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ETHERIFICATION OF GLYCEROL

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Abstract. *The etherification of glycerol with tert-butanol has been studied at the presence of catex Amberlyst 15 as catalyst. The maximum conversion of glycerol near 96% was reached at the temperature 90°C and at the molar ratio tert-butanol/glycerol = 4:1 after 180 min. Catalytic activity of Amberlyst 15 was compared with two large-porous zeolites (H-Y and H-BEA). The final conversion of glycerol was comparable with Amberlyst 15, but H-BEA was more active (twice amount of formed di-ethers near 45% against 25% with Amberlyst) was reached at 360 min of reaction. Dealkylation of di-ethers was not observed over zeolite catalysts. tert-Butyl ethers of glycerol can be used as oxygenate additives to diesel fuel.*

Key words*: etherification, tert-butyl ethers of glycerol, oxygenates, diesel fuel, catex, zeolites.*

Introduction

The environmental attack on improvement of the air mainly in the towns, has led in some countries to the production of special diesel fuels. These reformulated fuels have some improved qualitative parameters. There are produced from oil products petroleum fuels in combination with alternative components of nonoil source from renewable sources. Reformulated diesel fuel is more expensive in comparison with conventional fuels, but the main advantage of it is the reduction of particulate matter emission.

Diesel fuel of biogenic origin is produced from renewable sources, especially from vegetable oils. There are used methyl esters of rapeseed in Europe and from soybean oil in USA. Alternative fuels can be used independently, or in a mixture with kerosene and/or gas oil. The expenses on biodiesel fuel from renewable sources are higher in these days in comparison with conventional fuel. Ecofuels are more suitable from environmental point of view.

The methyl esters of vegetable oils are produced by transesterification of triglycerides at the presence of an alkaline catalyst. The main product are methyl esters of fatty acids from vegetable oil and as a by-product is glycerol. The preparation of the alkyl ethers of glycerol by etherification (0-alkylation) by alkenes, and preferentially by isobutylene, or C_4-fraction from pyrolysis and FCC at the presence of the acid catalyst, is one of the possibilities of the glycerol usage. The mixture of mono-, di- and tri- alkyl glycerol ethers is produced. These ethers and mainly di- and tri- alkyl glycerols are the most suitable as oxygenates to diesel fuels. The addition of these ethers has positive effect on the quality of final diesel fuel (high CN) and preferentially ethers are active by reduction of fumes and particulate matters, carbon oxides and carbonyl compounds in exhausts.

The limitation factor of vegetable oil methyl esters is Cloud Point, which value is for diesel fuel –16°C and for biodiesel around 0°C. The addition of ethers oxygenates decreases Cloud Point of diesel fuel. The addition of glycerol alkyl ethers to diesel, or biodiesel fuel decreases Cloud Point.

The mixture of alkyl ethers of glycerol is prepared [1] by etherification of glycerol by alkenes and preferentially by isobutylene at molar ratio of glycerol/isobutylene = 1:2 and up, at the temperature from 50 to 150°C on strongly acidic catex Amberlyst. The mixture of alkylethers is added to original diesel fuel with biodiesel or separately. The reduction of carbon oxide, hydrocarbons, aldehydes and particulate matters after application of alkyl ethers of glycerol to diesel fuel was proved. In [2] it was used p-toluene sulfonic acid as catalyst for etherification of glycerol. The etherifications are carried-out at the temperatures from 50 to 100°C at the surplus of isobutylene.

According to [3] the manufacture of tert-butyl ethers of glycerol is realized by etherification of glycerol with isobutylene in the liquid phase at the presence of large-porous zeolite catalyst at the temperature from 80 to 120°C, at the pressure between 0,6 to 2,1 MPa and at the molar ratio of glycerol/alkene from 1:1 to 1:5. The conversion of glycerol was near 99%.

The raw glycerol with some part of biodiesel fuel from transesterification of fatty acids from soybean oil with methanol is converted with isobutylene to the mixture of the ethers of glycerol and esters of fatty acids from soybean oil. The mixture of ethers and esters is added to the diesel fuel and such prepared reformulated diesel fuel (diesel with oxygenates) has lowered the Cloud Point and reduced emission of particulate matters [4].

Macho et al. [5] studied possibilities of utilization of isobutylene from C_4-fraction for etherification of different more hydroxylic alifatic compounds. They studies etherification glycol and glycerol at the presence of different acidic catalysts. Ostion catex was very active catalyst for this reaction. Autors studied kinetics of this reaction and also formation of secondary products.

Our paper presents some results of glycerol etherification with tert-butanol at the presence of Amberlyst 15 as catalyst. This catex is used as a catalyst for production of MTBE. The catalytic activity of Amberlyst 15 and two large-porous zeolites (H-Y and H-BEA) is compared in this work.

Experimental

Chemicals and Catalysts. Glycerol and tert-butanol were quality p.a.

Amberlyst 15 (Rohm and Hass, France). This catex has been activated by three-fold washing and decantation with 1M sul-

phuric acid and next with water and finally by methanol. Amberlyst was dried in vacuum at 60°C (acidity was 4,7 mmols H^+/g).

H-Y (Si/Al=15)-commercial zeolite (CBV 720) from Zeolyst Int. (S_{BET} = 710 m^2/g, $V_{mikro,t}$ = 0,286 cm^3/g, $S_{mezo,t}$ = 169 m^2/g, acidity (TPDA) = 0,56 mmol/g

H-BEA (Si/Al =12,5) - commercial zeolite (CP 814E) from Zeolyst, Int.

(S_{BET} = 700m^2/g, $V_{mikro,t}$ = 0,195 cm^3/g, $S_{mezo,t}$ = 309 m^2/g, acidity (TPDA) = 1,03 mmol/g.

Apparatus and Procedure

The etherification was carried out in a laboratory autoclave reactor ROTAMAG 100 with magnetic stirring and with regulated electric heating. 10g (0,1086 mol) of glycerol, 0,5g of catalyst and 32,2 g (0,4344 mol) of tert-butanol (mol.ratio TBA/G=4:1) were mixed in reactor. The reactor was twice flashed with nitrogen to replace air and it was heated to the reaction temperature.

Analytical Methods

The samples of reaction products were analysed by gas chromatography on CHROM-5 with FID and chromatograph was connected with PC-CSW. Analyses were carried out on chromatographic capillary column HP INNOWAX (30m×0,32 mm coated with film 0,5 μm). The used temperature programme: from 40 to 220°C (with gradient 10°C/min) and next 4 min isothermally.

Results and Discussion

Etherification (O-alkylation) of glycerol is acid - catalysed reaction with formation of mono-, di- and tri- alkyl glycerol ethers. The more probable is formation of 1- and 1,3- ethers (primary –OH groups) against 2- and 1,2- ethers. And more, primary –OH groups of glycerol are preferred for tert-butylation stericaly also, because tert-butyl groups are voluminous. Catalysts can be homogeneous (e.g. sulphuric acid, p-toluene sulfonic acid, ...) but more preferred are heterogeneous catalysts catexes and could be large-porous zeolites also). Catexes are frequent catalysts for production of technical ethers, e.g. MTBE. Classical homogeneous catalysts, e.g. sulphuric acid are not ecofriendly and are not suitable from technical reasons also.

Etherification of glycerol with tert-butanol as etherification agent was studied in this work. Etherification reactions were carried out in the liquid phase without solvent. The surplus of tert-butanol was used as etherification agent and tert-butyl ethers of glycerol are disolved in reaction mixture and etherification is carried out in homogenous phase.

The Influence of Temperature

tert-Butylations of glycerol catalysed by Amberlyst 15 were carried out at the range of temperature from 30 to 120°C.

From Figures 1 and 2 it can be seen that the maximum conversion of glycerol 95% was reached at 90°C in time of 180 min (at 70°C and equal time conversion of glycerol was 93%).

The etherification was more slower reaction at the lower reaction temperature, e.g. at 30°C the maximum conversion of

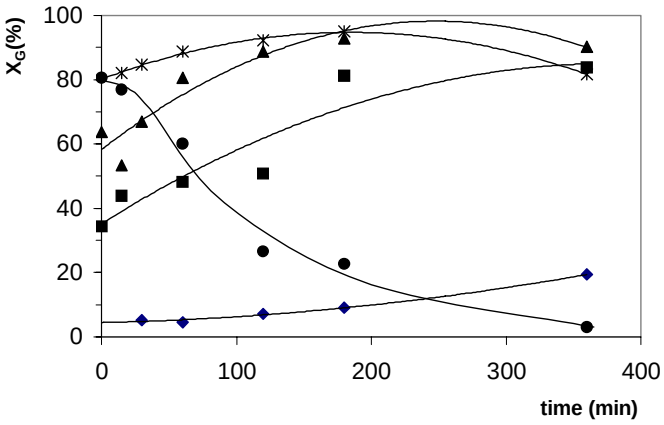

Figure 1. Influence of glycerol conversion on time for different temperatures, catalyst Amberlyst 15 (5 wt % / glycerol), TBA / G molar ratio = 4:1 (u - 30°C, n - 50°C, s - 70°C, v - 90°C, l - 120°C).

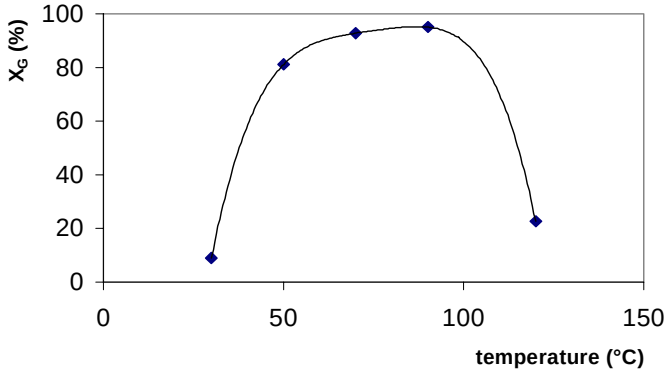

Figure 2. Effect of temperature on glycerol conversion at the reaction time 180 min

glycerol was only 19% (6 hours duration). There was observed the first increase of conversion at 120°C to 80% and next after the first 30 min decrease, what means that dealkylation of ethers with formation of glycerol, resp. mono- ether and isobutylene proceeds as back reactions.

The etherification of glycerol is complex reversible equilibrium reactions. It can be seen from Figures 3 and 4 at the temperature from 30 to 90°C the increase of mono-, di- and tri-ethers.1,2,3- Tri-tert-butyl ether was formed at used reaction conditions in the amount to 1 % mass only (reaction conditions were relatively mild).

The maximum of mono-ethers 87% was received at 180 min and at the reaction temperature 70°C (at 90°C and at the equal reaction time 69% mono-ethers was formed because of next etherification). The higher reaction temperature, surplus of the alkylation agent and longer reaction time leads to the increase of di- and tri- ethers.

The Influence of the Amount of Catalyst (Amberlyst 15)

From Figure 5 (the influence of glycerol conversion versus catalyst amount) is seen that maximum conversion of glycerol near 96 % at 90°C was reached after 2 hours at the amount of catalyst from 5 to 7,5 wt. % glycerol. The amount 5% of catalyst was used next in this work.

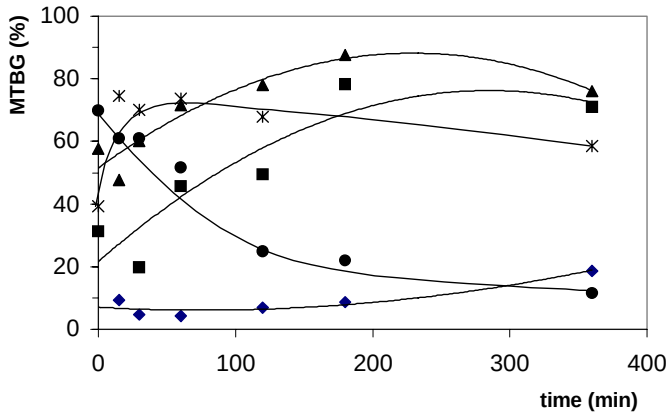

Figure 3. Influence of MTBG formation on time for different temperatures, catalyst Amberlyst 15 (5 wt.% / glycerol), TBA / G molar ratio = 4:1 (u - 30°C, n - 50°C, s - 70°C, v - 90°C, l - 120°C)

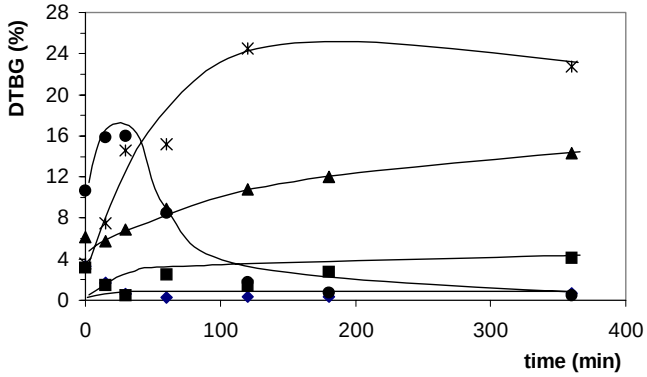

Figure 4. Influence of DTBG formation on time for different temperatures (u - 30°C, n - 50°C, s - 70°C, v - 90°C, l - 120°C)

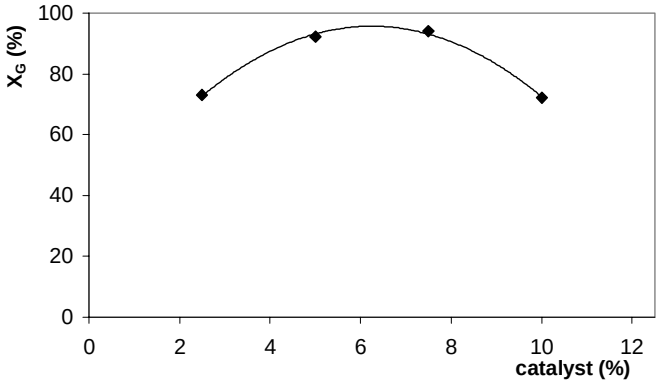

Figure 5. Effect of glycerol conversion on amount of catalyst (Amberlyst 15) T = 90°C, TBA / G molar ratio = 4:1, at the reaction time 120 min

The Influence of Catalyst Type

Figure 6 shows the comparison of three acidic catalysts (Amberlyst 15 and two large-porous zeolites H-Y and H-BEA) for etherification of glycerol. The highest conversion of glycerol was reached at the presence of Amberlyst 15 (96 % at 180 min) and with H-BEA similar at the equal time and conversion was constant with time in the next.

Zeolite H-Y was not so active as the next two catalysts Figure 6. Amberlyst was the most active for formation of monoethers and H-BEA for di-ethers (45% of di-tert-butyl ethers was formed with H-BEA zeolite and over Amberlyst only near 25% of di-ethers was formed at the same conditions as is shown in Figure 7.

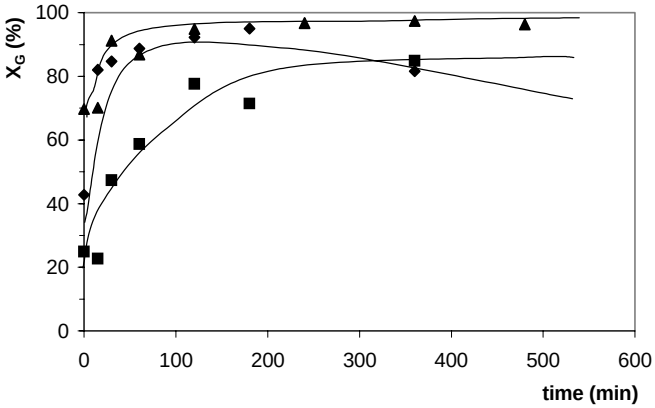

Figure 6. Influence of glycerol conversion on time for different catalysts T = 90°C, TBA / G molar ratio = 4:1, catalyst 5 wt % / glycerol (u - Amberlyst, n - zeolit H-Y, s - zeolit H-BEA)

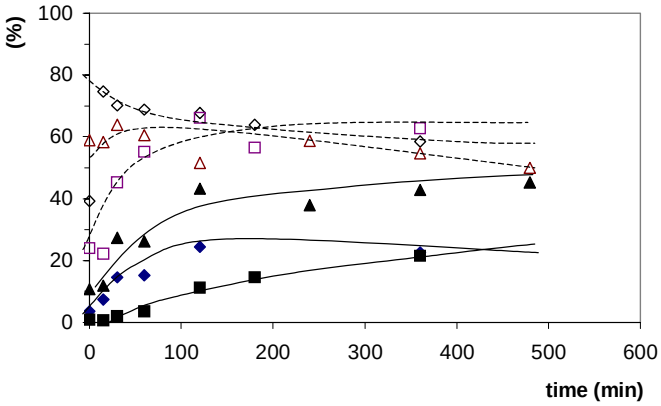

Figure 7. Distribution of MTBG and DTBG on time for different catalysts, T = 90°C, TBA / G molar ratio = 4:1, catalyst 5 wt % / glycerol (◇ - $MTBG_{Amb}$, □ - $MTBG_{H-Y}$, Δ - $MTBG_{H-BEA}$, u - $DTBG_{Amb}$, n - $DTBG_{H-Y}$, s - $DTBG_{H-BEA}$)

The dealkylation of ethers was observed in the case of Amberlyst but not for zeolite catalysts in the range of studied experimental conditions.

Conclusion

As the most active catalysts for tert-butylation of glycerol at the used reaction conditions were Amberlyst 15 (strongly

acidic catex used for production of ethers, e.g. MTBE) and large-porous zeolite H-BEA. The conversion of glycerol near 96 % at 180 min of reaction at 90°C and at mild surplus of alkylation agent to glycerol (1,3 mole of TBA, resp. isobutylene to 1 hydroxyl group of glycerol) was reached. Dealkylation of di-ethers was not observed over zeolite catalysts.

Abbreviations

G - glycerol, TBA - tert-butanol, MTBG - mono-tert-butyl-glycerol, DTBG - di-tert-butyl-glycerol, X_G - conversion of glycerol, CN - Cetane Number, FCC - Fluid Catalytic Cracking.

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