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Specific Features of Solketal Synthesis on KU-2-8 Cation-Exchange Resin

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Abstract—Technological specific features of the solketal synthesis on a KU-2-8 cation-exchange resin were improved. Data are presented on the mutual solubility of the components in the glycerol–acetone–water and glycerol–acetone–water–ethanol systems. It is shown that use of ethanol for homogenization of the starting reagents is more than twice more efficient than performing the process with delivery of an emulsion of the reagents or reaching a full solubility of glycerol in acetone due to the 20-fold excess of the latter at 35°C. It is shown that the delivery of a glycerol emulsion in acetone to an immobile bed of a heterogeneous catalyst working in the falling-film mode leads to flooding of the reactor at spraying densities exceeding 0.15 m^3 m^{-2} h^{-1}.

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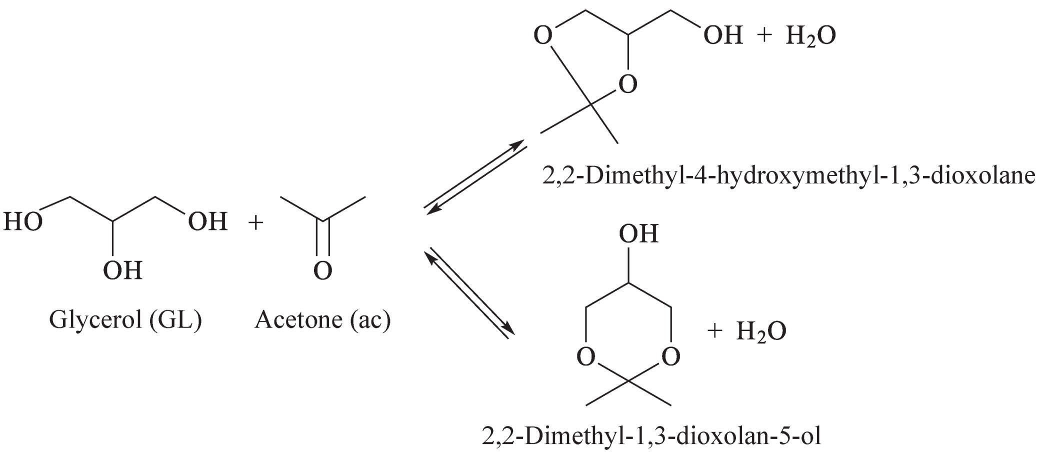
Solketal (SK, mixture of the isomers 2,2-dimethyl-4-hydroxymethyl-1,3-dioxolane and 2,2-dimethyl-1,3-dioxan-5-ol) is a promising high-octane additive improving the service properties of fuels for internal-combustion engines [1]. Solketal is formed in the condensation reaction of glycerol with acetone on acid-type catalysts:



(1)

KU-2-8 cation-exchange resin is one of the most promising catalysts, which exhibit a high activity [2] and are readily available and inexpensive.

The starting reagents, glycerol and acetone, have a very low mutual solubility and form emulsion under intensive mixing. The starting reaction mixture can be homogenized via addition of compounds well soluble in both glycerol and acetone, e.g., alcohols [3]. An advantage of ethanol over other alcohols is in its inertness toward the starting reagents and reaction products under the solketal synthesis conditions and the boiling point close

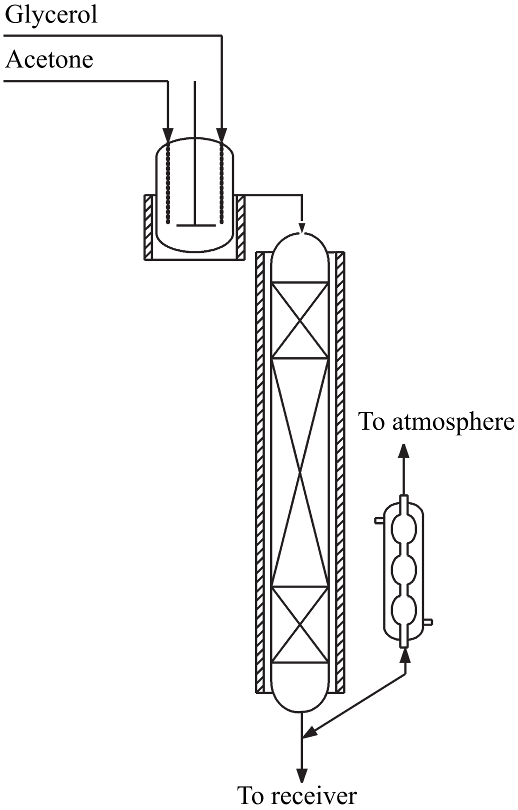


Fig. 1. Schematic of a laboratory installation for studying the process in a reactor with fixed catalyst bed.

to that of acetone, which hardly complicates the scheme of its evaporation from solketal and the organization of recycle in the synthesis stage.

It should be noted, however, that there are no published data on the influence of the ethanol concentration on the homogenization process of a mixture of glycerol and acetone at their various ratios and temperatures. In addition, it should be taken into account that the reagents are not absolutely dry and may contain up to 2 wt % water, which can affect the homogenization process: water also raises the mutual solubility of the starting reagents. A study of the process of mutual solubility in the glycerol–acetone–ethanol–water four-component system is a rather topical task in development of an industrial technology of solketal synthesis. In the end, the information obtained will be used to select the type of a reactor for synthesizing the oxygenate and the working conditions of the reactor.

EXPERIMENTAL

We used the following reagents: glycerol of special-purity grade (Kupavnareaktiv OOO, Russia), acetone of chemically pure grade (Ekos-1 ZAO, Russia), rectified ethanol, and distilled water. As the catalyst served KU-2-8 cation-exchange resin preliminarily dried with acetone on a water bath.

The mutual solubility of the components was studied in a three-necked glass vessel equipped with stirrer, reflux and a thermocouple cartridge, and electric heater. The reactor temperature was controlled and measured with a set of devices including a TRM-101 single-channel microprocessor programmed temperature-measuring and -controlling unit, solid-state relay, and laboratory autotransformer.

The vessel was charged with necessary amounts of acetone and glycerol and the stirrer was switched on. The reaction mixture was heated to a prescribed temperature. Water and(or) ethanol were batched with a syringe in an amount providing the disappearance of the emulsion (homogenization of the system).

The laboratory installation for studying the process in a reactor with fixed catalyst bed is shown schematically in Fig. 1. The reactor had the following parameters: inner diameter 2.6 cm; height of the catalyst bed, 47 cm; and catalyst mass 205 g. The catalyst was placed on a layer of glass packing constituted by rings in the form of a helix with 2–3 spiral turns 3–4 mm in diameter and 1 cm thick. The height of the packed bed was 3 cm.

To provide a uniform distribution of the reagent flow, the same packed bed with height of 5 cm was situated above the catalyst. The reagents were preliminarily mixed in a heated apparatus with a stirrer to form a stable emulsion.

The reaction products were analyzed on a Tsvet-800 gas chromatograph with ZB-WAX capillary column and flame-ionization detector.

RESULTS AND DISCUSSION

It is known that the solketal synthesis process is performed at a temperature of 35–55°C and glycerol-to-acetone ratio of 1 : (5–20) [4]. Under these conditions, a more or less stable emulsion of glycerol and acetone can be only obtained with intense agitation of the components of the mixture. Otherwise, the mixture of the reagents is a two-component system, with a layer of acetone over the lower layer of glycerol.

Because a heterogeneous catalyst, KU-2-8 resin, is used in the process, only two instrumentation variants of the synthesis stage are possible: a bulk reactor with high-intensity mechanical agitation of the reagents and the catalyst or a column-type apparatus filled with a fixed catalyst bed and sprayed with an emulsion of glycerol and acetone. Only these two kinds of apparatus can provide the maximum contact of the starting reagents with the catalyst surface and, as a consequence, a high rate of the condensation reaction.

The process in reactors with intense mechanical agitation is not considered here because of leading to disintegration (abrasion) of the catalyst and its contamination with fine particles of reaction products, which creates technological difficulties in the stage of isolation and purification of solketal, i.e., it is technologically unfeasible.

The process in a reactor with a falling film of preliminarily mixed reagents is devoid of the above shortcomings. It was experimentally demonstrated that, at a synthesis temperature of 35°C, the stratification of the emulsion of glycerol and acetone in a thin film at a spraying density of the catalyst bed of up to 0.15 $m^3\ m^{-2}\ h^{-1}$ does not lead to a significant decrease in the process rate. This is so because the insignificant thickness of the film and its sufficiently high motion speed provide an unobstructed contact of the reagents with the catalyst surface.

Raising the density of catalyst praying by a mixture of the starting reagents changes the course of hydrodynamic and, as a consequence, kinetic processes on the catalyst. Naturally, raising the flow rate of the emulsion leads to an increase in the thickness of the falling film. At a spraying density exceeding 0.15 $m^3\ m^{-2}\ h^{-1}$, the stratification results in that a thick glycerol layer is formed in the upper part of the catalyst bed, which substantially diminished the free-cross-section area of the reactor. As a result, the flow of reagents cannot freely pass any more through the catalyst bed and starts to fill the apparatus over the catalyst bed. Thus, the process of solketal synthesis in a reactor with a fixed catalyst bed and falling film of the starting reagents becomes inoperative at a high spraying density.

In addition, it should e noted that the solketal formation rate decreases with increasing spraying density already below its value of 0.15 $m^3\ m^{-2}\ s^{-1}$. It is clear that the thickness of the glycerol film increases gradually, and this film also gradually covers the increasingly large surface area of catalyst particles. As a result, the access of acetone to this catalyst surface is hindered and the rate of the condensation process is now determined by the rate of acetone diffusion across the glycerol layer. With the high solubility of the reaction products in glycerol taken into account, the rate of their diffusion from the catalyst surface has in all likelihood no noticeable effect on the solketal synthesis rate.

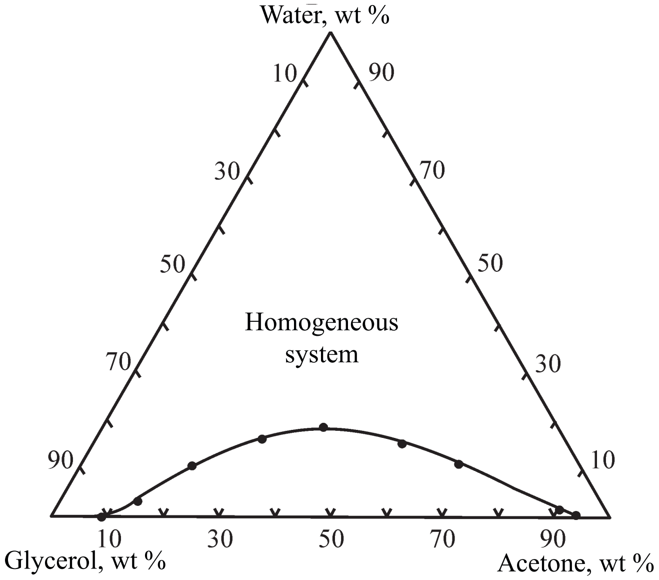


Fig. 2. Solubility diagram in the glycerol–acetone–water system at 35°C.

A solution to the appearing problems consists in passing to use of the starting reagents in the form of solutions. As noted above, introduction of certain amounts of ethanol and(or) water into the emulsion of glycerol and acetone makes it possible to obtain a homogeneous mixture of the reagents.

Depending on the quality of raw materials used to synthesize solketal, the starting mixture of the reagents will contain a certain amount of water.

The data on the effect of water concentration on the homogenization of the mixture of glycerol and acetone at 35°C are presented in Fig. 2.

Because the solketal formation reaction (1) is of equilibrium nature, raising the humidity of the starting raw material will lead to a decrease in the equilibrium degree of glycerol conversion. Hence follows that glycerol and acetone used in the synthesis process should be as dry as possible. However, the cost of glycerol steeply grows with its increasing concentration (purity), which inevitably affects the technical and economic parameters of the process. Fr example, the cost of glycerol of D-98 brand [GOST (State Standard) 6824–96] with 98% main substance is 30–50% less expensive than glycerol containing 99.3% main substance (GOST 6259–75).

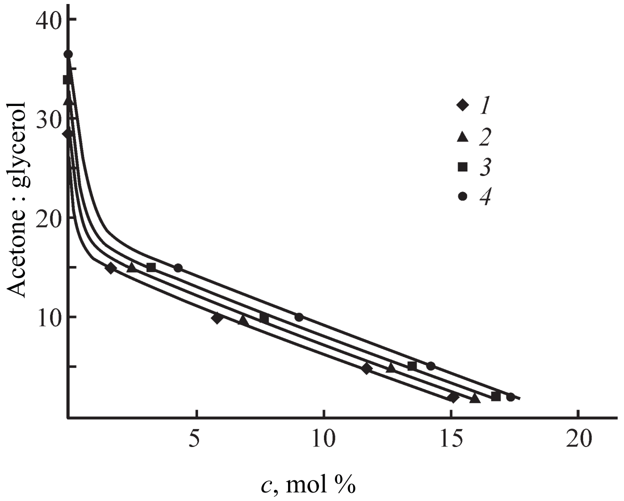


Fig. 3. Acetone : glycerol molar ratio at which, depending on the ethanol concentration *c*, the glycerol–acetone–ethanol–water heterophase mixture becomes a solution. *T* (°C): (*1*) 35, (*2*) 30, (*3*) 25, (*4*) 20.

To provide the maximum conversion of glycerol, reaction (1) is performed at 5–20-fold molar excess of acetone [4]. The excess amount of acetone is evaporated from the reaction products and recycled. The concentration of water in acetone being evaporated depends on the operation parameters of the rectification column. Calculations and experiments demonstrated that, when the reaction products formed in solketal synthesis are separated, the average moisture content of acetone is 1.3 wt %. This degree of acetone drying is acceptable for performing solketal synthesis with sufficiently high equilibrium degrees of glycerol conversion (≥90%).

Analysis of the data in Fig. 2 shows that, with 98% glycerol and 98.7% acetone used as raw materials, the starting mixture becomes homogeneous at a molar excess of acetone of 20-fold and more. Use of more humid reagents will make it possible to reduce the excess of acetone for homogenizing the mixture, but this will be accompanied by a decrease in the equilibrium yield of solketal.

It is necessary to take into account that such a significant excess of acetone will naturally lead to lower working concentrations of glycerol and, consequently, to a lower rate of the condensation reaction (1). In addition, the energy expenditure for acetone recycling will become several times higher.

One of the most rational ways to homogenize the glycerol–acetone mixture is by using an additional solvent, e.g., ethanol. This makes it possible to obtain a homogeneous mixture at a smaller excess of acetone.

The results of experiments on homogenization of a glycerol–acetone–ethanol–water mixture in the temperature range 20–35°C are presented in Fig. 3. The four-component mixture is homogeneous in the region lying above the curves, and heterophase in the lower lying region.

The effect of the ethanol concentration on the homogenization of the acetone–glycerol mixture can be described by a linear function (e.g., at 35°C $y = 16.18–0.96x$) at ethanol concentrations of 2–18 mol % and temperature in the range under study. The larger the excess of acetone, the smaller the amount of ethanol necessary for homogenizing the starting reagents. A decrease in temperature by every 5° requires an increase in the ethanol concentration by 0.7–1.1 mol %.

Table 1 lists data on how the concentration of water in a mixture of the starting reagents changes when an azeotrope of ethanol with water (96 wt % ethanol) is used for homogenization with 98 wt % glycerol and 98.7 wt % acetone.

Analysis of the data in Table 1 shows that addition of the ethanol azeotrope to the starting mixture has only a slight effect on the change in the concentration of water and, consequently, on the equilibrium degree of glycerol conversion. For example, when a mixture of acetone and glycerol is homogenized at their molar ratio of 5 : 1, addition of the ethanol azeotrope will lead to a decrease in the equilibrium degree of glycerol conversion by only 0.8% (calculated from the data of [5]).

Thus, the homogenization of the starting mixture of the reagents with ethanol is a rather effective way to intensify the process, which affects the yield of solketal only slightly.

Table 2 presents the results of a comparison of two methods for homogenization of the starting mixture of acetone and glycerol: with a 20-fold molar excess of acetone and with ethanol. The calculations were made for a temperature of 35°C with the use of published data on equilibrium constants [5].

It follows from a comparison of the data in Table 2 that use of ethanol for homogenization of the starting mixture leads to a decrease in the equilibrium degree of glycerol conversion in a single pass through the reactor by 7.5%, but makes it possible to reduce by a factor of 4.5 the expenditure for acetone recycling at an insignificant increase (by 5.5%) in the amount of glycerol in the recycle. At the same time, the product of glycerol and acetone concentrations becomes 2.6

Table 1. Change in the concentration of water in the starting reaction mixture at various molar ratios between acetone and glycerol in relation to the concentration of the introduced ethanol azeotrope

Acetone : glycerol molar ratio	Mass, g		Content in the mixture, wt %		Content of water without addition of ethanol, wt %
	mixture of glycerol and acetone	ethanol	ethanol	water	
15 : 1	100	1.3	1.23	1.40	1.37
10 : 1	100	4.8	4.40	1.52	1.40
5 : 1	100	9.7	8.49	1.69	1.47
2 : 1	100	12.9	10.97	1.88	1.61

Table 2. Comparison of methods for homogenization of the glycerol–acetone mixture

Homogeneous mixture of the starting reagents	Equilibrium degree of glycerol conversion, %	Amount in the recycle, kg per 1 kg of solketal			Product of the reagent concentrations $c_{ac}{\cdot}c_{gl}$ at the initial instant of time, mol mol
		acetone	ethanol	glycerol	
GL : AC molar ration of 1 : 20	91.25	9.96	–	0.128	8.85
With ethanol, GL : AC molar ratio of 1 : 5	83.70	2.18	0.33	0.135	23.11

Table 3. Results of experiments in an apparatus with fixed catalyst bed. GL : AC molar ratio 1 : 5

Parameter	Delivery of an emulsion	With ethanol, delivery of a homogeneous mixture
Flow rate of glycerol, g h^{-1}	15.7	33.5
Spraying density, m^3 m^{-2} h^{-1}	0.12	0.33
Volumetric flow rate, h^{-1}	0.25	0.70
Conversion of glycerol, %	62	65
Yield of the product per unit mass of the catalyst, g$_{SK}$ g$^{-1}_{cat}$ h^{-1}	0.067	0.15
Contact duration (per volume occupied by the catalyst), h	4.06	1.45

larger and, accordingly, the reaction rate grows because of the substantial increase in the content of glycerol at a GL : AC molar ratio of 1 : 5. The increase in the rate of the condensation process by at least a factor of 2.6 makes it possible to proportionally reduce the volume of the reaction unit or, accordingly, raise its output capacity.

The efficiency of homogenization of the mixture of the starting reagents with ethanol was experimentally confirmed in a column-type apparatus with a fixed bed of KU-2-8 ion-exchange resin in the falling-film mode. Table 3 lists the results of experiments with delivery of the emulsion of the starting reagents with nearly the maximum spraying density, or with that of a mixture homogenized with ethanol. In both cases, the GL : AC molar ratio was 1 : 5, and the temperature, 35°C.

If a homogenized mixture of the reagents is used, there are no limitations on the spraying density. At a higher spraying density and 2.8 times shorter contact duration, the homogenization of the starting mixture of the reagents enables a higher conversion of glycerol all other conditions being the sample. The yield of solketal per unit mass of the catalyst became 2.2 times higher.

Thus, when an emulsion of the reagents is delivered, the glycerol phase blocks about half of the active centers of the catalyst, thereby reducing its output capacity.

Despite the comparatively low conversion of glycerol in the reactor for solketal synthesis, recycling the starting reagent in the industrial technique will in the end provide a yield of the target product of no less than 97%.

CONCLUSIONS

The study demonstrated that the limited solubility of glycerol and acetone leads to stratification of the emulsion of the starting reagents in a film falling along the surface of KU-2-8 cation-exchange resin. This leads to blocking of active centers of the catalyst and impairs its output capacity. At a spraying density exceeding 0.15 m^3 m^{-2} h^{-1}, the adsorbed glycerol film becomes so thick that the free volume along the apparatus diameter becomes significantly smaller, which, in the end, causes flooding of the catalyst.

The homogenization of the starting mixture of the reagents helps to lift these restrictions. Data are presented on how the concentration of water and ethanol affects the solubility of glycerol in acetone. It was shown that use of ethanol for homogenization of the starting reagents is more than twice more efficient than performing the process with delivery of an emulsion of the reagents or with a 20-fold excess of acetone.

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