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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Technologies for Processing of Crude Glycerol from Biodiesel Production: Synthesis of Solketal and Its Hydrolysis to Obtain Pure Glycerol

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Abstract—Information on the volume of production of biodiesel and crude glycerol from it is analyzed. The possibility of using crude glycerol as a feedstock for preparing solketal is demonstrated. The specific features of the solketal synthesis from crude glycerol and of separation of the reaction products are described. A catalytic process is suggested for selective decomposition of solketal to glycerol to obtain purified glycerol of any required concentration up to 99.8 wt %. A flowsheet is suggested for processing of crude glycerol to obtain solketal and subsequently converting it to obtain pure glycerol.

Keywords: glycerol, solketal, biodiesel, fatty acids, sulfuric acid

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Active studies are being performed today to search for and bring into practice renewable power sources. Biodiesel is considered as a viable alternative to fossil fuels. Much interest in this product is largely due to its use in production of renewable natural raw materials, to its biodegradability, and to low level of pollutant emissions into the atmosphere [1, 2].

According to the estimates made by Abercade, in 2016 the world volume of biodiesel production reached 32.9 bln L, exceeding by 12.7% the level of the previous year. Such growth is due to a significant increase in the biodiesel amount produced in Argentine (by 29%), the United States (by 21%), and Indonesia (by a factor of 2.6). The total cost of the biofuel produced in 2016 is estimated at $24.8 bln, exceeding by 11.7% the level of the year 2015.

The major by-product in biodiesel production is crude glycerol. About 1 kg of crude glycerol is formed per 10 kg of biodiesel [3]. Thus, the total volume of bioglycerol production in 2016 was almost 3 mln t.

Thus, utilization or processing of the by-product, crude glycerol, becomes a serious problem at biodiesel production plants. Purified glycerol can be the main commercial product, but only a few plants in Asia and Latin America have facilities for glycerol purification. The purification is expensive, and the possible applications of crude glycerol are very limited.

Too large excess of crude glycerol from biodiesel production, on the one hand, will affect the market of refined glycerol and, on the other hand, can give rise to environmental problems associated with glycerol purification. The biodiesel production cost increases by $0.021/L per $0.22/kg decrease in the glycerol sale price [4]. Hence, commercial use of glycerol for producing high-value-added chemicals is extremely important for the financial efficiency of the biodiesel production. In this case, crude glycerol can be considered as a demanded by-product rather than production waste.

Purified glycerol is widely used in chemical industry as a feedstock for many processes including modern

Table 1. Specification of the main glycerol grades, accepted in the United States, and the corresponding requirements of the Russian state standards (GOST)

Glycerol grade	Glycerol content (USA), wt %	GOST requirements		Use of glycerol
		glycerol content, wt %	GOST, grade	
Crude glycerol	70–90	78–86	6823–2000	Production of distilled glycerol and other technical applications
Technical grade	99.5	88–94	6824–96, grades T-88, T-94	Production of distilled glycerol and other technical applications
Pharmacopoeia grade (USP)	99.5	≥94	6824–96, grade PK-94	For pharmacopoeia purposes and for food and cosmetic industry
Food grade (USP/FCC)	99.7	≥98	6824–96, grade D-98	For producing explosives (GOST 6884–96)

technologies for the production of epichlorohydrin [5] and oxygenates [6]. More than 2000 commercial items including pharmacological, medical, and food products are produced today using glycerol. Glycerol is used in cosmetology, military industry, and agriculture, including attempts of using it as forage for nonruminant animals, etc. [7].

Various vegetable and animal fats are used for biodiesel production. About 100 mln t of vegetable oils are produced annually in the world, and they are mainly used for food purposes. The production of vegetable oils cannot yet grow at a rate corresponding to the growth of the biodiesel production. Competition of biodiesel with the food market can hardly be avoided. However, today the main raw materials for biodiesel production are rapeseed, soybean, and palm oils. The choice of particular oil largely depends on the production region. As a rule, to reduce the biodiesel production cost, the oil that is the most readily available in the given region is chosen. Rapeseed and sunflower oils are used in the European Union, palm oil prevails in the biodiesel production in tropical countries, and soybean oil and animal fats are the main raw materials in the United States.

Biodiesel as an alternative diesel fuel contains a mixture of esters of higher fatty acids. The ester interchange of triglycerides (e.g., of vegetable oil) with methanol in the presence of such catalysts as NaOH or $NaOCH_3$ leads to the formation of the methyl ester (biodiesel) and glycerol phase.

Crude glycerol contains impurities of fatty acids, methanol, spent catalyst, and other chemicals; they can negatively affect the human health and the environment. Hence, glycerol, especially that intended for use in pharmaceutics (see, e.g., United States Pharmacopoeia, USP) and food industry (Food Chemical Codex, FCC), should meet definite requirements and standards.

The specification of the main grades of glycerol, accepted in the United States, and the requirements of the Russian state standards GOST 6823–2000 (Natural Crude Glycerol) and GOST 6824–96 (Distilled Glycerol) is given in Table 1.

Crude glycerol obtained from various raw materials will contain various impurities, and the purification technology will be largely determined by the application fields of the ready product. When glycerol is mainly used for technical purposes, certain contaminants are acceptable, whereas in most cases, e.g., when glycerol is used in food and pharmaceutical industries, high degree of purification is required.

The technologies developed for the purification of glycerol obtained as a by-product from biodiesel production are mainly based on adapted procedures used at soap-making plants in glycerol recovery from spent-soap lye. These processes include vacuum distillation, ion exchange, adsorption treatment with activated carbons, membrane separation, etc. The first step involves neutralization and phase separation of the reaction mixture to remove free fatty acids and some salts. The next step is the solution concentration

Table 2. Physicochemical parameters of crude glycerol from biodiesel production at OAO Mogilevkhimvolokno

Parameter	Value
External appearance	Dark brown liquid
Weight fraction of glycerol	75.6
Weight fraction of ash	3.8
Weight fraction of water	17.8
Weight fraction of soap (in terms of sodium oleate)	1.28
Weight fraction of fatty acids (in terms of oleic acid)	1.30
Weight fraction of methanol	0.2

by evaporation to remove methanol from the glycerol stream. The final step is a combination of different purification procedures including vacuum distillation, ion exchange, membrane separation, and adsorption.

As noted above, the technology for purification of crude glycerol is complicated and power-consuming, which does not allow many small and medium biodiesel producers to use it in the practice.

On the other hand, the price of purified glycerol in Europe in June 2017 was €850 per ton of 99.7% glycerol and €650 per ton of 99.5% glycerol. In the beginning of 2018, the price decreased to €550 and 500, respectively. The price of purified glycerol in Asia is today $390–400 per ton CFR (delivery terms: Cost and Freight) (in China, $420–460 per ton CFR). The price of 80% glycerol in Europe fluctuates between €150 and 275 (data of the Greenea: Market Watch consulting and broker company, April–March 2018).

The complexity of the technology for purification of crude glycerol and, as a consequence, the large difference in the product price depending on purity make it topical to develop new technologies for using crude glycerol for the production of high-value-added commercially demanded products. The use of crude glycerol as a raw material is particularly attractive for the Russian industry, because the biodiesel production in Russia makes no sense owing to large crude oil resources, and the available facilities for production of highly concentrated glycerol are extremely limited (the possible annual output does not exceed 5–6 thousand tons). Therefore, Russia imports today more than 60 thousand tons of glycerol annually, and this volume can increase by a factor of more than 2 with the planned construction of epichlorohydrin production plants. To compare, by 2022 only in Europe the annual glycerol consumption is expected to exceed 1190 thousand tons, and the global glycerol market will exceed $4 bln (data of Greenea: Market Watch, January 2017).

Among production of epichlorohydrin, large amount of glycerol can be demanded for the production of a new commercial product, solketal (SK), a promising octane booster improving the operation properties of fuels for internal combustion engines [8].

It should be noted that specifically crude, and not distilled, glycerol is an environmentally advantageous feedstock for producing high-value-added organic compounds.

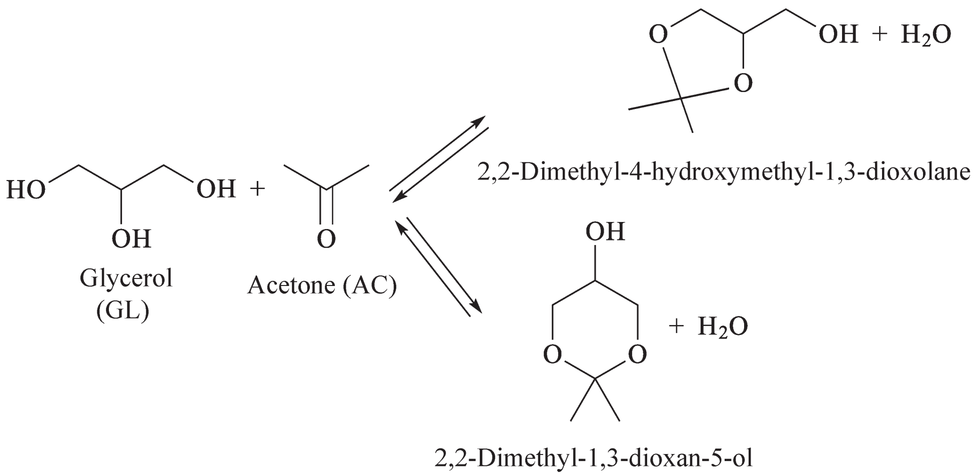
This study deals with the synthesis of solketal from glycerol formed as a by-product of biodiesel production and with the subsequent hydrolysis of the isolated solketal as an alternative procedure for purification of crude glycerol.

EXPERIMENTAL

As starting chemicals we used acetone (chemically pure grade), sulfuric acid (chemically pure grade), sodium hydroxide (analytically pure grade), distilled water, Amberlyst 35Wet resin, and crude glycerol from biodiesel production at OAO Mogilevkhimvolokno (Belarus) (for composition, see Table 2).

Fatty acids were removed from crude glycerol by adding sulfuric acid, vigorously stirring, and settling in a separation funnel. The lower glycerol layer was separated from the fatty acid layer and was subsequently used for the synthesis of solketal.

Scheme.



Experiments on the solketal synthesis from crude glycerol were performed in a 500-mL three-necked flask equipped with a thermometer, a reflux condenser, and a power-driven controllable-rate stirrer. The experiments were performed at 20–25°C; the stirrer rotation rate was 1500 rpm. Acetone was added in a 3–6.5-fold molar excess relative to glycerol.

After the solketal synthesis, a 5 wt % NaOH solution was added to the reaction mixture to neutralize the excess acidity to pH 7–7.5. Mineral salts and soaps precipitate in the course of the solketal synthesis and neutralization of the reaction products. After separating the precipitate on a blue ribbon paper filter, the reaction products were distilled on a glass column 20 mm in diameter and 500 mm high, packed with glass Raschig rings 4 mm in diameter and equipped with a unit for vapor condensation, for reflux with the possibility of controlling the reflux amount, and for condensate collection in a receiver at atmospheric pressure or in a vacuum.

The solketal decomposition into glycerol was performed in a 250-mL three-necked glass flask in the presence of sulfuric acid or Amberlyst 35Wet resin under the conditions of straight distillation of the acetone formed in the process or of fractional distillation on a column described above.

The organic reaction products were analyzed with a Tsvet-800 chromatograph equipped with a thermal conductivity detector under the following conditions: 2-m packed column, stationary phase 20% poly(ethylene glycol succinate) and 3% di(2-ethylhexyl) sebacate on Chromaton N-AW (0.25–0.315 mm fraction), vaporizer temperature 220°C, detector temperature 200°C, programmable column temperature 120–180°C. The water concentration was determined by gas chromatography on the same device using Polysorb-1 packing.

The concentration of fatty acids and soaps in the initial glycerol and reaction products was determined by conductometric titration. The analysis results were calculated in terms of oleic acid (as the major fatty acid component of rapeseed oil from which the biodiesel is produced at OAO Mogilevkhimvolokno) and sodium oleate.

The ash residue was determined according to GOST (State Standard) 7482–96.

RESULTS AND DISCUSSION

Solketal is formed by condensation of glycerol with acetone on acid catalysts. The reaction is shown in the scheme.

Hereinafter, the term solketal is applied to a mixture of these two isomers.

The initial crude glycerol has weakly acidic reaction (pH 5–6) due to fatty acid impurities. When crude glycerol is mixed with acetone, two liquid phases are formed because of limited mutual solubility of the components [9]. Vigorous stirring of this mixture for 24 h led to no changes in the reaction system, and solketal was not formed even in trace amount. That is, weak fatty acids cannot catalyze reaction (1).

It is known that sulfuric acid is an active catalyst of the solketal formation [10]. When using distilled glycerol,

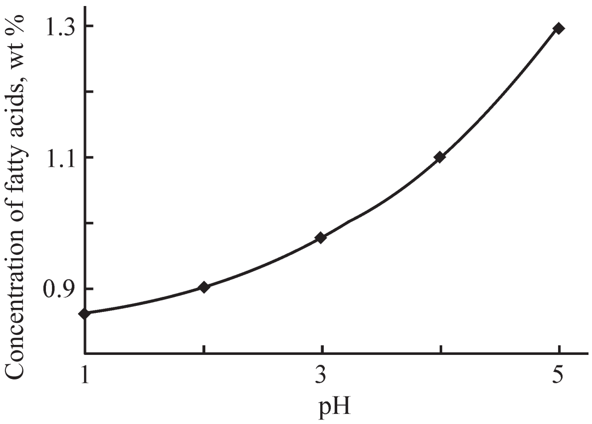


Fig. 1. Content of fatty acids in crude glycerol (in terms of oleic acid) as a function of pH.

catalytic concentrations of H_2SO_4 (about 0.01 wt %) are sufficient to ensure the acceptable reaction rate. When using crude glycerol, the required amount of sulfuric acid increases considerably, which is caused by its neutralization with soaps present in glycerol with the formation of fatty acids and sulfates. The solketal synthesis can be performed directly from crude glycerol after acidification of the mixture with sulfuric acid; however, in this case all the fatty acids remain in the reaction mixture, and they should be neutralized prior to distillation of the reaction products, which increases the NaOH consumption.

Preliminary treatment of crude glycerol with sulfuric acid, followed by separation of the fatty acids, which float up, is more appropriate. This not only reduces the alkali consumption for neutralization of reaction products, but also allows separation of the concentrated phase of fatty acids, which can become a commercial product after additional purification.

Figure 1 shows how the concentration of fatty acids (in terms of oleic acid) in crude glycerol depends on pH after the acidification with sulfuric acid and settling of the reaction mixture.

The lowest content of fatty acids in the glycerol layer was reached upon acidification of crude glycerol with sulfuric acid to pH 1–2. This pH value is recommended for the first step of the process.

The separated acidic solution of crude glycerol, when mixed with a 4–5-fold molar excess of acetone (relative to glycerol), forms an emulsion, which transforms into a homogeneous solution of reaction products after vigorous stirring for 2.5 h at 20–25°C, with more than 50% glycerol conversion. Homogenization of the reaction mixture considerably accelerates the reaction, which was limited in the emulsion by the component diffusion rate. The solketal concentration in the reaction mixture reached 25.1 wt % in 10 min after the formation of the homogeneous solution and did not change further with time; i.e., the equilibrium was attained. The equilibrium conversion of glycerol was 78%.

The dependence of the equilibrium conversion of glycerol on its molar ratio with acetone is shown in Fig. 2. As can be seen, when synthesizing solketal from crude glycerol, an increase in the molar excess of acetone over 5 influences the equilibrium concentration of glycerol insignificantly. On the other hand, larger excess of acetone leads to increased cost of its separation by fractional distillation. Therefore, approximately fivefold molar excess of acetone should be considered as optimum.

With the progress of the solketal synthesis and glycerol consumption, the volume of the glycerol phase decreases, and the mineral salts that were present in the initial crude glycerol in the dissolved form partially precipitate because of high acetone concentration in the second phase. By the moment of the equilibrium attainment in the experiment with a 4–5-fold molar excess of acetone, approximately 80% of the mineral compounds initially present in crude glycerol precipitated.

The solketal is isolated from the reaction products by fractional distillation. Because reaction (1) of solketal formation is reversible, prior to distillation of the reaction products the catalyst (sulfuric acid) should be removed from the system by neutralization. Otherwise, heating of the reaction mixture in the stripping section of the distillation column will lead to decomposition of solketal to acetone and glycerol.

The crude solketal is neutralized with a sodium hydroxide solution to pH 7–7.5. In the process, an additional amount of sodium sulfate precipitates, and small amounts of fatty acids present in the reaction mixture transform into soaps. The soaps formed are virtually fully adsorbed by crystals of mineral salts, which are separated by common methods.

The reaction products after neutralization and separation of the precipitate are subjected to fractional distillation. Excess acetone is distilled off first; it can be used again in the solketal synthesis. Then, water is distilled off, and solketal is distilled in a vacuum (T_b =

90°C at 10 mmHg). The solketal purity is no less than 99.5 wt %.

Thus, the available and relatively cheap crude glycerol does not require any preliminary purification or concentration and can be used directly for preparing solketal using sulfuric acid as a catalyst.

On the other hand, the reversibility of the solketal synthesis and relatively mild conditions of this reaction allow this process to be used as an alternative procedure for purification of crude glycerol formed as a by-product from biodiesel production.

The solketal prepared by the above procedure should be diluted with water, an acid catalyst should be added, and the equilibrium of reaction (1) should be shifted to the left by distilling off the low-boiling acetone formed by hydrolysis of solketal.

The conditions of our experiments on hydrolysis of solketal are given in Table 3. In the first experiment, we distilled the acetone off using a distillation column. As expected, the condensate obtained at 60°C was acetone with 0.5 wt % moisture content. In the process, the temperature of the bottoms increased to 190°C. Then, the temperature of the bottoms started to gradually decrease, and at 95°C the condensation of a water–acrolein mixture started.

The acrolein formation was practically avoided in the experiment with straight distillation in the presence of Amberlyst 35Wet resin. After the completion of the acetone distillation, as indicated by a sharp increase in the condensation temperature to 100°C, the bottoms was a pale yellow liquid consisting of glycerol with impurities of water (5 wt %), solketal (0.2 wt %), and acrolein (0.05 wt %). Because the process was performed in the straight distillation mode, the moisture content of the distilled acetone was 6–15 wt %; no impurities of acrolein and other compounds were detected in the condensate.

Replacement of Amberlyst resin by sulfuric acid in the straight distillation mode led to the formation of 1.4 wt % acrolein in the bottoms.

It is known that acrolein is produced from glycerol in a liquid-phase process at atmospheric pressure at $T > 150°C$ in the presence of homogeneous or heterogeneous acid catalysts (e.g., H_2SO_4, $KHSO_4$, initial and acid-promoted zeolites, γ-Al_2O_3, etc.) [11, 12].

Intense formation of acrolein in the course of acetone distillation in a column is due to high temperature of the bottoms (190°C), required for ensuring the vapor flow throughout the column height.

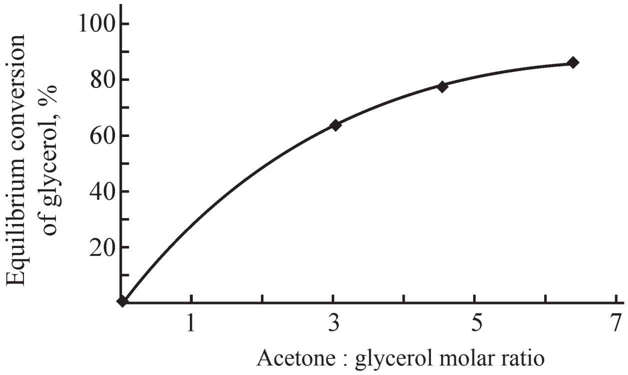


Fig. 2. Equilibrium conversion of crude glycerol (OAO Mogilevkhimvolokno) as a function of acetone : glycerol molar ratio.

In hydrolysis of solketal in the mode with straight distillation of acetone, heating to such high temperatures is not required, and the acetone distillation is complete at temperatures of up to 150°C. The acrolein formation can thus be avoided. However, in this case the distilled acetone is moist, and it should be additionally dried prior to the solketal synthesis.

The results of experiments in the presence of heterogeneous (Amberlyst 35Wet) and homogeneous (H_2SO_4) catalysts show that sulfuric acid is more active in the side reaction of the acrolein formation, which is apparently due to its stronger acid properties.

Our experiments show that heterogeneous acid catalysts are preferable for the for the solketal hydrolysis. The use of such catalyst, as compared to a homogeneous catalyst (e.g., H_2SO_4), does not require the subsequent neutralization of the reaction mixture; the catalyst is not consumed in noticeable amounts and exhibits high selectivity. Virtually no acrolein, the major and extremely undesirable by-product, is formed on Amberlyst resin. Acrolein is a colorless low-boiling liquid with strong order and strong lacrimating effect. This impurity can impart characteristic unpleasant odor to pure glycerol, which is inadmissible.

The concentrated glycerol formed after the solketal hydrolysis can be used for technical purposes without additional treatment or can be subjected to vacuum distillation to obtain a high-quality commercial product suitable for use in pharmaceutical and food industry.

Based on the data obtained, we suggested a flowsheet for the synthesis of solketal from crude glycerol as a by-product from biodiesel production and a procedure for

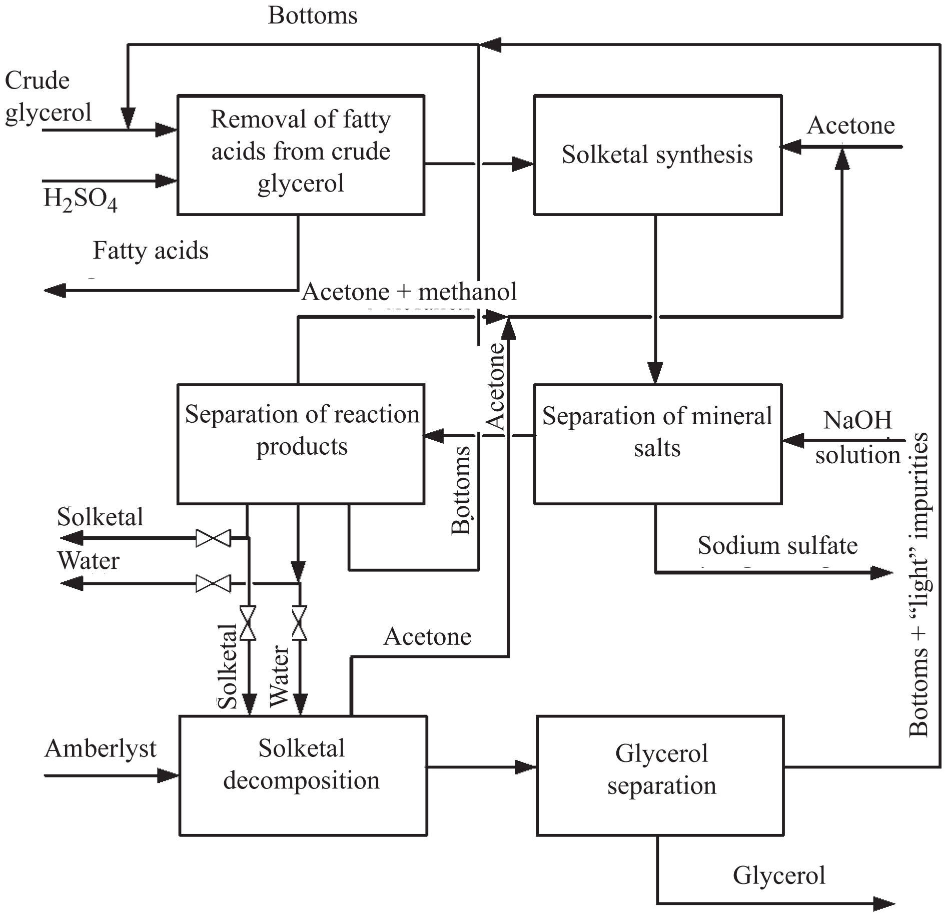
Table 3. Conditions of experiments on solketal hydrolysis

Run no.	Mode of acetone distillation	Reactants loaded				$T_{bottoms}$, °C (max)	$T_{condensate}$, °C
		catalyst	m_{cat}, g	m_{SK}, g	m_{H2O}, g		
1	Fractional distillation	Amberlyst 35Wet	2.5	164	25	190	60 and 95
2	Straight distillation	Amberlyst 35Wet	0.1	152	30	150	70–80
3	Straight distillation	H_2SO_4	0.02	152	30	136	70–80

glycerol purification via solketal (Fig. 3). The procedure that we developed allows preparing from crude glycerol a number of commercial products: solketal, glycerol, and fatty acid concentrate, which, if necessary, can be separated into individual acids or their mixtures.

CONCLUSIONS

Crude glycerol from biodiesel production can serve as a feedstock for producing solketal. It does not require any pretreatment or complication of synthesis conditions as compared to the process with distilled glycerol. The process occurs at room temperature in the presence of sulfuric acid as a catalyst. The sulfuric acid consumption is mainly determined by the content of soaps, which transform into fatty acids and sulfates under the action of the acid. The fatty acids themselves do not catalyze the solketal synthesis because of their low strength. The optimum molar ratio of acetone to glycerol, required for preparing solketal, is 5 : 1.



The equilibrium conversion of glycerol in this case is 80% at 20–25°C. The major fraction of mineral salts present in crude glycerol precipitates from the reaction products. After neutralization of the reaction mixture, the soaps that are formed from fatty acids dissolved in crude glycerol precipitate also. Solketal with the main substance content of no less than 99.5 wt % can be isolated from the neutralized reaction products by fractional distillation after separating the precipitate.

The solketal synthesized from crude glycerol can be used for producing glycerol of any quality, up to the level meeting the requirements of food and pharmaceutical industry. The reversibility of the solketal synthesis allows its hydrolysis to be performed with virtually 100% glycerol yield when the acetone formed in the process is distilled off. An acid catalyst is required for the solketal hydrolysis. Sulfuric acid exhibiting strong acid properties causes the formation of an appreciable amount of a by-product, acrolein, whose concentration in the glycerol obtained can reach 1.5%. With Amberlyst 35Wet resin used as a catalyst, the relative contribution of this side reaction can be reduced to a minimum, and the acrolein content of the glycerol obtained does not exceed 0.05 wt %. Additional vacuum distillation of glycerol allows obtaining a high-quality (up to 99.8 wt %) product.

A flowsheet for processing of crude glycerol to obtain solketal and then pure glycerol via solketal hydrolysis has been suggested.

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REFERENCES

1. Wan Omar, W.N.N., and Saidina Amin, N.A., *Biomass Bioenergy*, 2011, vol. 35, no. 3, pp. 1329–1338.
2. Magara-Gomez, K.T., Olson, M.R., Okuda, T., Walz, K.A., and Schauer, J.J., *Atmosph. Environ.*, 2012, vol. 50, no. 4, pp. 307–313.
3. Ardi, M.S., Aroua, M.K., and Awanis Hashim, N., *Renew. Sustain. Energy Rev.*, 2015, vol. 42, pp. 1164–1173.
4. Konstantinović, S.S., Danilović, B.R., Ćirić, J.T., Ilić, S.B., Savić, D.S., and Veljković, V.B., *Chem. Ind. Chem. Eng. Q.*, 2016, vol. 22, no. 4, pp. 461–489.
5. Dmitriev, G. and Zanaveskin, L., *Chem. Eng. Trans.*, 2011, vol. 24, part 1, pp. 43–48.
6. Dmitriev, G.S., Terekhov, A.V., Zanaveskin, L.N., Khadzhiev, S.N., Zanaveskin, K.L., and Maksimov, A.L., *Russ. J. Appl. Chem.*, 2016, vol. 89, no. 10, pp. 1619−1624.
7. Quispe, C.A.G., Coronado, C.J.R., and Carvolho, J.A., Jr., *Renew. Sustain. Energy Rev.*, 2013, vol. 27, pp. 475–493.
8. Mota, C.J.A., da Silva, C.X.A., Rosenbach, N., Jr., Costa, J., and da Silva, F., *Energy Fuels*, 2010, vol. 24, no. 4, pp. 2733–2736.
9. Dmitriev, G.S., Terekhov, A.V., Khadzhiev, S.N., and Zanaveskin, L.N., *Russ. J. Appl. Chem.*, 2016, vol. 89, no. 1, pp. 45–50.
10. Monbaliu, J.-C.M., Winter, M., Chevalier, B., Schmidt, F., Jiang, Y., Hoogendoorn, R., Kousemaker, M.A., and Stevens, C.V., *Bioresourse Technol.*, 2011, vol. 102, no. 19, pp. 9304–9307.
11. Patent JP 2006290815, Publ. 2006.
12. Katryniok, B., Paul, S., Carpon, M., and Dumeignil, F., *Chem. Sustain. Chem.*, 2009, vol. 2, no. 8, pp. 719-730.