Catalytic ethylation of glycerol and a consecutive tert-butylation of glycerol ethyl ethers over heterogeneous catalysts

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Abstract

The goal of the present work was to enhance the degree of alkylation of glycerol to ethyl – butyl ethers at a maximum use of bioethanol as an alkylation agent. While being less reactive, ethanol is a renewable. In the other hand the non-renewable isobutylene is more reactive. Etherification of bioglycerol with bioethanol was studied over H-Beta zeolite catalysts and over ion-exchange resins in acidic form. Selectivity to di- and tri- ethyl ethers of glycerol over H-Beta zeolite at 200° C after 8 hours was up to 49%, while over Purolite catalyst at 185° C (at the upper limit of its thermal stability) only 14%. Recyclation of the formed diethyl ether, as a by-product of glycerol ethylation, can significantly increase the yield of di- and triethyl ethers. To increase the yield of desired di- and tri- alkyl ethers, a consecutive tert-butylation of the remaining hydroxyl groups of glycerol by isobutylene at mild reaction conditions was used (over ion-exchange resin Purolite or Amberlyst 35 as catalysts at a reaction temperature 80°C). The best results of tert-butylation have been obtained over Purolite CT 169 DR (dry form) at 80°C after 8 hours. Overall selectivity to di-ethyl, tri-ethyl, di-tert-butyl, tri-tert-butyl and mixed di-ethyl-tert-butyl and ethyl-di-tert-butyl ethers of glycerol was 93,3%. Comparable results have been obtained over Amberlyst 35 Dry catalyst as well. The alkylation was carried out in two steps. The first step was ethylation of glycerol at 200°C over zeolite catalyst, and the second one was tert-butylation of the products of ethylation over ion-exchange resins as catalysts at 80°C. The mixture of di- and tri-alkyl ethers with very low concentration of mono-ethers can be potentially used as oxygenate additives to diesel fuels.

Keywords Zeolites ● Ethyl ethers of glycerol ● tert-Butyl ethers of glycerol ● Ion-exchange resins ● Alkenes

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1. Introduction

Extending fatty acid methyl esters (FAME) production leads to growing amount of bioglycerol in the market which has many possibilities of utilization. One is its conversion to lower aliphatic ethers (tert-butyl-, ethyl-, amyl-, isoamyl-, etc.) which have a potential to be used as oxygenates in motor fuels, preferentially in diesel fuels, to decrease the levels of toxic compounds in the exhaust gases.

As can be seen from many papers, the largest attention has been paid to tert-butylation of glycerol, because isobutylene is very reactive and etherification can be carried out at mild reaction conditions with good results [1,2,7-18]. Besides isobutylene, tert-butanol and C4-fraction as tert-butylation agents have also been used [3,4,5,10-15]. From among other alkylation agents, isoamylenes [4,5,12], isopropanol [22] and n-butanol [14] have been used for alkylation of glycerol. Unfortunately, all these reactants usually come from fossil sources. Moreover, they have very important utilization in the production of more valuable special chemicals than fuel components.

It would be more rational to use bioethanol [19-30] as etherification agent for glycerol. Ethanol is widely available and can be produced from different renewable resources at prices comparable to price of fuels. It is known that ethanol is not as reactive as isobutylene or tert-butanol. The reactivity of the alkylation agent is mostly given by the stability of formed carbocation [32]. Carbocation is more easily formed by dehydration of tert-butanol or protonisation of isobutylene and reacts preferentially with glycerol to ethers or with another isobutylene to dimer at temperatures between 65 and 90° C with high rate. Dehydration of ethanol requires significantly higher temperature (near 200°C) because the formation of carbocation relates to significantly higher consumption of energy.

Catalytic tert-butylation of glycerol by isobutylene requires mild reaction conditions (temperature 65 – 90° C and autogenous pressure). As catalysts are suitable ion–exchange resins and many other heterogeneous catalysts (zeolites, sulfonic mesostructured silicas, heteropolyacids, perfluorosulphonic ionomers and grafted silicas) [1-30] in acidic form.

Etherification of glycerol with ethanol requires significantly higher temperature as the formed reactive carbocation is stabilized only with one methyl group, the formation of which is thermodynamically less favorable.

As catalysts for ethylation of glycerol at such relatively high temperatures (near 200° C) wide-porous zeolites in acidic form are suitable among others [15-30].

Etherification of glycerol with ethanol is a set of consecutive reversible equilibrium reactions leading to the formation of five glycerol ethers (two mono-, two di- and one tri-ethyl ether) and by-products (water, diethyl ether, ethylene, etc.). For etherification of glycerol with ethanol a higher ethanol/glycerol molar ratio is used to prefer the formation of desired di- and tri-ethers, which have hydrophobic character and good solubility in diesel fuels. The formation of glycerol oligomers at high molar ratio of ethanol/glycerol is suppressed. In the other hand, without the presence of ethanol, at the same reaction conditions, high yields of glycerol dimers and oligomers were detected [31].

Glycerol has two primary hydroxyl groups with better steric availability and higher nucleophility in comparison with the secondary hydroxyl group. Thus, in the first step preferentially the primary hydroxyl groups react to form a mono-ethyl ether (MEG 1, Scheme 1). The secondary hydroxyl group reacts with ethanol to form another mono-ethyl ether (MEG 2). In the second step, from these monoethers, two types of di-ethers (DEG 1 and DEG 2) are formed, and in the next step tri-ethyl ether of glycerol (TEG, Scheme 1) is formed. In all steps water is formed as a by-product in equilibrium reversible reactions. As by-products, diethyl ether and ethylene are formed by dehydration of ethanol by parallel reactions. Principally both by-products can act as ethylation agents in parallel reactions.

Pariente [19] investigated the etherification of glycerol with ethanol in the presence of solid acid catalysts. The best result was achieved over grafted silica catalyst at 200° C. At the glycerol conversion of 68 % the selectivity to monoethers was 75 % and to diethers 25 %. With Amberlyst 35 as a catalyst at 160° C the conversion was 52 % and the selectivity to monoethers 90 % and to diethers 10 %, respectively. The best results were obtained at 200° C with H-Beta zeolite (Si/Al = 25). Selectivity to monoethers was 75 % and to diethers 25 % at the 57 % conversion of glycerol.

Yuan [20] reported glycerol etherification with ethanol catalysed by different homogeneous and heterogeneous catalysts. The most active was SiO_2-suported HPW. At 160° C after 20h and at a molar ratio EtOH/glycerol = 6:1, the highest conversion of glycerol was 97 % with selectivities to monoethers 62 %, diethers 28 % and triether (GtEE) 10 %.

Melero [21] optimized the reaction conditions of glycerol etherification with ethanol by experimental design. Over arenesulphonic acid functionalized mesostructured silica as a catalyst, the optimal reaction conditions for the highest conversion of glycerol (74 %) at the yield of all ethyl ethers 42% were: T = 200° C, EtOH/glycerol molar ratio 15, amount of catalyst 19 wt.% and reaction time 4 hours. However, the reported optimal concentration of catalyst (19 %) is very high.

Roze [22] studied etherification of glycerol with different aliphatic alcohols catalysed by Amberlyst 15 and 36, Montmorillonite K 10 and Beta zeolite at atmospheric pressure and at temperatures from 60 ° C up to their boiling points. At these very mild reaction conditions the etherification of glycerol with ethanol failed.

A Canadian patent [23] over Beta zeolite (Si/Al = 40) at the temperature of 100° C and molar ratio of EtOH/glycerol = 5:1 after 5 hours claimed 92 % conversion of glycerol and 85 % yield of ethyl ethers. These results per se seem questionable, as experiments carried out by other authors at 100 °C over similar zeolite catalysts practically failed.

Pinto [24] compared different catalysts for etherification of glycerol with ethanol. The best results were obtained over Amberlyst 15 at 180° C, EtOH/glycerol molar ratio 3:1 after 4 hours. The conversion of glycerol was 96 % and the selectivity to ethyl ethers 80 %. It should be mentioned that the used temperature, 180° C, is over the declared thermal stability of Amberlyst 15 (140 – 150° C, Rohm and Haas).

Yadav [25] published a kinetic study of glycerol etherification with ethanol using strongly acidic cation exchange resin. Glycerol mono-ethyl ether was the major product of the reaction. The apparent activation energy of glycerol and ethanol was 105 and 111 kJ/mol, respectively. The conversion of the reactants calculated from the kinetic model matched reasonably with experimental data.

Lemos [26] studied catalytic glycerol etherification with ethanol over series of catalysts in a continuous reactor. Amberlyst 15 showed the best performance in terms of glycerol conversion and yield of ethers. A central composite design was used to optimize the performance of Amberlyst 15. The optimized value for glycerol conversion was 91 % and yield of ethers was 13 % under different reaction conditions. The other by-products formed from glycerol at its high conversion and low ether yields are not mentioned. In another work Lemos et al. [30] published optimization of glycerol etherification with ethanol in a fixed bed high pressure reactor using a three-factor central composite design over Amberlyst 15 as catalyst. The reaction temperature and catalyst amount were statistically significant in glycerol conversion and ethers yields. By further refinement of the data for the same reaction and same catalyst Marinho [35] claimed that the maximum glycerol conversion, up to 97%, is achieved at the reaction conditions 269 °C and 2.5 MPa.

Veiga [27] reported catalytic performance of USY, H-ZSM-5 and H-Beta zeolites for glycerol etherification with ethanol and tert-butanol. The best results were obtained with USY-650-L-2 and H-Beta zeolites with glycerol conversion up to 70% with high selectivity to mono-ethers. Hydrophobicity/hydrophilicity of the catalyst surface and reactants was crucial to glycerol conversion. Veiga in another work [28] published detailed identification of all ethers formed in the etherification of glycerol with ethanol or tert-butanol, considering the mass spectra of isolated products and the comparison of the retention times. Veiga [29] also studied etherification of glycerol, 1,2-propylene glycol and ethylene glycol with ethanol or 1-octanol using USY, H-Beta and H-ZSM-5 zeolites. The catalytic activity was correlated with zeolite hydrophobicity index. Higher conversions were achieved with more hydrophobic zeolites.

Frusteri [34] reported Hyflon® Ion S4X perfluorosulphonic ionomers as acid precursors for butylation of glycerol. Compared with Amberlyst A-15 catalyst the authors claim a superior activity in terms of yields of di- and tri-alkyl ethers of glycerol. However, the usage of pure isobutylene as an alkylating agent limits the utilization of bioethanol. Recent reviews [36,37] propose a variety of alkylating agents, the promising being alkenes and alcohols. Hence, a combination of consecutive alkylation steps is a promising route for the glycerol utilization, where both the quality of the resulting fuel additives, as well as the maximal utilization of bioderived resources (e.g. alcohols) are taken into account.

In the present work we focused on the catalytic ethylation of glycerol with bioethanol (both renewable reactants) and on the consecutive tert-butylation of formed glycerol ethyl ethers to enhance selectivity to di- and tri-alkyl ethers of glycerol as potential oxygenate additives to diesel fuel. This is an improved approach as ethylation mostly gives high selectivity to mono-ethyl ethers of glycerol, which are not suitable as additives to hydrophobic diesel due to their hydrophilic character. However, after tert-butylation of the primary product (with high proportion of mono-ethyl ethers), a mixture of tert-butyl- and mixed ethyl-tert-butyl ethers of glycerol can be obtained with high selectivity to desired di- and tri-ethers.

2. Materials and methods

As catalysts for the ethylation of glycerol zeolite H-Beta CP 814 Q (Table 1) and ion-exchange resin Purolite CT 169 DR were used (Table 2). For the next tert-butylation ion-exchange resins Purolite CT 169 DR and Amberlyst 35 Dry (Table 3) were used as catalysts. Zeolite H-Beta was calcined during 6 hours at 500°C prior the utilization.

Table 1 Characteristics of zeolite H-Beta CP 814 Q (from Zeolyst Int.)

Zeolite	Si/Al ratio	$S_{BET, L}$ (m^2/g)	$V_{mikro,t}$ (cm^3/g)	Acidity mmolH$^+$/g	Pore size (nm)
H-Beta CP 814 Q	25	730	0,225	0,68	0,77x0,67 0,55 - 0,56

$S_{BET,L}$ = specific surface of zeolites calculated on the base of linearized BET isotherm [33], $V_{micro,t}$ = volume of micropores calculated from t- line.

Table 2 Characteristics of ion - exchange resin Purolite CT 169 Dry (from Purolite)

Catalyst	Acidity (mmol H$^+$/ g)	Particle size (mm)	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)	Density g/cm^3	Thermal stability (°C)
Purolite CT 169DR	4,7	0,425 – 1,200	35 - 50	0,3 - 0,5	25,0 – 42,5	1,2	to 180

Table 3 Characteristics of ion-exchange resin Amberlyst 35 Dry (from Rohm and Haas)

Catalyst	Acidity (mmolH$^+$/g)	Water cont. (wt. %)	Particle size (mm)	Surface area (m^2/g)	Pore diameter (nm)	Pore volume (cm^3/g)
35Dry	≥5,2	≤3,0	1,18	50	30	0,35

Sorption characteristics of zeolites have been measured by the method of nitrogen adsorption at the temperature of liquid nitrogen. Micromeritics ASAP 2000 has been used as equipment. The samples of zeolite have been activated 12 h at the temperature 450° C and pressure 10-40 mbar.

Adsorption – desorption isotherms were measured by static volumetric method. Sorption characteristics of zeolites were calculated from isotherms by commercial software.

Total acidity of zeolites has been determined by TPDA method. After calcination of the zeolite sample, ammonia has been adsorbed 15 min at 100°C. Physiosorbed ammonia has been blown–out by nitrogen at 100° C (5 h). Chemisorbed ammonia has been desorbed in the flow of nitrogen in the temperature interval from 100 to 650° C (gradient 10°C/min) and trapped in HCl, the resulting solution was analyzed by potentiometric titration.

As chemicals were used: ethanol (p.a.) dry, glycerol (p.a.), tert-butanol (p.a.), isobutylene (99 %), diethyl ether (p.a.) all from Aldrich.

Glycerol mono - ethyl ether was prepared by ethylation of glycerol sodium salt (prepared from glycerol and sodium at 80° C) with ethyl iodide at 80° C for 5 hours. Reaction products have been isolated by distillation at 2 kPa. The main fraction was glycerol mono-ethyl ether 1. This fraction has been extracted by n-heptane to separate nonpolar by-products and after extraction it was vacuum distilled at 2 kPa. The purity of glycerol mono - ethyl ether was 95 % (determined by GC). For comparison, a commercial standard was used as well.

Glycerol di-ethyl ether (1,3-dietoxy – 2 – propanol) has been obtained as a standard from Alfa Aesar Co.

Etherifications were carried out in stainless steel laboratory autoclave (volume 250 cm^3) with regulated electric heating and magnetic stirrer. All experiments were carried out at 1000 rpm to eliminate the influence of external mass transfer.

Glycerol (12g), ethanol (90,1 g) and catalyst (10 wt.%/glycerol) were added to the reactor. After flushing with nitrogen, the reactor was heated to reaction temperature. The working temperature was 180 – 200° C (with zeolite catalyst) and 175 – 185° C (with Purolite catalyst). The pressure in the reactor during etherification was autogenous. After the catalytic test the reactor was cooled to laboratory temperature and the catalyst was filtered-off from reaction products. Diethyl ether and unreacted ethanol were distilled-off from reaction products and the residing liquid was analyzed by GC. The consecutive tert-butylation of mixed glycerol ethyl ethers has been done with isobutylene or tert-butanol (molar ratio of isobutylene or tert-butanol/free –OH group in reaction mixture was 2).

Tert-butanol and catalyst (Amberlyst 35 or Purolite CT 169 DR) were added to the reaction products obtained from the first reaction step. After flushing the reactor with nitrogen and heating to 80 or 90°C the stirring of reaction mixture was started. If isobutylene has been used as tert-butylation agent, after flushing the reactor with nitrogen, the isobutylene was introduced from a pressurized steel ampule. After 8 hours of reaction time the reactor was cooled to the laboratory temperature and after gassing-off the unreacted isobutylene, diisobutylene was distilled-off from the reaction mixture, the catalyst was filtered-off and the resulting liquid was weighted and analyzed by gas chromatography.

The identification of the products has been done by GC/MS 2010 Shimadzu equipped with EI and capillary column (HP- 1, 50 m x 0,2 mm). Helium was used as carrier gas (1 ml/min). The temperature program ranged from 60° C with the slope of 10°C/min up to 260° C.

For the quantification of products, a gas chromatograph Shimadzu GC-2014 has been used. It was equipped with capillary column OPTIMA WAX (30m x 0,53mm x 2 μm). The temperature program was as follows: 60°C (5 min) isothermally, then the temperature ranged to 220° C with a gradient 10° C/min and the last 10 min isothermally at 220° C. The method of internal standard has been used. Retention times of all presented ethyl-, tert-butyl- and mixed ethyl-tert-butyl ethers of glycerol are in the Table S4. The concentration of glycerol in the reaction products was not possible to determinate exactly for widening of its peak, and thus, the amount of unreacted glycerol in the reaction products was calculated from mass balance of used glycerol and formed glycerol ethers.

3. Results and discussion

The main idea of this work is to enhance the formation of di- and tri-ethers of glycerol. These higher ethers are more hydrophobic than mono-methyl ethers and have higher solubility in low polar diesel fuel as oxygenate additives.

The problem of glycerol etherification with ethanol is in the relatively low reactivity of ethanol. They have higher polarity and, thus, hydrophilic character and their miscibility with diesel is limited. The high selectivity to mono-ethyl ethers of glycerol in comparison with tert-butyl ethers is a result of higher reactivity of isobutylene/tert-butanol in comparison with ethanol.

To overcome this problem, we have suggested a solution by consecutive tert-butylation of prepared mixture of ethyl ethers of glycerol with high concentration of glycerol mono-ethyl ethers. The formed higher ethers are soluble in low polar fuels and can be used as potential oxygenates to motor fuels. After tert-butylation and removing of catalyst the reaction products can be directly used as oxygenate additive to diesel.

Possible ethylation and tert-butylation reactions are depicted in Scheme S1.

The possible reactions of glycerol and its ethyl-ethers by diethyl ether and ethylene, which also leads to the formation of ethyl ethers, are not presented in the Scheme S1.

During ethylation and consecutive tert-butylation, five tert-butyl ethers (two mono-, two di- and one tri-tert-butyl ether) can be formed [8], (Scheme S2).

The advantage of this procedure is the maximal utilization of bioethanol and bioglycerol from renewable resources, and in the second step the mono-ethyl ethers are tert-butylated to a mixture of di- and tri- alkyl ethers of glycerol as possible oxygenate additives to diesel.

3.1 Ethylation of glycerol

In the first part of this work catalytic ethylation of glycerol with bioethanol, diethyl ether and mixture of ethanol and diethyl ether over heterogeneous catalysts has been studied. Ethylation proceeded in the batch reactor over wide-porous zeolite H-Beta and over acidic ion-exchange resin Purolite CT 169 (dry form with thermal stability up to 180° C). All possible five ethyl ethers were identified and determined in the reaction products. As by-products, diethyl ether, ethylene and water were detected. Their formation is due to the ethanol dehydration. As by-products of glycerol dehydration 2,6-hydroxymethyl-dioxane, acetol and acetic aldehyde has been identified. Polyglycerols have not been formed in measurable amounts at high concentration of ethanol and in the presence of water (formed in the reaction).

3.1.1 Comparison of catalysts and the influence of reaction temperature

Based on previous studies [18, 26, 28] zeolite H-Beta and ion-exchange resin Purolite CT169 were tested for the ethylation of glycerol with ethanol. Over H-Beta zeolite with module 25 23.7 and 25.4% glycerol conversion with selectivities to di- and triethers 12.1 and 49.4% were achieved at 180 and 200 °C, respectively. Over Purolite CT169 catalyst the corresponding data were 21.1 and 21.8% conversion with 10,6 and 11,0% selectivities at 170 and 180 °C (see Tab. S5 and S6).

3.1.2 The influence of reaction time

As it is seen in Table 7, reaction time 8 hours is sufficient for studied ethylation reaction of glycerol at the given reaction conditions to obtain equilibrium composition of reaction mixture at 200 °C. Etherification of glycerol with ethanol in the closed system (autoclave reactor) is a system of reversible reactions which are determined by main equilibrium of O-alkylation reactions of glycerol and a formation of two mono-, two di- and one tri-ethyl ether of glycerol and diethyl ether, ethylene and water as a by-products (Scheme 1). Diethyl ether and ethylene can react with formed ethers and glycerol in parallel reversible reactions. Water has poisoning effect on catalyst, as its –OH group competes with –OH groups of polar reactants (glycerol and ethanol) on polar acidic sites of catalyst.

Table 7 The influence of reaction time

Reaction time (h)	2	4	6	8	10
Distribution of products (mol %)					
TEG	0,1	0,3	0,0	1,0	0,0
DEG 1	0,8	3,7	4,8	6,9	7,2
DEG 2	0,6	2,7	3,4	4,6	4,8
MEG 1	8,7	8,8	10,6	11,1	11,0
MEG 2	1,8	1,6	1,8	1,8	1,7
G	88,0	82,9	79,4	74,6	75,4
Conversion, selectivity and yield (%)					
X (G)	12,0	17,1	20,6	25,4	24,6

S (D+T)	12,3	39,4	39,7	49,4	48,5
Y (D+T)	1,5	6,7	8,2	12,5	12,0
S (M)	87,7	60,6	60,3	50,6	51,5

Reaction conditions: catalyst zeolite Beta Q: 10 wt. % related to glycerol, molar ratio EtOH/G = 15, temperature 200 °C.

3.1.3 The influence of water on glycerol ethylation

As the poisoning effect of water on alkylations is often reported in the literature, the influence of different amount of added water to dry reactants (glycerol and ethanol) has been studied in detail. In industrial conditions preferably ethanol with cca. 4.5% of water can be used. Additional water will be formed as a reaction product of etherification. The problem of the influence of water is complex, as the reaction mixture is a gas-liquid mixture. Great part of water and ethanol, diethyl ether and ethylene are the form of vapor in the autoclave reactor at the reaction temperature 200°C (at the end of reaction after 8 hours the autogenous pressure was 4.5 MPa). Moreover, it is known that small amount of water may have activation effect, but more water generally has poisoning effect on zeolite catalysts [25]. This small amount of water creates new Brönsted acid sites from Lewis acid sites, which can be catalytically more active in the acid-catalysed reactions (etherification, alkylation, esterification, etc.) in liquid phase for higher mobility of protons in comparison with fixed Lewis sites.

Hence, it is important to know the influence of added water to the reactants for ethylation of glycerol.

In the Table 8 one can see the influence of added water on glycerol etherification with ethanol over H-Beta zeolite catalyst at 200 °C.

As it is seen, addition of small amount (0.5 wt. %) of water to dry glycerol and ethanol had low effect on studied reaction. There is no positive effect of this concentration of water on catalyst activity. At 3.5 wt.% the negative effect of water on the formation of di- and triethers was evident. The water adsorbed on Brönsted acid sites of zeolite catalyst inhibits its catalytic activity. It is important to bear in mind this effect, as industrially manufactured ethanol usually contains only 95,5 % of ethanol.

Table 8 The influence of water for glycerol ethylation

Ethylation agent	G (dry)	G (dry)+ 0,5 wt.% water /G	G (dry)+ 3,5 wt.% water /G
Distribution of products (mol %)			
TEG	1,0	0,0	0,0
DEG 1	6,9	7,0	5,1
DEG 2	4,6	4,9	3,7
MEG 1	11,1	12,0	14,2
MEG 2	1,8	1,8	2,5
G	74,6	74,2	74,5
Conversion, selectivities and yield (%)			

X (G)	25,4	25,8	25,5
S (D+T)	49,4	46,3	34,5
Y (D+T)	12,5	11,9	8,8
S (M)	50,6	53,7	65,5
H_2O formed (%)	38.9	37.6	34.3
H_2O total (%)	38.9	40.2	52.2

Reaction conditions: zeolite Beta Q 10 wt. % related to glycerol, EtOH/G molar ratio = 15, temperature 200° C, reaction time 8 h. Ethanol and glycerol were used in the dry form.

The initial addition of water to the reaction suppresses the extent of alkylation, thus, the amount of water formed during the reaction is decreasing from calculated 38.9 to 34.3 mol% relative to the initial amount of glycerol (Tab. 8). However, the amount of total water present in the reaction mixture (formed + initially added water) increased from 38.9 to 52.2%. The increase of the water content in the reaction mixture shifts the equilibrium of the alkylation toward monoethyl ethers.

3.1.4 Ethylation of glycerol with different ethylation agents

Diethyl ether is a by-product formed by reaction of two ethanol molecules over acidic catalysts. Conversion of ethanol to diethyl ether during glycerol ethylation depends on reaction conditions, mainly on reaction temperature and time. It yields mostly up to 20 %. Diethyl ether also can act as ethylation agent for glycerol. Hence, we tested several ethylation systems.

The results of different methods of glycerol ethylation: with dry ethanol, diethyl ether alone, mixture of ethanol - diethyl ether and of diethyl ether - water at 180 °C are compared in Table 9.

It is seen, that when only diethyl ether was used as ethylation agent at given reaction conditions, conversion of glycerol was only 6 %, but the selectivity to di- and tri-ethers achieves 39 %. In this case the low solubility of less polar diethyl ether in polar glycerol (observed solubility <2%) hinders the reaction rate, however, in the other hand, the presence of diethyl ether helps the formation of a phase comprising less polar di- and tri ethers and diethyl ether. When diethyl ether and water was used as alkylation agent, the selectivity to di- and tri- ethers decreased to 17 % because of partial poisoning of zeolite catalyst with polar water and increased polarity of both, glycerol-water and diethyl ether-water phase. Hence, the addition of polar water further decreases the solubility of less polar di-and triethylethers of glycerol in the diethyl ether-water phase. In the other hand, water can partially hydrolyze diethyl ether to ethanol, what increases the polarity of the reaction mixture and, thus, increases the selectivity to more hydrophilic monoethyl ethers of glycerol.

The highest increase of glycerol conversion and of selectivity to di- and tri-ethers in comparison with pure ethanol was obtained when a mixture of ethanol and diethyl ether was used as ethylation agent. In this experiment

15 g of diethyl ether was added to 90 g of ethanol, which theoretically corresponds to 17,5 % conversion of ethanol to diethyl ether. The presence of ethanol increases the solubility of diethyl ether in the reaction mixture, and, thus, increases the molar ratio of alkylation agents to glycerol, which shifted the equilibrium to the side of higher glycerol ethers. Parallel to it, the polarity of initial reaction mixture is lowered by the presence of diethyl ether in comparison with ethanol, which increases the solubility of low polar higher ethylethers in the reaction mixture and in this way helps their formation. From the measured results follows, that recycling of the formed diethyl ether to the initial reaction mixture can significantly increase the selectivity and yield of valuable di- and tri-ethers of glycerol.

Table 9 Ethylation of glycerol with different ethylation agents

	EtOH 90 g	DEE 72 g	DEE + H_2O 72 g + 7 g	EtOH+DEE 74 g + 13 g
Distribution of products	(mol %)			
TEG	0,1	0,2	0,1	1,0
DEG 1	1,4	1,3	0,8	7,2
DEG 2	1,3	0,8	0,4	5,7
MEG 1	17,2	3,1	5,5	14,3
MEG 2	3,6	0,5	0,8	3,5
G	76,3	94,3	92,4	68,4
Conversion, selectivities and yield (%)				
X (G)	23,7	5,7	7,6	31,6

S (D+T)	12,1	38,3	16,7	43,8
Y (D+T)	2,9	2,2	1,3	13,8
S (M)	87,9	61,7	83,3	56,2

Reaction conditions: catalyst zeolite H-Beta (Q) 10wt.% /G, temperature 180°C, reaction time 8 h, glycerol 12 g

3.1.5 Recyclation of zeolite H-Beta catalyst

The zeolite catalyst after etherification from each experiment has been filtered-off, washed with dry ethanol and dried at room temperature overnight. The next day the catalyst was dried 5 hours at 130° C and calcinated 6 hours at 500° C before next run in air.

As one can see, the activity of catalyst decreases after recyclation. The conversion of glycerol was 22.5 % and 19.9 %. after 2. recyclation, respectively. Selectivity to di- and tri-ethers decreased from 49.4 to 33.3 %.

Table 10 Recyclation of catalyst H-Beta Q in glycerol ethylation with ethanol

	Basic run	1. recyclation	2. recyclation
Distribution of products (mol %)			
TEG	1,0	0,3	0,2
DEG 1	7,0	4,4	3,6
DEG 2	4,6	3,3	2,8
MEG 1	11,1	12,3	11,2
MEG 2	1,8	2,2	2,1

G	74,6	77,5	80,1
Conversion, selectivities and yield (%)			
X (G)	25,4	22,5	19,9
S (D+T)	49,4	35,5	33,3
Y (D+T)	12,5	8,0	6,6
S (M)	50,6	64,5	66,7
$S_{BET, L}$ (m^2/g)	730	452	410
Acidity (mmol H^+/ g)	0,68	0,55	0,52

Reaction conditions: catalyst zeolite H-Beta Q 10wt.% related to glycerol, temperature 200° C, EtOH / G molar ratio = 15, reaction time 8 h.

As reported recently [38] in the FTIR spectra of the used catalysts, peaks belonging to C-H and C=O bonds (at 1380, 1480, 2850–2980 cm^{-1} and 1720 cm^{-1}, respectively) were discernible, which disappeared after calcination. It was also found that the peak belonging to Si-O-Al (950 cm^{-1}) in the used catalyst weakens, and the signal belonging to the Si-O-Si bond (1210 cm^{-1}) intensifies.

Such dealumination is also manifested in the reduction of the specific surface and in the reduction of acidity, which is not restored after calcination (see Tab. 10). This phenomenon is then responsible for the gradual reduction of the catalytic activity.

3.2 Consecutive tert-butylation of glycerol ethylation products

The main idea of this work is to increase the yield of desired di- and tri-ethers of glycerol. The etherification of glycerol should be done using as high portion of a renewable etherification agent as possible. By using ethanol, only equilibrium composition of the reaction products can be obtained, with high content of monoethylethers, but not satisfactory content of higher ethers. In a closed reactor the removal of water formed by the reaction represents a technical problem. As was seen in Table 7, at 200°C and at a molar ratio of ethanol/glycerol = 15 after 8 hours, selectivity to di- and tri-ethers is 49 % and to mono-ethers 51 %.

Consecutive catalytic tert-butylation of free hydroxyl-groups of mono- and di-ethyl ethers with isobutylene or tert-butanol can be done at mild reaction conditions (temperature down to 80° C) and with high selectivity to di- and tri-ethers. The result of this procedure is the mixture of ethyl-, tert-butyl- and mixed ethyl-tert-butyl- ethers of glycerol with very high selectivity to di- and tri-ethers of glycerol (Scheme 1).

In the Table 11 tert-butanol and isobutylene are compared for the tert-butylation of ethylated products. As a catalyst for ethylation H-Beta zeolite, and for tert-butylation acidic ion-exchange resin Purolite CT 169 was used.

As can be seen, higher yields of desired products were obtained with isobutylene (i-Bu) as a tert-butylation agent. The results are consistent with the fact that if tert-butanol (TBA) is used, the formed water has poisoning effect on the catalyst. After tert-butylation of ethylated product with isobutylene at 90° C after 8 hours over Purolite CT 168 catalyst a total selectivity to di- and tri-ethers was 87.5 %, what is an increase of the selectivity to higher ethers by about 50 % after the second alkylation step.

Table 11 Comparison of tert-butylation agents for consecutive tert-butylation of ethylated products

	Ethylation*	Tert-butylation	Tert-butylation
Catalyst	H-Beta Q	Purolite	Purolite
Molar ratio	EtOH/G=10/1	TBA/-OH=2/1	i-Bu/-OH=2/1
Temperature (°C)	200	90	90
Distribution of products		(mol %)	
TEG	1,3	0,4	0,4
EDTBG		1,4	5,8
DETBG		0,9	10,6
TTBG		0,1	1,9
DEG 1	4,3	2,1	1,4
ETBG 1		7,4	11,6
DTBG 1		5,3	8,8
DEG 2	3,2	1,1	0,5
ETBG 2		2,8	1,7
DTBG 2		1,2	1,0
MTBG 1		12,4	3,2
MTBG 2		0,5	1,2
MEG 1	13,2	3,4	1,4
MEG 2	2,2	0,2	0,4

G	75,9	60,7	50,1
Conversion, selectivities and yield (%)			
X (G)	24,1	39,3	49,9
S (D+T)	36,2	57,9	87,8
Y (D+T)	8,7	22,8	43,8
S (M)	63,8	42,1	12,2

Reaction conditions: catalyst 10 wt. % related to glycerol, time for each alkylation 8 h, *composition of reaction products of ethylation after removing ethanol, diethyl ether, water and other volatile components, consecutively used for tert-butylation.

In the Table 12 two acidic ion-exchange catalysts are compared (Amberlyst 35 and Purolite CT 169) for tert-butylation of the ethylated glycerol. In these experiments isobutylene has been used as tert-butylation agent at a temperature 80°C.

As can be seen, in the terms of glycerol conversion, Purolite is more active than Amberlyst, but the selectivity to total di- and tri-ethers of glycerol is the same, 93 %. The increase in di- and tri-ethers selectivity after tert-butylation is nearly 56 %.

Table 12 Comparison catalysts for consecutive tert-butylation of ethylation products

	Ethylation	Tert-butylation	Tert-butylation
Catalyst	H-Beta Q	Purolite CT 169	Amberlyst 35 Dry
Molar ratio	EtOH/G=10/1	i-Bu/-OH=2/1	i-Bu/-OH=2/1
Temperature (° C)	200	80	80
Distribution of products		(mol %)	
TEG	1,3	0,8	0,8
EDTBG		6,6	6,7
DETBG		9,4	8,5
TTBG		2,5	1,7
DEG 1	4,3	1,5	1,5
ETBG 1		7,9	6,9
DTBG 1		7,0	4,7
DEG 2	3,2	0,3	0,3
ETBG 2		1,1	1,0
DTBG 2		0,9	0,4
MTBG 1		1,2	1,1
MTBG 2		0,6	0,2
MEG 1	13,2	0,6	0,8
MEG 2	2,2	0,2	0,2
G	75,9	59,4	65,1
Conversion, selectivities and yield (%)			
X (G)	24,1	40,6	34,9
S (D+T)	36,2	93,5	93,5
Y (D+T)	8,7	38,0	32,6
S (M)	63,8	6,5	6,5

Reaction conditions: catalyst (10 wt. % related to glycerol), time for each alkylation 8 h

It is seen that mono-ethyl ethers of glycerol were alkylated with isobutylene to ethyl-tert-butyl- and ethyl-di-tert-butyl glycerols and di-ethyl glycerols to di-ethyl-tert-butyl glycerols with selectivities exceeding 90%. All these reactions are reversible, proceeding to equilibrium, and the reaction products after ethylation and tert-butylation are ethyl ethers, tert-butyl ethers and mixed ethyl-tert-butyl ethers with high concentration of di- and tri-ethers of low polarity, which are therefore suitable as oxygenate additives to motor fuels, preferentially to diesel. As reported by Noureddini [39], a mixture of 24 wt% monoethers, 62 wt% diethers and 14 wt% triethers was completely miscible with diesel either with or without FAME up to the limit 22% over the full range of temperatures that were investigated for the cloud point. Decreasing the selectivity to monoethers to 6.5% by a 2-step alkylation guarantees an improvement in the miscibility with diesel fuels.

4. Conclusion

Glycerol and ethanol are renewable raw materials, which is a great advantage in the preparation of glycerol ethyl ethers. It is therefore advantageous to use ethyl ethers as renewable components of fuels. Isobutylene, on the other hand, is mostly a fossil raw material, which is also a desired raw material for specialty chemicals. However, the relatively low reactivity of ethanol compared to isobutylene is a setback. Therefore, it is advisable to replace part of the valuable isobutylene with ethanol as an alkylating agent. Optimal reaction temperature for ethylation of glycerol with ethanol is around 200° C, higher molar ratio of ethanol/glycerol promotes the formation of ethyl ethers, and as catalyst for this reaction zeolite H-Beta with Si/Al ratio = 25 was found suitable. At these conditions the selectivity to desired di- and tri-ethers after 8 hours (equilibrium composition) is 49.4 % at ethanol/glycerol molar ratio = 15 and 36.2 % at ethanol/glycerol = 10, respectively.

By recycling diethyl ether (a dehydration product of ethanol) the yield of di-and tri- ethylethers can be increased at reaction temperature 180 °C from 2.9% to 13.8 %, the selectivity to these ethers increases from 12.1 % to 43.8 % and the conversion of glycerol increases from 23.7 % to 31.6 % over catalyst zeolite H-Beta (Q).

In the proposed concept of increasing the selectivity of di- and triethers, a consecutive alkylation was proposed: first ethylation of glycerol, and a subsequent tert-butylation of ethylated products with isobutylene, which is a more reactive alkylating agent compared to ethanol, under mild reaction conditions. Tert-butylation of glycerol ethylation products on an acidic ion exchange resin (Purolite CT 169 or Amberlyst 35) at 80 °C after 8 hours increased the selectivity to di- and triethers from 36.2% to 93.5%.

The final mixture of ethyl-, tert-butyl- and mixed ethyl-tert-butyl ethers of glycerol can be potentially used as oxygenate additive to motor fuels, preferentially to diesel.

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Graphical abstract

H-Beta zeolite

1. Ethylation: bioethanol + bioglycerol → glycerol ethyl ethers

200° C **Selectivity (Di- + Tri- ethyl ethers ≈ 50 %)**

Ion-exchange resins

2. Consecutive tert. butylation: glycerol ethyl ethers + isobutylene

80° C ↓

Mixture of ethyl-,tert-butyl-, mixed ethyl- tert-butyl ethers of glycerol **Selectivity (Di- + Tri- alkyl ethers) ≈ 93 %**