Досліджено трансестерифікацію тригліцеридів соняшникової олії аліфатичними спиртами C_2-C_4 у присутності катіоніту КУ-2-8 у Н-формі та з іммобілізованими іонами металів і аніоніту АВ-17-8. Визначено вплив будови спирту, виду іоніту, іммобілізованого катіону металу, мольного співвідношення реагентів, температури реакції, вмісту каталізатора у реакційній суміші на швидкість реакції трансестерифікації та конверсію тригліцеридів

Ключові слова: трансестерифікація, аліфатичні спирти C_2-C_4, тригліцериди, іоніт, іони металів

Исследована переэтерификация триглицеридов подсолнечного масла алифатическими спиртами C_2-C_4 в присутствии катионита КУ-2-8 в Н-форме и с иммобилизованными ионами металлов и анионита АВ-17-8. Определено влияние строения спирта, вида ионита, иммобилизованного катиона металла, мольного соотношения реагентов, температуры реакции, содержания катализатора в реакционной смеси на скорость реакции переэтерификации и конверсию триглицеридов

Ключевые слова: переэтерификация, алифатические спирты C_2-C_4, триглицериды, ионит, ионы металлов

RESEARCH INTO TRANSESTERIFICATION OF TRIGLYCERIDES BY ALIPHATIC ALCOHOLS C₂–C₄ IN THE PRESENCE OF IONITES

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1. Introduction

The products of transesterification of triglycerides are methyl, ethyl, propyl, butyl esters of fatty acids, mono- and diacylglycerols. These substances are used as biofuel, softeners, raw materials for the synthesis of higher fatty alcohols and surfactants (SAS), plasticizers of varnish and dye materials and polymers, etc. [1].

Main technique to obtain the esters of unsaturated fatty acids are the processes of transesterification of triglycerides by lower alcohols. Methanol is used as alcohol most often. However, C_2-C_4 alcohols are known to be applied as reagents in the processes of transesterification [2]. Such facts are not numerous, however, disparate, and unsystematic.

The main application of methyl esters of fatty acids is biofuel. However, they are also used in the production of sucrose polyesters, which are used as neutral SAS or as food low-calorie oil. A significant part of methyl esters is used in the production of alkanol-amides, which are used as SAS, emulsifiers, thickeners, and plasticizers [1]. Higher aliphatic alcohols, obtained by the hydration of these esters, depending on the length of the carbon chain, are used in the pharmaceutical industry ($C_{16}-C_{18}$) or as lubricants and plasticizers (C_6-C_{12}).

A wide range of catalysts, which are used to intensify transesterification at present, are characterized by both advantages and significant shortcomings [1].

When it comes to avoiding a number of shortcomings (low activity, homogeneity of catalysts), of special interest are the studies into regularities of transesterification of triglycerides with alcohols C_2-C_4 in the presence of heterogeneous ionites of different nature.

The advantage of using ionites is the possibility of obtaining catalysts that contain active centers of varying nature, chemically bound with the carrier, non-soluble in the reaction mixture. Specifically, both H^+- and OH^--ions are immobilized on the solid matrix. This allows performing both acidic and basic catalysis of the transesterification process. Replacement of H^+-ions with cations of metal creates a virtually new active catalytic center on the ionite.

Accordingly, determining the activity of a metal cation, immobilized on the ionite in the process of transesterification of triglycerides by lower aliphatic alcohols is a relevant scientific task. It is also important to establish influence of the alcohol structure, the type of cationite and a metal ion on the indicators of reaction, to determine optimal conditions for the process of transesterification (the content of a catalyst in the reaction system, molar ratio of reagents, and the temperature of reaction).

2. Literature review and problem statement

In the process of transesterification of triglycerides (TG), homogeneous base [1], homogeneous acidic [3], and heterogeneous catalysts [1, 4] are used.

As homogeneous base catalysts, hydroxides, oxides, alkoxides and carbonates of alkali metals, first of all, of sodium and potassium, are used [1]. The benefits of using these catalysts include low cost, high yield of monoesters, moderate temperature and relatively low duration of the transesterification reaction. An essential drawback of homogeneous base catalysts is their sensitivity to the content of free fatty acids (FFA) and water in raw materials. That is why, in order to achieve high values of the rate of transesterification reaction and conversion of TG, the total FFA content in a raw material must not exceed 1 % by weight [2].

As homogeneous acidic catalysts of TG transesterification, the Bronsted acids, mainly sulfate and aryl sulfonic acids, are used [3]. The shortcomings of these catalysts include lower activity in comparison with homogenous base catalysts, higher temperature (larger than 373 K) and longer duration of reaction (over 3 hours) [3]. Another disadvantage of acidic homogeneous catalysts is the need for a significant excess of alcohol to achieve high TG conversion. This complicates alcohol regeneration and decreases productivity of reactive volume [5]. However, when raw materials with a high content of FFA and water are used, the homogeneous acid catalysts are more effective than the homogeneous base catalysts. That is why acidic catalysts can be used for the transesterification of used oils and fats [5].

The above shortcomings of homogeneous catalysts are inherent to a lesser extent for heterogeneous catalysts of transesterification reaction [2]. Specifically, the use of heterogeneous catalysts has several advantages: the absence of stage for the neutralization of catalyst in the reaction mixture, lower corrosive impact on equipment, easy separation of a catalyst from the reaction mixture [6].

It is proposed to apply, as heterogeneous catalysts of transesterification, the compounds of acidic and base character, in particular, a mixed zirconium-aluminum catalyst (Lewis acid) [7], and carbonates of alkali and alkaline earth metals, oxides of alkaline earth metals [3, 8].

Heterogeneous catalysts of transesterification demonstrate high activity, provide high yield of methyl esters at transesterification of used oils and fats that contain more than 12 % by weight of FFA [8].

Products of partial carbonation of carbohydrates, such as D-glucose, sucrose, cellulose, starch, etc., were explored as heterogeneous catalysts [9].

Ion exchange resins demonstrate activity in transesterification reaction, comparable with activity of base homogeneous catalysts [9, 10].

High catalytic activity in reaction of TG transesterification by ethanol at 333–373 K was demonstrated by ion exchange resins produced by Mitsubishi Chemical company (PA308, PA306, PA306s, HPA25) [11]. However, in the experiment, there was a noticeable decrease in the activity of these catalysts due to the formation of unsaturated fatty acids (UFA) due to a direct ion exchange reaction between hydroxide-ion with the residue of triglyceride acid.

It is known that the cations of Sn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Al^{3+} and Cu^{2+}, applied by the method of ion exchange from the saturated solutions of respective salts on the cationite CU-2-8, are the catalysts of transesterification of dibutyladipate by cyclohexanol [12]. These catalysts also show high activity in the reaction of TG transesterification by ethanol, propane-2-ol [14] and butane-1-ol [15].

Thus, it is a promising task to establish general regularities in the TG transesterification reaction in the presence of heterogeneous catalysts and to determine optimal conditions for the transesterification process.

3. The aim and objectives of the study

The aim of present research is to establish regularities in the transesterification of triglycerides of sunflower oil (TGSO) by aliphatic alcohols C_2–C_4 in the presence of ionites and to determine optimal conditions for obtaining monoesters of UFA and these alcohols.

To accomplish the set aim, the following tasks must be solved:

– to determine regularities in the process of TG transesterification by aliphatic alcohols C_2–C_4 in the presence of the cationite CU-2-8 with the immobilized ions of metals and the anionite AV-17-8;

– to determine effect of the type of ionite and the immobilized metal ion on TG conversion and the rate of transesterification reaction;

– to establish optimal conditions for the process of TG transesterification by alcohols C_2–C_4.

4. Materials and methods of research into transesterification of triglycerides by aliphatic alcohols C_2–C_4

4. 1. The examined materials and equipment used in the experiment

We used in the transesterification reaction the sunflower oil (DSTU 4492:2005) and such aliphatic alcohols C_2–C_4 with normal and isostructure as ethanol (DSTU 4221:2003), propane-1-ol (TU 2632-106-44493179-07), propane-2-ol (GOST 9805-84), butane-1-ol (GOST 5208-81) and 2-methylpropane-1-ol (GOST 9536-79).

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Ethanol with a concentration of 96.2 % by volume was dried with fried magnesium sulfate (GOST 4523-77).

We used as catalysts the cationite CU-2-8 (GOST 20298-74) in H-form and the cationite CU-2-8 with the ions of Co^{2+}, Zn^{2+}, Ni^{2+}, Sn^{2+}, Cu^{2+} (Fig. 1), immobilized on it, as well as the anionite AB-17-8 (GOST 20301-74).

Metal ions were immobilized by means of the exchange reaction between the cationite CU-2-8 in the H-form and a solution of salt of the respective metal. There was such a concentration of salt in the solution that the molar ratio of the cation of metal of salt:H^+ was not less than 1:1. After the ion exchange, cationite with immobilized ions of metals was washed 3–4 times with distilled water and dried in the air to constant mass.

For the cationite CU-2-8, static ione-exchange capacity (SIEC) was determined in line with GOST 20255.1-89.

A batch of 1±0.0001 g of the cationite CU-2-8 in H-form or with the immobilized ions of metals was weighed in a flask with a tight stopper (250 cm³); next, we added 100 см³ of NaOH solution and left the flask for not less than 10 hours. Over this period, the content of the flask was agitated sev-

eral times. 25 cm³ of the solution was taken with a pipette and titrated with HCl solution in the presence of phenolphthalein.
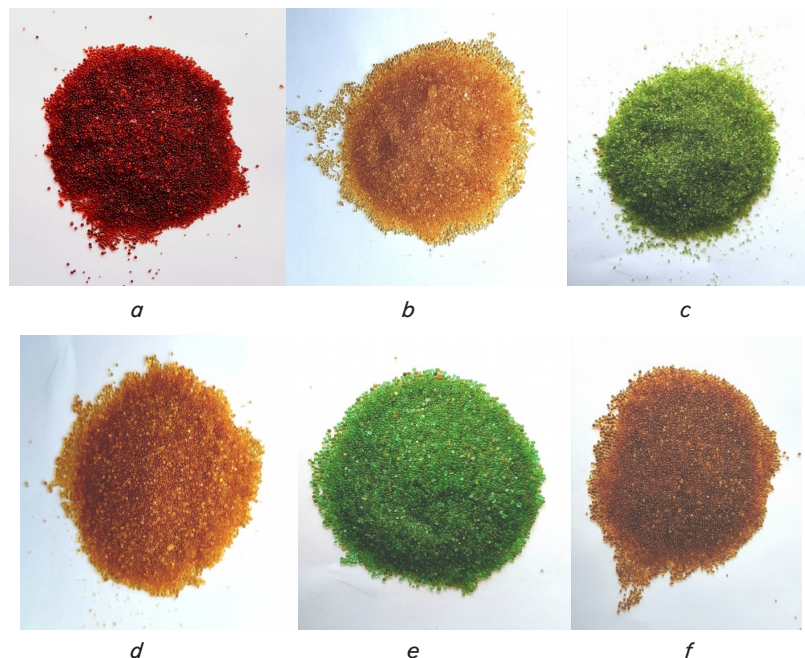

Fig. 1. Images of the examined catalysts: a – CU-2-8/Co^{2+}; b – CU-2-8/Zn^{2+}; c – CU-2-8/Ni^{2+}; d – CU-2-8/Sn^{2+}; e – CU-2-8/Cu^{2+}; f – CU-2-8/H^{+}

The value of full exchange static capacity of the cationite, in conversion to mmol H^{+}/g, was calculated from formula:

$$SIEC = \frac{n\left(V_{NaOH}C_{NaOH} - V_{HCl}C_{HCl}\right)}{m},$$

where n is the ratio of the total volume of the examined solution to the volume, taken for analysis; V_{NaOH} is the volume of NaOH solution, added to the cationite, cm³; C_{NaOH} is the molar concentration of NaOH solution, mol/dm³; V_{HCl} is the volume of HCl solution on titration, cm³; C_{HCl} is the molar concentration of HCl solution, mol/dm³; m is the weight of a cationite batch, take for analysis, g.

The dosage of the catalyst for the transesterification reaction and for the ion exchange in the course of obtaining the cationite CU-2-8 with the immobilized metal cations was determined based on SIEC. SIEC of the cationite CU-2-8 in H-form was 1.9 mmol H^{+}/cm³; that of the cationite with immobilized ions of metals (on conversion to mmol H^{+}/cm³): 1.4 for CU-2-8/Zn^{2+}, 1.4 for CU-2-8/Ni^{2+}, 1.7 for CU-2-8/Sn^{2+}, 1.5 for CU-2-8/Co^{2+}, 1.9 for CU-2-8/Cu^{2+}, respectively.

The obtained values of SIEC indicate a sufficiently high degree of immobilization of metal cations and close values of the number of active centers at the same dosage of catalysts for the reaction.

The content of C$_2$–C$_4$ alcohols in the products of transesterification reaction was determined using the gas-liquid chromatograph "Tsvet-100" (made in the USSR) equipped with a thermal conductivity detector.

Control of the flow of the TG transesterification reaction was carried out according to consumption of alcohol.

The rate of the TG transesterification reaction was calculated as the ratio of a change in the TG concentration until the moment of this change.

Moisture content of the cationite was determined by drying the batch to a constant mass at a temperature of 105 ºC.

4. 2. Procedure for the experiment and for determining a composition of the reaction mixture, acidic number, and chromaticity of the reaction mixture

Regularities of transesterification of TGSO by aliphatic alcohols C$_2$–C$_4$ were examined at a temperature of 353–383 K, molar ratio of alcohol:TG from 4:1 to 10:1, and the content of catalyst of 0.5–8 % by weight.

Experiments were carried out in the reaction device, which included a heat-resistant round-bottom flask, a reverse refrigerator, a mechanical stirrer, and a thermometer. Temperature of the heat carrier and the reaction was maintained within ±0.5 K. The samples of the reaction mixture were taken over the assigned intervals of time in order to determine chromatographically the concentration of alcohol.

Based on the calculated amount of alcohol that had reacted, TG conversion was determined recalculated to glycerol trilinoleate, the main component of sunflower oil. The formation of mono- and diglycerides in the transesterification reaction was not taken into consideration.

For the chromatographic analysis of alcohol content in the products of reaction, a column of 2 m in length and 3 mm in diameter, filled with a immobile phase of 5 % Silicone SE30 on Chromaton N-AW, was used. Helium was a gas-carrier, its consumption was 3 dm³/h, volume of the analyzable sample was 2 µl. Other parameters of chromatographic analysis are given in Table 1.

Table 1

Parameters of chromatographic content of alcohols

Alcohol	Strength of current of detector, mA	Temperature, K		
		evaporator	detector	column
Ethanol	120	483	443	353
Propane-1-ol				
Propane-2-ol				
Butane -1-ol	140	498	483	373
2-Methylpropane-1-ol				

Acidic number of the reaction mixture was determined according to procedure [16].

5. Results of research into transesterification of triglycerides by aliphatic alcohols C$_2$–C$_5$

Results of research into effect of the type of ionite and metal ion, immobilized on the cationite CU-2-8, on the con-

version of TG and the rate of transesterification reaction are given in Table 2.

Effect of the character of ionite and metal ion, immobilized on the cationite CU-2-8 on the conversion of triglycerides and the rate of transesterification reaction. Content of catalyst is 2 % by weight

Ionite/cation (anion)	Molar ratio alcohol:TG	Tempera-ture of reaction, K	Reaction rate, r·10⁴, mol/(dm³·s)		Conversion of TG, %	
			30 min	60 min	30 min	final
Ethanol						
CU-2-8/Co^{2+}	4:1	353	1.6	1.1	32.9	57.1
CU-2-8/Zn^{2+}	4:1	353	2.7	1.5	56.0	69.3
CU-2-8/Ni^{2+}	4:1	353	1.6	1.0	33.5	58.9
CU-2-8/Sn^{2+}	4:1	353	3.3	1.8	68.9	86.6
CU-2-8/Cu^{2+}	4:1	353	1.6	1.1	33.4	45.6
CU-2-8/H^{+}	4:1	353	3.2	2.1	64.6	90.6
AV-17-8/OH^{-}	4:1	353	0.9	0.6	17.8	82.2
Propane-1-ol						
CU-2-8/Co^{2+}	4:1	353	–	1.9	–	99.9
CU-2-8/Zn^{2+}	4:1	353	–	1.6	–	73.5
CU-2-8/Ni^{2+}	4:1	353	–	2.0	–	99.7
CU-2-8/Sn^{2+}	4:1	353	–	1.8	–	97.6
CU-2-8/H^{+}	4:1	353	–	1.2	–	67.4
AV-17-8/OH^{-}	4:1	353	–	1.1	–	62.9
Propane-2-ol						
CU-2-8/Co^{2+}	4:1	353	–	0.92	–	57.0
CU-2-8/Zn^{2+}	4:1	353	–	0.54	–	70.0
CU-2-8/Ni^{2+}	4:1	353	–	0.78	–	57.9
CU-2-8/Sn^{2+}	4:1	353	–	0.81	–	75.0
CU-2-8/H^{+}	4:1	353	–	1.05	–	80.8
Butane-1-ol						
CU-2-8/Co^{2+}	10:1	383	0.2	0.3	7.8	68.0
CU-2-8/Ni^{2+}	10:1	383	0.9	0.6	28.9	79.1
CU-2-8/Sn^{2+}	10:1	383	0.2	0.3	7.9	67.0
CU-2-8/Cu^{2+}	10:1	383	0.2	0.2	7.1	41.7
CU-2-8/H^{+}	10:1	383	–	0.6	–	85.4
2-Methylpropane-1-ol						
CU-2-8/Zn^{2+}	10:1	373	–	–	–	8.8
CU-2-8/Ni^{2+}	10:1	373	0.2	0.23	7.4	52.6
CU-2-8/Cu^{2+}	10:1	383	–	–	–	28.9

Data in Table 2 demonstrate that the best catalysts of TG transesterification are the cationite CU-2-8 with immobilized ions of Sn^{2+} (ethanol, propane-2-ol), Sn^{2+}, Co^{2+} or Ni^{2+} (propane-1-ol), Ni^{2+} (butane-1-ol) and the cationite KU-2-8 in H-form (propane-2-ol, butane-1-ol).

The highest TG conversion is achieved by the reaction with propane-1-ol. During ethanolysis, at molar ratio of ethanol:TG of 4:1, TG conversion on the best catalysts reaches 86–90 %. A slightly lower TG conversion is reached in the reaction with butane-1-ol; in this case, it is 79.1–85.4 %. At interaction with secondary alcohol (propane-2-ol) and alcohol with a branched chain (2-methylpropane-1-ol), TG conversion is lower than that in the reaction with the respective primary alcohols with a linear chain (Table 2).

However, with an increase in the length of an alcohol chain, a decrease in reaction rate is also observed (Table 2).

For each of the examined alcohols, the difference in the reaction rate in the presence of catalysts with various immobilized ions of metals is by 2–3 times.

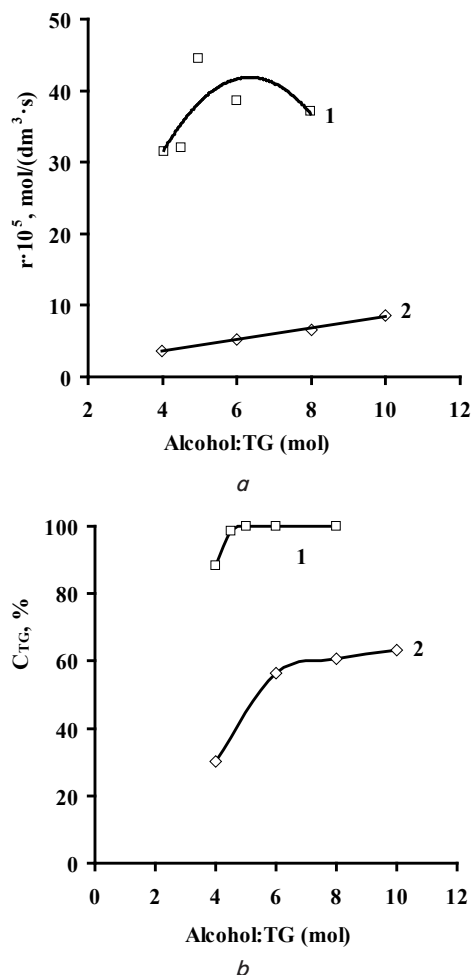Molar ratio of reagents also impacts the initial rate of transesterification reaction (Fig. 2, *a*).

Fig. 2. Dependence of initial rate (*r*) of transesterification reaction (*a*) and conversion of triglycerides in 180 min (*b*) on molar ratio of alcohol:TG: 1 — ethanol, catalyst — CU-2-8/H^{+}; 2 — butane-1-ol, catalyst — CU-2-8/Ni^{2}. Temperature is 353 K, catalyst content is 2 % by weight

In the interaction of ethanol with TGSO, the extreme dependence of the reaction rate on the ratio of reagents is observed. Maximum rate corresponds to molar ratio of ethanol:TG of 5:1. At a decrease or an increase in the ethanol excess, a decrease in reaction rate is observed. The dependence of the rate of reaction of TGSO transesterification by butane-1-ol on molar excess has a different character – the rate increases linearly with an increase in molar ratio of butane-1-ol:TG. At the same time, with an increase in molar excess of alcohol, TG conversion, reached in the same period of time, increases in both cases, while for the case of ethanolysis, the time it takes to achieve an equilibrium TG conversion decreases as well.

At the same time, the character of dependence of TG conversion on the molar ratio alcohol:TG for ethanol and butane-1-ol is similar (Fig. 2, *b*).

Dependence of the rate of reaction of TG transesterification with ethanol and butane-1-ol on the concentration of catalyst

(CU-2-8/ Ni^{2+}) takes an extreme shape (Fig. 3). Moreover, it is characteristic that the maximum rate of reaction in both cases is achieved at the catalyst content of approximately 2 % by weight. It should also be noted that at the interaction between butane-1-ol and TGSO, this extremum is expressed less clearly. The similar character of curves was also observed for the dependence of TG conversion on the catalyst concentration [14].
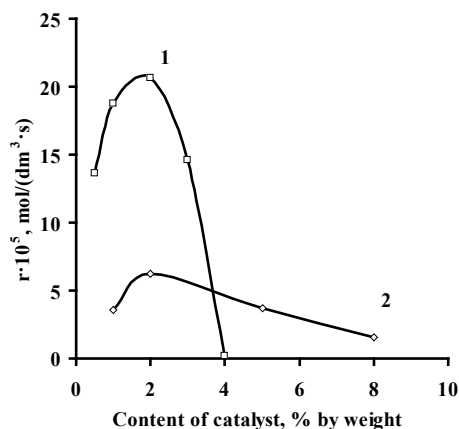

Fig. 3. Dependence of initial rate of reaction (r) of TG transesterification on the catalyst content in the reaction mixture: 1 — catalyst — CU-2-8/H^+, ethanol: TG — 4:1 (mol); 2 — catalyst — CU-2-8/Ni^{2+}, butane-1-ol: TG — 10:1 (mol). Temperature is 353 K

It was also established that the initial rate of reaction of TG transesterification by butane-1-ol changes almost linearly with an increase in temperature (Fig. 4).
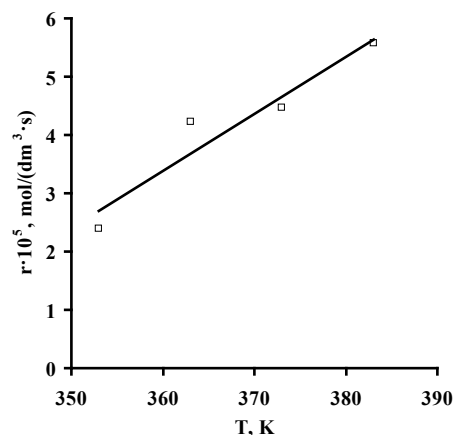

Fig. 4. Dependence of initial rate of reaction (r) of TG transesterification by butane-1-ol on temperature: catalyst CU-2-8/Ni^{2+}, butane-1-ol:TG — 4:1 (mol), catalyst content is 2 % by weight

Moreover, the obtained results show that an increase in the temperature of TG transesterification reaction by butane-1-ol significantly influences the rate of reaction, but has much less influence, as it was shown previously, on the conversion of TG [17]. At the same time, TG conversion, reached over 180 min of transesterification by butane-1-ol, in the examined interval of temperatures is practically the same. A further increase in the temperature of reaction is impractical, because at approaching the boiling temperature of alcohol, the amount of it that is in the form of vapor increases, which is undesirable from a technological point of view.
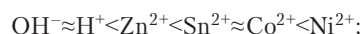
6. Discussion of results of research into transesterification of triglycerides by aliphatic alcohols C_2-C_4

By the initial rate of reaction of TGSO transesterification by alcohols C_2-C_4 (Table 2), the activity of the examined catalysts changes in the following sequence:
– ethanol:

$$OH^-<Ni^{2+}\approx Co^{2+}\approx Cu^{2+}<Zn^{2+}<H^+\approx Sn^{2+};$$

– propane-1-ol:

$$OH^-\approx H^+\leq Zn^{2+}\leq Sn^{2+}\approx Co^{2+}\leq Ni^{2+};$$

– propane-2-ol:

$$Zn^{2+}<Ni^{2+}\approx Sn^{2+}\leq Co^{2+}\leq H^+;$$

– butane-1-ol:

$$Cu^{2+}\leq Sn^{2+}\approx Co^{2+}\leq Ni^{2+}\approx H^+.$$

It is obvious that the high rate of TG transesterification by alcohols C_2-C_4 is achieved when applying the cationite CU-2-8 with immobilized ions of Ni^{2+}, Sn^{2+}, Co^{2+} and the cationite CU-2-8 in H-form. This regularity leads to the results of TGSO transesterification by ethanol. In this case, the catalyst CU-2-8 with immobilized ions of Ni^{2+} and Co^{2+} demonstrates low activity and does not make it possible to achieve high conversion of TG. These results can be probably related to the fact that the reaction mixture of TGSO-ethanol is heterophasic, in contrast to the use of other alcohols. That is why, in this case, the influence of mutual solubility of components of the reaction mixture in different phases can manifest itself, which would affect the conversion of reagents.

According to the achieved conversion (Table 2), the examined catalysts are arranged in the following sequence:
– ethanol:

$$Cu^{2+}<Co^{2+}\approx Ni^{2+}<Zn^{2+-}OH\leq Sn^{2+}\leq H^+;$$

– propane-1-ol:

$$OH^-\approx H^+\leq Zn^{2+}<<Sn^{2+}\approx Co^{2+}\approx Ni^{2+};$$

– propane-2-ol:

$$Co^{2+}\approx Ni^{2+}<Zn^{2+}\approx Sn^{2+}\approx H^+;$$

– butane-1-ol:

$$Cu^{2+}\leq Sn^{2+}\approx Co^{2+}\leq Ni^{2+}\approx H^+.$$

It is obvious that in most cases the given sequences of changes in the initial rate of reaction and TG conversion correlate with each other. Noticeable differences are observed only for propane-2-ol. The structure of alcohol probably causes such a difference in the activity and TG conversion that was reached in the presence of the examined catalysts. Specifically, the high rate of transesterification reaction does not make it always possible to achieve high TG conversion.

At the same time, with an increase in length of the alcohol chain, the rate of transesterification reaction and TG conversion decreases (Table 2). The obtained results correlate well with the data on a decrease in the activity of alcohols at an increase in their length in the presence of acidic catalysts [18].

An increase in the proportion of alcohol in the reaction mixture naturally allows increasing the reaction rate (Fig. 2, *a*). However, with an increase in the ratio of ethanol:TG from 4:1 to 4.5:1, almost total TG conversion is achieved (Fig. 2, *b*). A further increase in the content of alcohol in the reaction mixture decreases the time it takes to achieve complete conversion of triglycerides, but also is the reason for a decrease in specific productivity of the process. The increase in the ratio of butane-1-ol:TG from 4:1 to 10:1 makes it possible to increase TG conversion over 180 min from 31.2 % to 63.2 % (Fig. 2, *b*). The indicated impact is most vividly pronounced at a change in this ratio from 4:1 to 6:1. A further increase in the molar ratio of butane-1-ol:TG has a much less impact on TG conversion. This effect can be explained by the fact that with an increase in molar ratio of alcohol:TG, the acting concentrations of reagents decrease, which naturally affects the reaction rate and TG conversion that is achieved over a given period. Therefore, a subsequent increase in the excess alcohol in the reaction of TG transesterification by butane-1-ol will be ineffective.

It is obvious that the cause of extreme dependences of the rate of reaction of TGSO transesterification by ethanol and butane-1-ol and the achieved TG conversion on the concentration of a catalyst is water, which is contained in the cationite. At an increase of the content of a catalyst in the reaction system, the amount of water also increases. Since the established water content in most catalysts is quite high (Table 3), then, when adding a considerable amount of a catalyst to the reaction mixture, the amount of water in molar terms relative to the quantity of reagents will also be high. This will ultimately affect the rate and equilibrium of transesterification reaction.

Table 3

Content of water in the examined catalysts

Catalyst	Content of water, % by weight
CU-2-8/Ni^{2+}	17.4
CU-2-8/Cu^{2+}	16.9
CU-2-8/Zn^{2+}	17.6
CU-2-8/Sn^{2+}	15.3
CU-2-8/H^{+}	13.3
AV-17-8/OH^{-}	16.8

Bases on the results of study conducted, it is possible to propose optimal conditions for the process of TGSO transesterification by alcohols $C_2 - C_4$ (Table 4).

Thus, the examined catalysts of TGSO transesterification by alcohols $C_2 - C_4$ make it possible to conduct the reaction under mild conditions over 45–360 min depending on alcohol.

It is also necessary to note that complexes of ions of metals with cationite are stable under conditions of the reaction. This is proved by the absence of a change in coloration of the obtained catalysts and the reaction mixture in the process of transesterification.

The obtained results indicate the prospects for industrial application of the examined catalysts, especially during TG transesterification by ethanol and propane-1-ol. However,

under conditions of industrial implementation of the process, it is advisable to use a reactor with the bulk layer of a catalyst. Such changes to the conditions of the process would require better understanding of the impact of a hydrodynamic mode, especially for the case of the heterophasic system ethanol–TG.

Table 4

Optimal conditions of TGSO transesterification by different alcohols in the presence of examined catalysts. Content of catalyst is 2 % by weight

Alcohol	Catalyst	Temperature of reaction, K	Molar ratio alcohol: TG	Duration of reaction, min	Conversion of TG, %
Ethanol	CU-2-8	353	5:1	45	99.9
Propane-1-ol	CU-2-8/Ni^{2+}	353	4:1	180	98.8
	CU-2-8/Sn^{2+}	353	4:1	180	97.1
	CU-2-8/Co^{2+}	353	4:1	240	99.9
Propane-2-ol	CU-2-8	353	4:1	240	80.8
	CU-2-8/Sn^{2+}	353	4:1	240	75.0
Butane-1-ol	CU-2-8	383	10:1	360	79.1
	CU-2-8/Ni^{2+}	383	10:1	360	85.4

The prospects for development of the study conducted include extending the range of cations of metals, immobilized on the cationite, and imply searching for the conditions that would make it possible to increase TG conversion when using propane-2-ol and butane-1-ol.

7. Conclusions

1. We determined the effect of the type of ionite and the metal ion, immobilized on the cationite CU-2-8, on the reaction of transesterification of triglycerides of sunflower oil by alcohols $C_2 - C_4$. It was shown that the cationite CU-2-8 with immobilized ions of Sn^{2+}, Co^{2+} or Ni^{2+} and the cationite CU-2-8 in H-form demonstrate the highest activity. It was established that an increase in the content of cationite in the reaction mixture that is higher than optimal, leads to a decrease in the reaction rate due to inhibition by water that is present in the catalyst. It was shown that an increase in the molar ratio of alcohol:TG makes it possible to increase the conversion of triglycerides.

2. It was established that the rate of reaction of transesterification and conversion of triglycerides depend on the type of a metal ion, immobilized on the cationite CU-2-8. It was shown that the cationite CU-2-8 with immobilized ions Sn^{2+}, Co^{2+} and Ni^{2+} demonstrates the highest activity in the reaction of transesterification of triglycerides of sunflower oil by alcohols $C_2 - C_4$.

3. Optimal conditions for the process of transesterification were determined. It was shown that the optimal content of a catalyst is 2 % by weight. It was established that it is appropriate to carry out the reaction of transesterification of triglycerides by ethanol, propane-1-ol and propane-2-ol at 353 K and at the molar ratio of alcohol:TG of (4–5):1, and by butane-1-ol – at 383 K and at the molar ratio of butane-1-ol:TG of 10:1. Under such conditions, the conversion of triglycerides in reaction with ethanol and propane-1-ol is ~99 % over 45 min and 180 min, respectively, and with less reactive propane-2-ol butane-1-ol, it is ~80 %.

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