

## Etherization of glycerol with alcohols on cationic resins

S.Q. Amirov\*, G.A. Aliyeva, F.R. Rahimova, A.F. Mammadova

Azerbaijan State Oil and Industry University, 16/21 Azadliq Ave., Baku, Azerbaijan  
e-mail: [firengizrehimova@gmail.com](mailto:firengizrehimova@gmail.com)

---

### Abstract

Etherization of glycerin with alcohols was carried out in the presence of acidic catalysts. Self-etherization of all alcohols is observed. Esters of various compositions are obtained on acid catalysts as the main product. Several samples of catalysts (Amberlyst-35, Al<sub>2</sub>O<sub>3</sub>, CPS and CPS) were used for the experiment.

**Keywords.** Glycerin, isobutyl alcohol, catalyst, diisobutyl, mono-, di- and triisobutyl glycerol esters.

---

Received: 24 january 2022

Accepted: 27 april 2022

Published: 26 may 2022

---

### 1. Introduction

The significant expansion of the production of various products and, above all, fuels based on renewable raw materials raises the question of developing methods for the effective use of glycerin, one of the by-products of these industries. The global glycerin market has been characterized by rapid development in recent decades: in 2003, the total production volume amounted to about 200 thousand tons, and by 2012 exceeded 2 million tons. While the average price of distilled glycerin for 10 years (from 2000 to 2010) decreased by 10 times (from \$ 4,000/ton to \$ 450/ton), crude glycerin completely turned into unprofitable waste at the beginning of the 21st century due to the intensive development of biodiesel production [1] (in 2009, 64% of the glycerin produced accounted for the production of biodiesel [2]).

The high content of free glycerin exceeded the demand, which sharply raised the question of finding qualified processing methods. On the basis of glycerin, highly demanded semi-finished products and industrial synthesis products can be obtained using a number of processes described below:

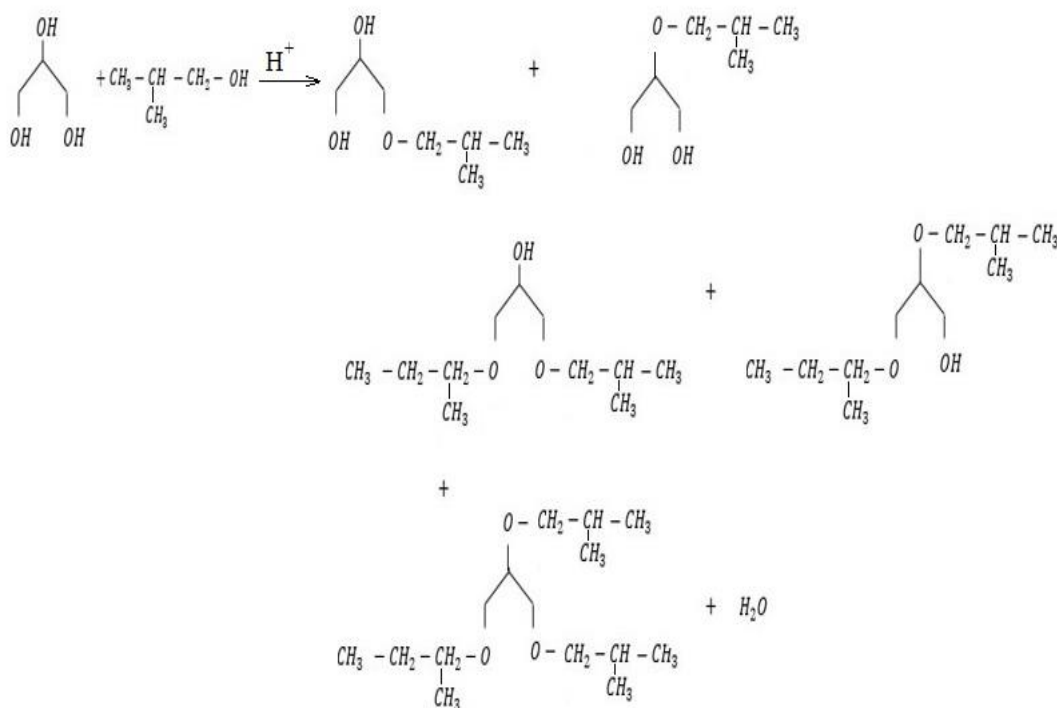
- production of acrolein from glycerol by catalytic dehydration at 250-350°C on acid catalysts (zeolites, perfluorosulfopolymer nafion, aluminum oxide, heteropoly acids) [3,4];
- production of epichlorohydrin from glycerin by chlorination with hydrochloric acid (Epicerin process) [3,5,6];
- the process of catalytic hydrogenation of glycerol to 1,2- and 1,3-propylene glycol [7-9];
- oxidative processes with the production of glyceric acid [10,11], glycolic acid [12] and hydroxyacetone [13,14].

The greatest attention of researchers in this field is attracted by glycerol ethers and esters, oligo - and polyglycerols, glycerol acetals and ketals. These glycerin derivatives are considered promising components for motor fuels [15] and lubricants [16]; for solvents,

coatings and refined organic synthesis processes [17, 18] for the paint and varnish industry; for surfactants [19, 20] and hydrotropic [21, 22] substances, components for household chemicals and cosmetics [23, 24], biologically active compounds [25, 26]. The interest in this field of research is due to the widespread use of glycerin, as well as the fact that glycerin is a raw material obtained from renewable raw materials.

There are many potential applications of glycerin esters. Addition to fuel as additives, use as a solvent, cryogenic substance, use as an antibacterial agent are the main areas of use of these substances [9, 27]. From the reaction of glycerin with isobutylene or with trichlubutyl alcohol in the presence of an acid catalyst, trichlubutyl-glycerine ether is obtained, which makes it possible to add as a mixture to diesel fuel [10].

The etherization of glycerin with various alcohols is carried out by acidic catalysts. Mono- and diglyceride esters with a yield of 61% to 96% are obtained from their interaction. The process of alkylation of glycerol with alcohols in the presence of various types of acidic heterogeneous catalysts may be of great interest. The purpose of this process is to obtain mono-, di- and trialkylglycerin esters by the following reactions (Fig.1):



**Scheme 1.** Etherization of glycerol with isobutyl alcohol in the presence of an acid catalyst

## 2. Experiments

Ionizing resins are polyelectrolytes with ionogenic groups in the form of covalently crosslinked insoluble fine particles. The particles have either a dense internal structure without discrete pores (gel resins, microporous resins) or a multi-channel porous structure (macromolecular or macronutrient resins). Usually, these ionites are obtained on the basis of styrene and divinylbenzene, which is a building component that controls the porosity of particles [28]. Ionizing materials are divided into cationites, anionites and amphoteric. Most of the cationites belong to insoluble polyfunctional acids and include the groups -COOH; -SO<sub>3</sub>H; -OH; -SH. Anionites, however, are insoluble bases with the main groups -NH<sub>2</sub>; -NH<sub>3</sub>OH; -NHR; -NR<sub>2</sub>. Ionogenic groups are introduced into the ionite composition during the

chemical treatment of monomers or the finished polymer.

In the process under study, ionizing resins were used along with catalysts of various acidic nature. But the studied resins were ion-exchange resins obtained industrially [23].

In the process of glycerol etherization, cationic resins synthesized using simplified technology based on a polymer frame made from both unused polystyrene and waste polystyrene were used for the first time. Let's conditionally designate the unused polystyrene frame cationite as C-PSY, and the unused polystyrene frame cationite as C-PST.

To improve the complex properties of the polymer frame, its functionality, hardening and subsequent sulfonation, new samples of polystyrene and waste polystyrene were modified into a laboratory capillary viscometer (IIRT-1) by a mechanochemical method with polyvinyl chloride. Polyvinyl chloride is a polymer with an active functional group-Cl in the composition (29-30%).

The proposed method of obtaining ionizing resin while maintaining the technology of obtaining a polymer frame allows to reduce energy consumption, improve the quality of the resulting cationite by increasing the volume of static and dynamic changes [31].

Some properties of the ionizing materials used are given in Table 1 [32, 33].

№	Sulfocationite based on polymer body, (%) mass.		Swelling coefficient in water	SEC based on NaOH, mg-equi/g	DEC based on CaCl <sub>2</sub> , mg-equi/g	mechanical durability after 10 hours of shaking, %
	Polymer sample	PVC				
New industrial polystyrene and polyvinyl chloride were used to obtain the polymer carcass (modification temperature 140°C).						
1	99	1	6,31	7,65	0,96	100
2	97	3	6,38	7,98	0,97	100
3	95	5	6,38	8,00	0,96	100
Domestic waste polystyrene and polyvinyl chloride were used to obtain the polymer carcass (modification temperature 140°C).						
4	99	1	1,04	5,9	0,59	90
5	97	3	0,75	5,6	0,62	90
6	95	5	0,49	6,7	0,79	90

**Table 1.** The main indicators of sulfocationites obtained in various compositions

The analysis of the composition of the reaction products was carried out on a chromatograph with a flame ionizing detector of the Russian production “Crystallux 4000 M”. Chromatographic analyses were carried out on a capillary calon (active phase: 5% phenyl -95% dimethylpolysiloxane, 30 m × 0.25 mm), in a helium gas-forming medium, in a temperature programming mode of 70-250 °C, at a temperature rise rate of 10C/min.

#### ***Conditions of the etherization reaction with isobutyl alcohol***

To compare the catalysts, the process was carried out in a three-phase tubular laboratory installation equipped with a mechanical mixer, a Dina-Stark water separator with reverse water cooling, a drip GIF and a thermometer.

The etherization reaction of glycerin and isobutyl alcohol in the presence of an acid heterogeneous catalyst was carried out in a three-bladed tube equipped with a thermometer, a stirrer and a Dean-Stark water separator with reverse cooling of water. The reactions were carried out at a temperature of 110c for 2 hours with the participation of both the c-PSY catalyst and the c-PST catalyst. As a result of numerous experiments, it turned out that the highest result in the direction of obtaining glycerol ether of isobutyl alcohol, which is the target product, is observed with the participation of C-PSY, taken as a catalyst. When an

excess of isobutyl alcohol is obtained from reacting substances as a result of self-etherization of isobutyl alcohol, a large amount of Di-isobutyl ether is obtained during the reaction, which, in turn, reduces the yield of monoisobutylglycerin ether, which is the target product. Therefore, when the substances entering the reaction are taken in a ratio of 1:1 (mol), the self-ether reaction proceeds with little ether, the reaction leads to the complete conversion of glycerin and the production of monoalkylglycerin ether with a high yield.

Tables 1, 2 and 3 below show the conditions for the preliminary preparation of catalysts, respectively, as well as data on the characteristics and degree of acidity of the catalysts.

Catalyst	Prerequisites, (°C)	Time / Condition
Amberlist-35	105 (10 °C *min-1)	Overnight-vacuum
$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	300 (5 °C *min-1)	2 hours
K-PSY-3 (3-VX mass share, %)	110 (10 °C *min-1)	Overnight-vacuum
K-PST-33-VX mass share, %)	110 (10 °C *min-1)	Overnight-vacuum

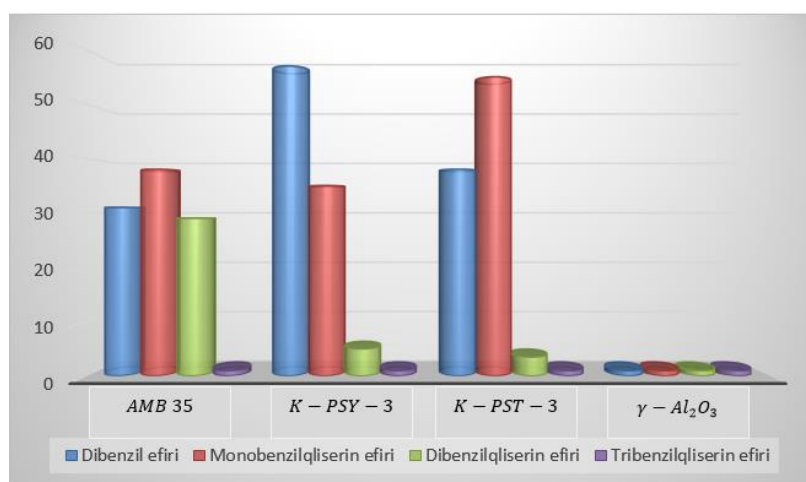
**Table 2.** Pre-preparation conditions of heterogeneous catalysts

Catalyst	Area / (m <sup>2</sup> *q <sup>-1</sup> )	Acidity <sup>a</sup> / (mmol n-butylamine *g-1)
Amberlist-35	50	5,2 <sup>b</sup>
K-PSY-3	45	4,2
K-PST-3	45	3,2
$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	210	0,3

**Table 3.** Surface area and acidity of Catalyst

a-as a result of adsorption of n-butylamine at 150 °C, b-reported by the manufacturer.

Isobutyl alcohol is separated from the reaction mixture in a rotary evaporator, and ether concentrate is obtained on the basis of isobutyl alcohol, which is also separated separately by vacuum rectification.



**Figure 1.** The yield of the products of the reaction of glycerin with isobutyl alcohol at 110 °C and for 2 hours

The c-PSY catalyst and the C-PST catalyst showed the highest results compared to other catalysts. The yield of isobutyl glycerol esters formed in reactions involving these catalysts is higher than the yield of diisobutyl ether.

$\gamma$ -Al<sub>2</sub>O<sub>3</sub> is practically inactive as a catalyst in this reaction. This inactivity can be explained by its low degree of acidity. On the other hand, the high activity of the Amberlyst-35, CPS and CPS catalyst in the production of isobutyl glycerol esters may be due to their high acidity. Thus, it becomes obvious that the acidity of the catalyst plays the biggest role in this reaction.

Among these catalysts, we have witnessed that the C-PST ionite catalyst also exhibits quite high activity. In the presence of this catalyst, esters of isobutyl glycerin with a good yield were obtained.

### 3 . Results and discussion

Thus, glycerol was abstracted with benzyl alcohol in the presence of heterogeneous acid catalysts, and in the presence of c-PST and c-PSY catalysts, the production of monoisobutylglycerol ether with high yield was found. When using c-PSY ionite as a catalyst, a diisobutyl ether with a higher yield than monoisobutylglycerin ether is obtained as a catalyst.  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is practically inactive in this reaction.

### References

1. B. Katryniok, Green Chemistry **12** (2010) 2079.
2. M. Gupta, N. Kumar, Renewable and Sustainable Energy Reviews **16**(7) (2012) 4551.
3. <https://www.cdc.gov/niosh/npg/npgd0302.html>//The National Institute for Occupational Safety and Health, Glycerine: (mist) Retrieved 2016, 2017-04-15.
4. R. Christoph, B. Schmidt, Ullmann's Encyclopedia of Industrial Chemistry (2006).
5. Bryan. Biodiesel Magazine (2011) 25.
6. J. Bonnardeaux, Report for the Western Australia Department of Agriculture and Food (2006) 5.
7. S. Carretin, P. McMorn, P. Johnston, K. Griffin, C. Kiely, G. Hutchings, Phys. Chem. Chem. Phys. **5**(6) (2003) 1329.
8. G. Brett, Q. He, C. Hammond, P. Miedziak, N. Dimitratos, M. Sankar, G. Hutchings, Angew. Chemie **50**(43) (2011) 10136.
9. C. Mota, C. Da Silva, N. Rosenbach, J. Costa, F. Da Silva, Energy and Fuels **24**(18) (2010) 2733.
10. Patent EC №EP0718270A2. 1995.
11. E. Alptekin, M. Canakci, Appl. Therm. Eng. 2017.
12. S.V. Koshchii, Russ. J. Appl. Chem. **75**(9) (2002) 1434.
13. S. Queste, P. Bauduin, D Touraud, W. Kunz, J. Aubry, Green Chem. **8**(9) (2006) 822.
14. P. Gaudin, R. Jacquot, P. Marion, Y. Pouilloux, F. Jérôme, ChemSusChem **4** (2011) 719.
15. P. Gaudin, R. Jacquot, P. Marion, Y. Pouilloux, F. Jérôme, Catal. Sci. Technol. **1**(4) (2011) 616.
16. K. Klepáčová, D. Mravec, M. Bajus, Appl. Catal. A Gen. **294**(2) (2005) 141.
17. M. Pico, A. Romero, S. Rodríguez, A. Santos, Ind. Eng. Chem. Res. **51** (2012) 9500.
18. A. Behr, L. Obendorf, Engennier Life Sci. **2** (2003) 185.
19. W. Kiatkittipong, P. Intarachoen, N. Laosiripojana, C. Chaisuk, P. Praserttham, Comput. Chem. Eng. **35**(10) (2011) 2034.
20. F. Frusteri, F. Arena, G. Bonura, C. Cannilla, L. Spadaro, O. Di Blasi, Appl. Catal. A Gen. **367** (2009) 77.
21. M.D. Gonzalez, Y. Cesteros, P. Salagre, Appl. Catal. A Gen. **450** (2013) 178.
22. J. Melero, G. Vicente, M. Paniagua, G. Morales, P. Muñoz, Bioresour. Technol. **103**(1) (2012) 142.
23. B. Pinto, J. De Lyra, J. Nascimento, C. Mota, Fuel. **168** (2016) 76

24. K.Y. Nandiwale, S.E. Patil, V.V. Bokade, *Energy Technol.* **2**(5) (2014) 446.
25. F. Liu, K. De Oliveira Vigier, M. Pera-Titus, Y. Pouilloux, J. Clacens, F. Decampo, F. Jerome, *Green Chem.* **15**(4) (2013) 901.
26. P. Gaudin, R. Jacquot, P. Marion, Y. Pouilloux, F. Jérôme, *ChemSusChem* **4** (2011) 719.
27. C. Cannilla, G. Bonura, L. Frusteri, F. Frusteri, V. Lucia, *Catal. Sci. Technol.* **5** (2015) 187.
28. A. Tsuji, K. Rao, S. Nishimura, A. Takagaki, K. Ebitani, *ChemSusChem* **4** (4) (2011) 542.
29. F.A. Amirov, G.A. Aliyeva, F.R. Rahimova, G.F. Rustamova, 11 th Word Conference on “Intelligent systems for Industrial Automation, Tashkent, Uzbekistan (2021).
30. G.A. Aliyeva, F.R. Rahimova, G.F. Rustamova, 9th Rostocker International Conference: “Technical Thermodynamics: Thermophysical Properties and Energy Systems”, Germany (2020) 62.
31. F.A. Amirov, I.Q. Abdullayeva, G.A. Aliyeva, AR Patents № I 2021 0101
32. G.A. Aliyeva, F.R. Ragimova, Proceedings of the XXXIII International Scientific and Technical Conference "Chemical reagents, reagents and processes of low-tonnage chemistry". dedicated to the memory of Academician of the Academy of Sciences of the Republic of Bashkortostan D.L. Rakhmankulov, Ufa (2020) 82.