaled 78.2 wt. % (KOH sample (II)) and 76.8 wt. % (KOH sample (III)).

Azeotropic distillation of water from KOH (I) with benzene gave no result. Water was not isolated at all.

All samples of KOH for the synthesis had good solubility in *n*-butyl alcohol with a mild auto heating of the mixture, in contrast to the research work [24], wherein the authors emphasized on poor solubility of KOH in *n*-butyl alcohol and necessity to heat the mixture for dissolution of alkali.

To remove water from the KOH/butanol reaction mixture, we used Dean-Stark receiver (Figure).

In the previous experiment, 6.79 g of water in 180 g of butanol were dissolved. Further azeotropic distillation with Dean-Stark receiver separated 6.8 cm<sup>3</sup> as a lower layer, which corresponded to value of the added water. Butanol migrated to the upper layer. Hence, we can claim that volume of the lower layer correctly indicated the amount of separated water.

As we can see from the data in the Table, water separated from the reaction media exceeded the maximum possible amount of free water in KOH. The maximum amount of free water was calculated as the difference between the KOH sample weight and actual presence of KOH, calculated from KOH content in the KOH sample. Besides, according to the results of titration of the actually loaded KOH, almost its whole amount was transferred into the solution (98.0–99.9 %).

Potassium butylate synthesis was carried out in five different flasks: 1–3 in 250 cm<sup>3</sup> flasks, 4 and 5 in 500 cm<sup>3</sup> flasks with chemical grade *n*-butyl alcohol for sample KOH (I) and technical grade *n*-butyl alcohol for samples KOH (II) and KOH (III). During first two hours, water separation from the reaction medium was hardly observed. After that, a more active water separation began.

Interestingly, with the increase of oil bath temperature, water separation stopped as the heating medium temperature exceeded 165 °C, while the intensity of mixture boiling was still rising. Contrastingly, in butanol–water mixture, the intensity of water separation was escalating with the increase of temperature.

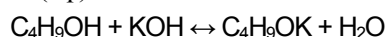
We assume that such difference can be explained by the shift of the reaction equilibrium to the side of the starting materials (hydroxide and alcohol) as a consequence of dis-

## Potassium butylate synthesis conditions

Reactor	Sample of KOH	Weight of KOH, g	Weight of free H <sub>2</sub> O in KOH, g	Separated water, cm <sup>3</sup>	Yield of KOBu, %	Content of eq. KOH, %	t, °C	Δτ, h	V <sub>av</sub> , cm <sup>3</sup> /h
1	(III)	20.08	4.66	5.4	15	8.72*	147–165	7.5	0.72
1	(II)	20.04	4.37	5.5	25	7.82	146–163	7.0	0.79
1	(III)	20.00	4.64	7.3	54	6.99*	153–156	7.5	0.97
1	(III)	20.05	4.65	7.6	60	7.48*	150–155	8.0	0.95
1	(II)	20.12	4.39	7.5	62	9.07	143–149	6.5	1.15
1	(II)	20.00	4.36	7.8	69	8.84	142–149	4.5	1.73
2	(III)	20.03	4.65	6.2	32	7.99*	153–156	7.5	0.83
2	(III)	20.08	4.66	6.5	37	7.63*	150–155	8.0	0.81
3	(II)	20.09	4.38	5.2	16	9.38	143–149	6.5	0.80
3	(II)	20.01	4.36	5.2	17	10.56	142–149	4.5	1.16
3	(II)	20.04	4.37	7.7	75	9.78	146–163	7.0	1.10
4	(II)	24.01	5.23	7.35	35	6.73	137–141	6.5	1.13
4	(I)	10.06	1.46	2.5	38	7.44	139–145	4.0	0.63
4	(II)	19.97	4.35	7.1	55	4.61	137–139	7.5	0.95
4	(II)	25.12	5.48	9.1	58	7.35	139–142	8.0	1.14
4	(II)	20.04	4.37	8.0	72	5.71	142–149	10.0	0.80
4	(II)	18.98	4.13	7.8	77	4.85	133–145	10.0	0.78
4	(I)	13.11	1.90	4.75	79	4.45	137–142	4.0	1.19
4	(I)	13.06	1.89	4.8	81	3.68	130–142	4.0	1.20
4	(I)	20.02	2.90	7.4	82	5.56	133–139	4.5	1.64
5	(II)	18.96	4.13	7.7	75	5.24	133–137	5.5	1.40

\* – samples with determined amount of alkali by titration

sociation of potassium butylate and thus water separation does not occur (eq.).



The most intensive water separation was observed when we maintained the minimal temperature, which ensured condensation in the Dean-Stark receiver (that was the least reflux ratio). This can be expressed as the highest possible average water separation speed (V<sub>av</sub>) at the minimal process temperature (see the table).

The fact that amount of water separated from the reaction media exceeded the maximum amount of free water in KOH indicates that reaction of potassium butylate formation occurred successfully (eq.), whereas the reaction of dibutyl ether formation from butyl alcohol in alkali media is hardly probable. Moreover, density of dibutyl ether is lower than that of *n*-butyl alcohol, and density of the obtained solutions was always higher than alcohol density.

Based on the amount of separated water, potassium butylate yields ranged between 15–82 %. All obtained catalyst solutions had a color from yellow to brown and demonstrated high catalytic activity in reaction of refined/unrefined sunflower oil transesterification with *n*-butyl alcohol at ambient temperature with yields of main products reaching 92–98 %, which was accompanied with a spontaneous separation of the glycerol layer.

Therefore, Dean-Stark method makes it possible to carry out synthesis of potassium butylate with the use of *n*-butyl alcohol as an azeotrope-forming agent, which at the same time is a reagent for triglyceride transesterification reaction. In this case, it is not necessary to use an additional

component for catalyst formation and to conduct further withdrawal of this component from the medium. Moreover, the possibility to utilize the non-conforming potassium hydroxide (which contains abnormal water quantity) into the catalytic solution and to achieve successful transesterification with a subsequent quick separation of the products.

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## Особливості одержання бутилату калію як каталізатора процесу переестерифікації

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Синтезовано бутилат калію на основі *n*-бутилового спирту та гідроксиду калію із використанням методу Діна-Старка. Показано двояку роль бутилового спирту в процесі одержання бутилату як реагента синтезу та як азеотроп-утворюючого агента для видалення води з реакційного середовища. Підтверджено його високу активність як каталізатора переестерифікації соняшникової олії при кімнатній температурі.

## Особенности получения бутилата калия как катализатора процесса переэтерификации

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Синтезирован бутилат калия на основании *n*-бутилового спирта и гидроксида калия с использованием метода Дина-Старка. Показана двоякая роль бутилового спирта в процессе получения бутилата как реагента синтеза и как азеотроп-образующего агента для удаления воды из реакционной среды. Подтверждена его высокая активность как катализатора переэтерификации подсолнечного масла при комнатной температуре.