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STUDY OF A CONTINUOUS PROCESS OF GLYCEROLYSIS OF RAPESEED OIL WITH THE SOLID BASE CATALYSTS

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Abstract. Glycerolysis of rapeseed oil over several solid bases using fixed bed flow reactor has been studied. It was found that Mg-Al hydrotalcite and Al_2O_3 supported CaO–ZnO demonstrate high activity in this reaction. The yield of monoglycerides reaches 70 % with 96 % oil conversion at 513 K. It was shown that pores size of a catalyst is an important factor of intensification of the glycerolysis process. It was found that turpentine additive decreases the reaction temperature due to higher solubility of glycerol in oil.

Keywords: solid base catalysts, hydrotalcite, rapeseed oil glycerolysis, monoglycerides.

1. Introduction

Glycerol as co-product of biodiesel production is now a reasonable raw material for obtaining different commodity chemicals including monoglycerides of fat acids. The transesterification process of oil and fats with glycerol has been applied since long in industry for production of mono- (MG) and diglycerides (DG), which are used as emulsifiers and surfactants in a wide range of food, pharmaceutical, and cosmetic products [1]. MG and DG are also important modifying agents in the manufacturing of alkyd resins, polymers, and lubricants [2]. Mainly, MG and DG are produced in batch processes at the temperatures higher than 473 K using NaOH, KOH, or $Ca(OH)_2$ as a catalyst [1, 3]. Recently, a continuous alkaline-catalyzed process for the glycerolisis of soybean oil was proposed [3]. However, alkali in the reaction product must be neutralized by acid.

Now a development of the environmentally friendly heterogeneous processes based on solid catalysts for transesterification of vegetable oils with glycerol as well as with methanol for biodiesel production becomes topical [4, 5]. The basic oxides such as MgO, $MgO-Al_2O_3$, ZnO, CeO_2, La_2O_3, Sepiolite-Na–Cs, MCM-41-Cs, and calcined hydrotalcites have been studied in the oil glycerolysis batch processes [6-8]. MgO turns out to be a suitable catalyst in that process [6, 7]. We have studied a continuos glycerolysis of rapeseed oil over solid bases using a flow reactor with fixed-bed of a catalyst. Such insoluble mixed oxides as hydrotalcite, calcined hydrotalcite, $MgO-TiO_2$, $MgO-La_2O_3$, $MgO-ZrO_2$ and alumina-supported ZnO, ZnO-MgO, CaO-ZnO were used as catalysts.

2. Experimental

2.1. Materials

Hydrotalcite carbonate (Mg:Al = 3:1) samples were prepared by co-precipitation method according to [9]. The samples were dried at 393 K. To obtain $MgO-Al_2O_3$ mixed oxides, the hydrotalcite samples were calcined at 673 K for over 2 h. The $MgO-La_2O_3$, $MgO-TiO_2$ and $MgO-ZrO_2$ samples were prepared by usual co-precipitation method. The required amounts of $Mg(NO_3)_2 \cdot 6H_2O$ and $La(NO_3)_2 \cdot 9H_2O$ were dissolved in water and then the mixed metal nitrate solution (atomic ratio Mg:La = 3:1; total concentration of Mg^{2+} and La^{3+} – 1.4 M) was added to ammonium solution under vigorous stirring at pH = 12. The resulting mixture was heated up to 358 K and aged for 4 h under vigorous stirring. The slurry was filtered and thoroughly washed. The precipitate was extruded to form granules and dried at 393 K. In such a way the $MgO-ZrO_2$ samples (Mg:Zr = 6:1) were prepared using water solution of $ZrOCl_2 \cdot 8H_2O$. For synthesis of $MgO-TiO_2$ samples (Mg:Ti = 3:1) preliminarily prepared 3M water solution of $TiCl_4$ was used. 22.3 ml of this solution (0.067 mol of Ti) was added to 300 ml solution of $Mg(NO_3)_2 \cdot 6H_2O$ (0.2 mol of Mg). The solution with pH = 1.5 was added to ammoniun solution (0.67 mol of NH_4OH in 500 ml of H_2O, pH = 12) at vigorous stirring. After drying at 673 K for 1h (heating rate 5°/min), the samples were crumbled, and the fraction of granules with diameter 0.5–1 mm was used for catalytic testing.

The supported samples were prepared *via* impregnation of granulated γ-Al_2O_3 ("Alvigo-KS", Ukraine) by aqueous solutions of metal nitrates (ZnO-MgO/Al_2O_3 samples) or metal acetates (ZnO/Al_2O_3 and CaO-ZnO/Al_2O_3 samples). The fraction of Al_2O_3 granules of 0.5–2.0 mm was pre-dried at 523 K for 1 h and used for impregnation. After impregnation the samples were dried 393 K and treated at 773–973 K.

2.2. Catalysts Characterization

The specific surface area of the samples was determined using N_2 adsorption/desorption method at 77 K by standard BET method (Quantachrome Nova 2200 e Surface Area and Pore Size Analyzer). Prior to each measurement, all samples were degassed at 393 K. XRD patterns of the samples were recorded with DRON-4-07 diffract meter (CuK$_\alpha$ radiation).

The strength of basic sites (H$_-$) of prepared oxides was determined using 0.1 % cyclohexane solution of 2,4 dinitroaniline (pK$_{BH}$= +15.0), 4-chloro-2-nitroaniline (pK$_{BH}$ = +17.2), 4-nitroaniline (pK$_{BH}$ =+18.4), aniline (pK$_{BH}$ =+ 27.0) and triphenylmethane (pK$_{BH}$ =+ 33.0) indicators (Aldrich).

To determine the total concentration of basic sites [B] on the surface of prepared mixed oxides we have used the method of inverse titration of 2,4-dinitrophenol by KOH solution in the presence of bromthymol blue as indicator. 10 ml of 0.05 N solution of 2,4-dinitrophenol in toluene was added to 200–300 mg of calcined at 523–973 K sample and stirred for 30 min. The suspension was stored in closed glasses for over 24 h to establish equilibrium. The aliquots were titrated with 0.01 N solution of KOH. Traditionally benzoic acid solution in benzene is used for determination of site content in solid bases [10]. However we have not obtained recurrent results on site concentrations due to possible salt formation of benzoic acid with strong basic sites. Therefore benzoic acid was replaced by 2,4-dinitrophenol.

2.3. Reaction Procedure

Rapeseed oil with 99.5 % triglyceride content and glycerine with a normal purity of 99 % were used without further purification. The glycerolysis of rapeseed oil was carried out in a fixed-bed continuous flow Pyrex reactor (i.d. 8 mm), inserted in an electric oven and operating at atmospheric pressure. A catalyst (1.2 cm^3) was previously activated at 523 K under argon flow. The rapeseed oil and glycerol were introduced into the upright reactor over two glassed capillaries separately within the total LHSV= 0.4–2.7 h^{-1} using a syringe pump Orion M 361 (Thermo Electron Corporation). Mainly the experiments were performed at molar ratio oil: glycerol = 1: 4.

The reaction products were collected every 2 h and analyzed by high-pressure reverse liquid chromatography method (Waters System Breez Model 717 chromatograph

with a refractometric detector). The column used was Symetry C_{18} 150 × 4.6 mm with silicagel 5 μ; eluent – THF: acetonitrile = 30:70 vol %. ^{13}C NMR spectra of the products were recorded on a FT-NMR Bruker Avance 400 spectrometer.

3. Results and Discussion

The textural parameters and data on the strength and concentration of basic sites of the studied oxides are presented in Table 1. All samples show a low temperature N_2 adsorption isotherm of type IV in the classification of IUPAC, which is typical of mesoporous solids. The studied samples are characterized by relatively strong basic sites (+17.2$\leq$ H$_-$ $\leq$+27.0) with the concentration of 0.55–1.57 mmol/g (Table 1).

The results on oil conversion over the studied catalysts and MG selectivity are given in Table 2. High oil conversion at the level of 75–95 % was observed for the middle basic hydrotalcite sample (H$_-$ $\leq$+17.2). However, after preliminary calcination of this sample at 673 K, when the destruction of layered hidrotalcite lattice with formation of amorphous mixed MgO-Al_2O_3 oxide is observed [9], the activity of such material decreased up to 25 % oil conversion. Three-time decrease of pore sizes occurs under calcination of the Mg-Al hydrotalcite (Table 1). As is known triglycerides are large molecules with the length of C_{18} chain about 2.5 nm. Obviously, only large pores (R > 5 nm) of a catalyst can provide effective access for triglyceride molecules to active surface sites. Therefore we attribute high activity of the hydrotalcite to the largest size of its pores among the studied samples.

The supported catalysts showed quite good activity in the glycerolysis reaction with 65–73% oil conversion (Table 2). The highest oil conversion (73 %) was observed for ZnO-CaO/Al_2O_3 sample.

The prepared mesoporous MgO-TiO_2, MgO-ZrO_2, and MgO-La_2O_3 samples with the strength of basic sites H$_-$ $\leq$ +27 should be classified as strong solid bases (Table 1). Owing to the strong basicity and high surface area, the synthesized oxides were supposed to show high activity at lower temperatures than the hydrotalcite. However, MgO-TiO_2 and MgO-ZrO_2 provided low oil conversion (15–18 %) at 473 K. The MgO-La_2O_3 mixed oxide kept high activity (85 %) during 2 h and then was blocked by high viscous products (Table 2). At increasing temperature of the reaction to 513 K formation of the highly viscous polymeric compounds on the surfaces of MgO-TiO_2, MgO-ZrO_2, and MgO-La_2O_3 owing to glycerol polymerization was observed. The activity of the solid bases in glycerol oligomerization at 523 K was reported [11]. Thus, strong basic mixed oxides are unsuitable catalysts for the glycerolysis of rapeseed oil.

Table 1

Textural properties and basicity of the studied catalysts

Sample	Me atomic ratio	Deposited phase, wt %	T_{calc}, K	Crystalline phase	S, m²/g	Pore volume, cm³/g	BJH desorption pore radius, nm	H_	[B], mmol/g
$Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$	3:1	—	523	Hydrotalcite carbonate	130	0.50	6.3	≤+17.2	0.55
$MgO-Al_2O_3$	3:1	—	673	MgO (periclase) + amourphous	260	0.40	2.4	≤+17.2	0.90
$MgO-TiO_2$	3:1	—	673	MgO (periclase) + amourphous	280	0.60	1.9	≤+27.0	0.85
$MgO-ZrO_2$	6:1	—	673	MgO (periclase) + amourphous	220	0.60	1.9	≤+27.0	1.10
$MgO-La_2O_3$	3:1	—	673	MgO, La_2O_3	150	0.70	1.7	≤+27.0	1.57
ZnO/Al_2O_3	—	19	773	—	230	0.70	3.3	≤+17.2	0.75
$ZnO-CaO/Al_2O_3$	2:1	22	973	—	150	0.50	3.3	≤+17.2	0.82
$ZnO-MgO/Al_2O_3$	1:1	21	873	—	175	0.60	3.9	≤+17.2	0.81
Al_2O_3	—	—	873	γ-Al_2O_3	270	0.70	4.8	≤+1.5	0.57

Table 2

Results on glycerolysis of rapeseed oil over the studied oxides

Catalyst	T_r, K	Time contact*, h	Oil conversion, %	Selectivity to MG**, %
Hydrotalcite	513	1.6	96	70
		0.6	79	57
$MgO-Al_2O_3$	513	0.6	25	80
ZnO/Al_2O_3	513	1.1	68	55
$ZnO-MgO/Al_2O_3$	513	1.1	65	50
$ZnO-CaO/Al_2O_3$	513	1.1	73	53
		1.6	85	55
$MgO-TiO_2$	473	1.1	15	70
$MgO-ZrO_2$	473	1.1	18	60
$MgO-La_2O_3$	473	1.1	85***	85
Al_2O_3	513	1.1	7	18

Notes: * τ = 1/total LHSV; ** calculated from chromatographs; *** reaction duration up to 2 h

The hydrotalcite and $CaO-ZnO/Al_2O_3$ samples, which demonstrated the highest catalytic activity in the process of the continuous rapeseed oil glycerolysis, have been studied more in detail. In Fig. 1, the data on oil conversion and MG selectivity over hydrotalcite at different temperatures are given. With the temperature rising from 453 to 533 K, the conversion of rapeseed oil on the hydrotalcite increased from 22 to 97 % correspondingly. However, brown product was obtained at 533 K in contrast to pale yellow products formed at lower temperatures. The effect of reaction temperature on MG selectivity was minor (Fig. 1).

The effect of time contact on oil conversion and glyceride selectivity was studied also (Fig. 2). The oil conversion more than twice increased when time contact was prolonged from 0.2 to 1.1 h. These data are closely to the results obtained by authors [6] with MgO catalyst after 5 h of reaction time (96 % oil conversion and 66 % MG selectivity). According to stability test on catalytic activity the hydrotalcite catalyst has been provided oil conversion on the level of 80–85 % during 6 h at 513 K.

The supported $ZnO-CaO/Al_2O_3$ catalyst provides the high oil conversion at 493–513 K also (Fig. 3). Minor increase in selectivity to MG is observed at different time contact τ (Fig. 3b). However with rising τ from 0.8 to 2.4 h the conversion of oil increases from 63 to 90 % (Fig. 3a). Changes in oil:glycerol molar ratio in the range from 1:4 to 1:13 did not lead to a marked increase in the selectivity to MG.
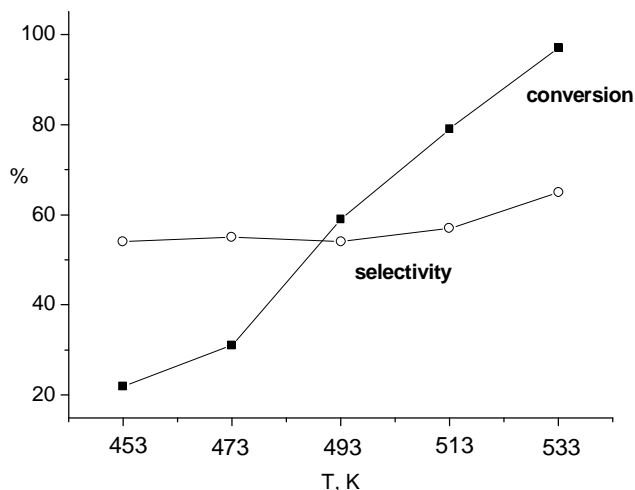
Fig. 1. Oil conversion and selectivity to monoglycerides at different temperatures with hydrotalcite ($\tau = 0.6$ h)
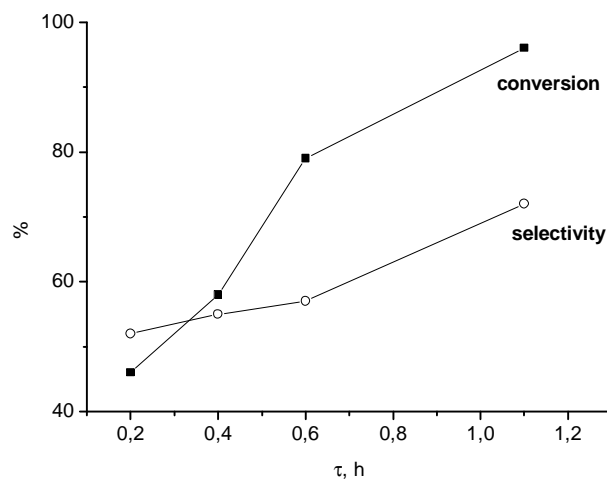

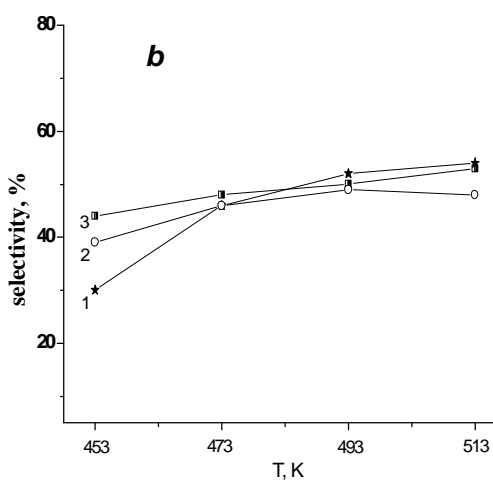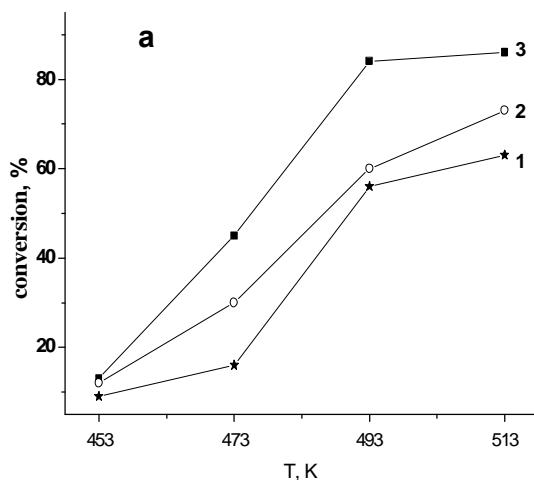**Fig. 2.** Oil conversion and MG selectivity at different time contact on hydrotalcite at 513 K

Fig. 3. Rapeseed oil conversion (a) and selectivity (b) at different temperatures over ZnO-CaO/Al$_2$O$_3$ at contact time 0.8 (1); 1.1 (2) and 1.6 (3) h

^{13}C NMR spectroscopy is a useful method for identification of MG- and DG-isomers in the glycerolysis product. Analysis on shift and intensity of the signals from two different carbons in the ester groups at 172–175 ppm and 61–72 ppm is more informative. So, in the ^{13}C NMR spectrum of rapeseed oil the signals of carboxyl groups at 173.1 and 172.7 ppm and the signals at 62.2 and 69.3 ppm, corresponding to carbon atoms of the glycerol fragment, are observed (Fig. 4). In spectrum of the products the lines at 174.0 and 173.7 ppm, relating to *a*-MG and to 1,3-DG, were appearing (Fig. 4). The signals of initial triglyceride fragment at 173.1 and 172.7 ppm, and at 62.2 and 69.2 ppm were practically disappearing. At the same time the lines at 63.4, 65.1 and 70.2 ppm, which correspond to the carbon atoms   with attached

hydroxyl groups in *a*-MG molecules, were recorded. According to ^{13}C NMR spectra of glycerol *a*-monostearate, glycerol *a*-monolaurate (www.aist.go.jp/ RIODB/SDBS), these signals can be assigned to HO–[*]CH$_2$–CH(OH)–CH$_2$OOR (63.4 ppm), HO–CH$_2$–CH(OH)–[*]CH$_2$OOR (65.1 ppm) and HO–CH$_2$–[*]CH(OH)–CH$_2$OOR (70.2 ppm). The authors of [6] have also observed mainly the formation of *a*-MG (not β-MG) at glycerolysis of rapeseed oil. Thus, at first stage of the glycerolysis process *a*-MG and 1,3-DG, as intermediate by-product, are formed. Then diglycerides, through the second reaction with glycerol, transform to *a*-MG (Scheme). Therefore the mixture of DG and MG is the common reaction product (Table 2).
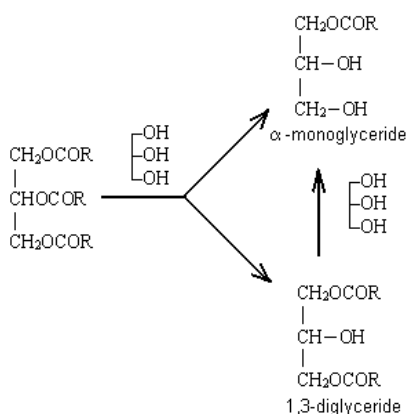
It is known that low mutual solubility of the hydrophilic glycerol in the hydrophobic triglyceride oil (~ 4 % at room temperature) limits the effectiveness of glycerolysis process. The solubility of glycerol to 40–45 % is reached at 513–523 K. We have added turpentine to rapeseed oil for better solubility of glycerol. Turpentine is a complex mixture mainly of terpene hydrocarbons $C_{10}H_{16}$ with T_b = 428–453 K which is used as a common solvent for paints on the basic of vegetable oils. Addition of 4 wt % of turpentine results in the increasing oil conversion from 12 to 20 % at 1453 K in the presence of ZnO-CaO/Al_2O_3 catalyst. Perhaps other higher-boiling emulsifiers could provide high oil conversion at T = 473–513 K.

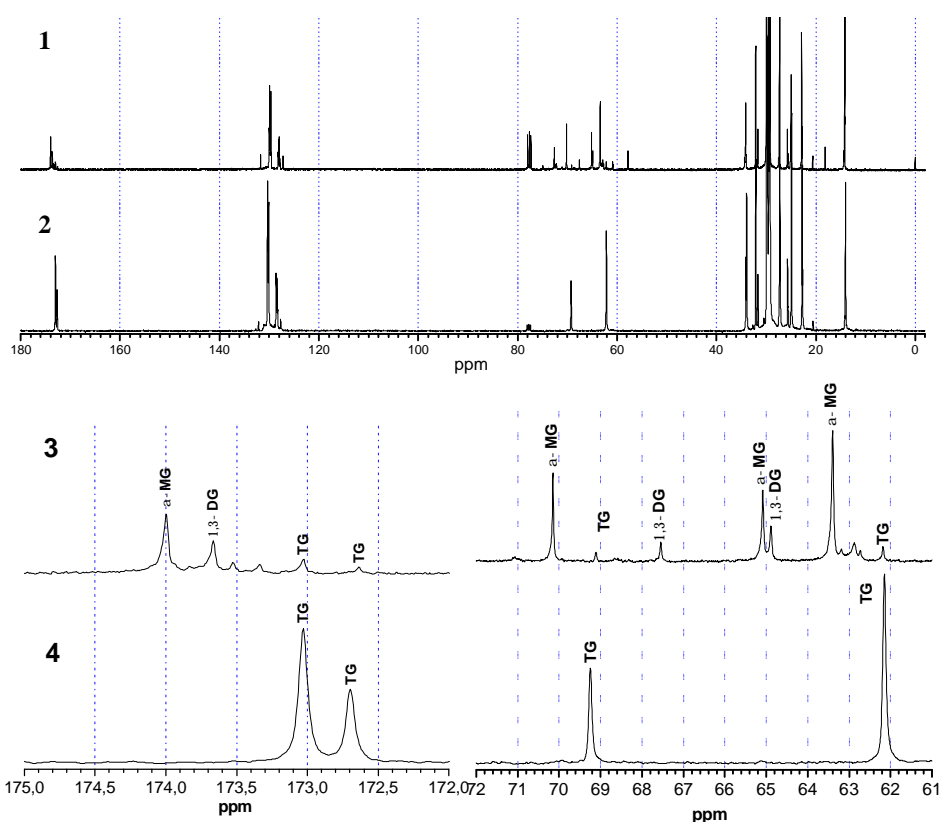**Fig. 4.** ^{13}C NMR spectra of rapeseed oil (2, 4) and glycerolysis products over ZnO-CaO/Al_2O_3 (1, 3) at 180–0, 175–172 and 72–61 ppm shift regions

4. Conclusions

On the basis of the obtained results it is possible to consider three main factors which affect glycerolysis process. These are basicity (strength and content of basic sites), catalyst pores radius, and solubility of glycerol in oil. The basic oxides with the strength of basic sites on the level of H. = +17.2 can abstract a proton from glycerol molecules forming active anions, which attack carbon atoms in carboxylic groups of rapeseed oil. Prepared hydrotalcite and ZnO–CaO/Al_2O_3 catalysts at 513 K produce monoglycerides with 69 % and 57 % yields, respectively. Addition of terpentine to rapeseed oil allows to somewhat decrease the reaction temperature due to better glycerol solubility. Strong basic oxides (H. = +27.0) are unsuitable for the transesterification process because they can also catalyze glycerol oligomerization reaction.

By an example of initial and calcined hydrotalcites it was shown that pores size of a catalyst is an important intensification factor of the glycerolysis process. The catalysts with wide pores (R > 5 nm) can provide the effective access of large triglycedide molecules to active surface sites.

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ВИВЧЕННЯ НЕСТАЦІОНАРНОГО ПРОЦЕСУ ГЛІЦЕРОЛІЗУ РІПАКОВОЇ ОЛІЇ НА ОСНОВНИХ КАТАЛІЗАТОРАХ

Анотація. Досліджено процес гліцеролізу ріпакової олії на твердих основних каталізаторах в проточному реакторі зі стаціонарним шаром каталізатора. Знайдено, що Mg-Al-гідротальківт і CaO-ZnO/Al$_2$O$_3$ проявляють високу активність в цій реакції. Вихід моногліцеридів досягає 70 % при 96 % конверсії олії за 513 К. Показано, що розмір пор каталізатора є важливим фактором в процесі гліцеролізу. Знайдено, що додавання скипидару дозволяє знизити температуру реакції завдяки збільшенню розчинності гліцерину в олії.

Ключові слова: тверді основні каталізатори, гідро-тальківт, гліцероліз ріпакової олії, моногліцериди.