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Effect of reaction conditions on the etherification between glycerol and tert-butyl alcohol over beta zeolite

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ABSTRACT

Introduction: Glycerol tert-butyl ethers (GTBEs) can be used as diesel additives due to their physico-chemical properties, such as flash point, viscosity, and cetane number. GTBEs were produced from the reaction between tert-butyl alcohol and glycerol using a stirred reactor at moderate temperatures. This study aims to discuss the effect of reaction conditions on the etherification between glycerol and tert-butyl alcohol. Methods: In this work, the etherification of glycerol and tert-butyl alcohol was performed using beta zeolite ($SiO_2/Al_2O_3 = 360:1$) under different reaction conditions, including different molar ratios, catalyst loadings, reaction times, and reaction temperatures, to evaluate glycerol conversion and product selectivity. Beta zeolite was characterized by infrared spectroscopy, X-ray diffraction, and NH₃-TPD. **Results:** The results showed that the suitable conditions for the synthesis of GTBEs using beta zeolite were a temperature of 80 °C, a tert-butyl alcohol/glycerol feed ratio of 12:1, a catalyst loading of 1:3 weight of glycerol, and a reaction time of 6 hours. Under these conditions, the highest glycerol conversion was 81.35%, the selectivity of the diether was 32.44%, and the overall yield of the diether was 26.39%. Conclusion: Reaction conditions are important factors in tailoring glycerol conversion and product selectivity in the reaction between glycerol and tert-butyl alcohol.

Key words: Beta zeolite, diesel additive, etherification, glycerol, tert-butyl alcohol

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INTRODUCTION

² The development of industries is driving an increase 3 in energy demand. Diesel, a vital energy source 4 for transportation, power generation, construction, 5 manufacturing, and farming, is predominantly de-6 rived from petroleum resources. However, an alterna-7 tive source, biodiesel, can be produced from green re-⁸ sources through transesterification of glycerides with 9 alcohols^{1,2}. This process also yields glycerol as a 10 byproduct. The growing demand for bioenergy, in-11 cluding biodiesel, has led to a surge in glycerol pro-12 duction. Consequently, there is significant interest in ⁵Hong Bang International University, Ho₁₃ converting glycerol into valuable products, particu-14 larly within the biodiesel industry.

> 15 Currently, glycerol can be converted into several 16 products, including syngas, solketal, glycerol car-17 bonate, glyceric acid, tartonic acid, propanediols, ¹⁸ acrolein, and glycerol ether ^{3,4}. Among these, ethers of glycerol, such as di-tert-butyl glycerol ethers and 20 tri-tert-butyl glycerol, can be used as diesel addi-²¹ tives^{3,5}. Several studies have explored the etherifica-²² tion of glycerol with tert-butanol^{6–9}. Five main prod-23 ucts, including two mono-tert-butylglycerol ethers 24 (monoethers), two di-tert-butyl-glycerol ethers (di-25 ethers) and one tri-tert-butylglycerol (triether), were

obtained from glycerol etherification with tert-butyl 26 alcohol (Scheme 1). 27

Acid catalysts, including Amberlyst⁶, Y zeolite^{8,10}, FAU, MOR, MFI, Beta zeolites¹⁰⁻¹², and ²⁹ tungstophosphoric acid^{7,13}, were investigated. 30 Amberlyst-15 showed high conversion of glycerol 31 (at 90-100 °C) because of the high number of 32 Brønsted acid sites⁶. Among Beta, Faujasite, MFI 33 and Mordenite zeolites, Pariente et al.¹⁰ reported that ₃₄ Beta zeolite with an intermediate aluminum content 35 (Si/Al = 25) is effective for glycerol etherification with $_{36}$ ethanol. Beta zeolite with Si/Al = 25 showed a higher 37 glycerol conversion and diether selectivity among 38 the investigated zeolites¹⁰. Specifically, nanobbeta ³⁹ zeolite (SiO₂/Al₂O₃ = 25) resulted in ~95% glycerol $_{40}$ conversion and ~99% glycerol conversion toward 41 diethers and triethers¹¹. In this research, we studied 42 the etherification of glycerol with tert-butanol using 43 a beta zeolite with a high Si/Al ratio that typically 44 contains mainly Brønsted acid sites and explored the 45 effects of the reaction conditions on this etherification 46 reaction. 47

MATERIALS AND METHODS

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Scheme 1: The scheme of glycerol etherification with tert-butanol

49 Materials

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Commercial beta zeolites with a SiO2/Al2O3 ratio of 360 were purchased from Alfa Aesar and denoted as beta 360. Glycerol (Fisher, 99%), ethanol (Fisher, 99.8%) and tert-butyl alcohol (Shanghai Zhanyun Chemical Co., Ltd., AR grade) were used without any pretreatment. Dodecane (Fisher, 95%) was used as an internal standard. 56

Catalyst characterization 57

The ATR-FT-IR spectra of the zeolite samples were 58 characterized by a Bruker VERTEX70 instrument 59 coupled with a Platinum Diamond ATR in the wavenumber range of 400-4000 cm⁻¹, with a reso-61 lution of 4 cm^{-1} and an accumulation of 32 scans. 62 The sample was placed on the ATR crystal, and the spectrum was recorded in air. The background spec-64 trum was taken before sample analysis. The catalyst 65 surface was analyzed by an X Shimadzu 6100 (Japan) 66 instrument operating at a voltage of 40 kV and a cur-67 rent of 30 mA with CuK_{α} radiation at a wavelength of 0.15406 nm. The 2θ ranged from 10° to 60° , with 60 each step being 0.02°, and the scanning speed was 70 $0.05^{^\circ}\mbox{/sec.}$ The sample was powder and placed in 71 72 the sample holder. The ammonia-temperature programmed desorption (NH₃-TPD) profile was measured as described in a previous study¹⁴. The NH₃-74 TPD profile was measured using a calorimeter (Sensys 75 76 DSC, SETARAM instrument, Cranbury, NJ, USA). 77 After pelletizing and collecting particles ranging from 180 to 250 μ m, the sample (30 mg) was pretreated 78 at 300 $^{\circ}$ C for 30 min in Ar and then cooled to 100 70 C. The sample was saturated with NH₃ by a flow of 20 mL/min containing 2000 ppm NH₃ balanced 81 ⁸² in Ar for 90 min. After that, the physisorbed NH₃ was removed from the sample by flushing with Ar for 60 min. Temperature-programmed desorption mea-84 surements were performed by increasing the tempera-85 ture from 100 to 700 °C (heating rate 10 °C/min). The 86 mass number, m/z = 17, was recorded to follow the 87 88 desorption of NH₃ using a mass spectrometer (HPR-89 20 QIC, Hidden Analytical, Warrington, UK).

Glycerol etherification reaction

A 100 cm³ glass batch reactor was used to carry out the liquid phase etherification process between glyc-92 erol and tert-butyl alcohol at a stirring frequency of 93 600 cycles per minute. To maintain a consistent temperature in the glass, the reactor was placed in a water 95 bath. The experiments were performed under differ-96 ent reaction conditions: (i) tert-butyl alcohol/glycerol 97 (TBA/G) molar ratio; (ii) reaction time (iii) reaction 98 temperature ranging from 60 °C to 90 °C; and (iv) catalyst loading (0.045–0.45 g). The experimental proce- 100 dure involved adding glycerol (0.45 g), catalysts and tert-butyl alcohol to the reactor. n-Dodecane was 102 also added to 10 wt.% glycerol as an internal standard 103 for subsequent sample analysis. The reactor was then 104 sealed and stirred at a constant temperature. The reac- 105 tion was stopped by immersing the reactor in a coldwater bath to allow all of the gas phase chemicals to 107 condense into a completely liquid mixture. Approximately 2 mL of ethanol was added to the mixture to 109 homogenize the remaining glycerol with tert-butyl alcohol. The product was then centrifuged at 8000 revolutions per minute for 10 minutes to remove the solid 112 catalysts. The liquid sample was diluted with ethanol 113 before analysis. All reactions were performed in trip- 114 licate. 115

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All products that were diluted in ethanol and 116 aliquoted were subsequently analyzed for glycerol 117 conversion, diethers and tri-ether selectivity by gas 118 chromatography (GC). The liquid mixture was an- 119 alyzed using an Agilent 7890A gas chromatography 120 (GC) instrument equipped with a flame ionization de- 121 tector (FID) for product quantification. An automatic 122 liquid sampler (ALS) G4513A automatic liquid sam- 123 pler (ALS) Agilent 7693A ALS with G4513A Injector 124 was used, and 1 μ L of sample was injected at a split 125 ratio of 40:1. An HP-5 capillary column (length, 30 126 m; inner diameter, 0.32 mm; film thickness, 0.25 μ m) 127 was used for product separation under the following 128 oven temperature profile: from 45 °C to 85 °C (with 129 a heating rate of 10 °C/min), held for 2 minutes, then 130 heated to 250 °C and held for 2 minutes. 131

132 The glycerol conversion and product selectivity were

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calculated as follows:
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The conversion of glycerol = $\frac{n_{0,glycerol} - n_{1,glycerol}}{...} \times 100\%$ 134 $n_{0,glycerol}$

The selectivity of monoether = $\frac{\Sigma A_{monoether}}{\Sigma A_{total ether}} \times 100\%$ 135

- The selectivity of diether = $\frac{\Sigma A_{diether}}{\Sigma A_{totalether}} \times 100\%$ 136
- The yield of ether = Glycerol conversion (%) \times ether 137
- 138 selectivity (%)
- ¹³⁹ n_{0.glvcerol}: initial mole of glycerol (mol).
- ¹⁴⁰ n_{1. glycerol}: mole of glycerol remaining after reaction 141 (mol).
- ¹⁴² $\sum A_{monoether}$: total area of monoether peaks from GC 143 data.
- ¹⁴⁴ $\sum A_{diether}$: total area of diether peaks from GC data.
- ¹⁴⁵ $\sum A_{Total \ ether}$: total area of all glycerol tert-butyl ether peaks from GC data. 146
- ¹⁴⁷ To determine the peak of each compound, the products were analyzed by gas chromatography-mass 148 spectrometry (GC-MS) on an Agilent 6890 instru-149 ment equipped with a 5973 inert mass selective de-150 tector (MSD). An injector was used to inject 1 μ L of 151 sample at a split ratio of 30:1. A GSBP-5MS capillary 152 column (length, 30 m; inner diameter, 0.25 mm; film 153 thickness, 0.25 μ m) was used for product separation 154 under the following oven temperature profile with a 155 starting point at 60 °C and was held for 4 minutes. 156 The mixture was heated to 90 °C at a heating rate of 10 157 C/min, held for 1 minute, then continuously heated 158 to 150 °C and held for 5 minutes. GC-MS analysis, as 159 shown in Figure 1 revealed that the glycerol etherifi-160 cation reaction with tert-butyl alcohol produced mo-161 noether and diether and did not produce triether in 162 this study using beta 360 zeolite.

RESULTS 164

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Characterization of the catalyst

166 Figure 2A shows that beta 360 presented three main peaks at 1300-900 cm⁻¹, 850-650 cm⁻¹, and 465- $_{168}$ 400 cm⁻¹¹⁵. The peaks in the range of 1300–900 cm⁻¹ are assigned to the asymmetric stretching of the 169 T-O-T bridges, where T represents tetrahedrally co-170 171 ordinated Si or Al atoms. There are three peaks in this range at 1230, 1073, and 952 cm^{-1} . The peak 172 at 799 cm^{-1} is assigned to the bending mode of the 172 T-O-T bridges. The last range, which represents the out-of-plane deformation of the T-O-T bridges, con-175 $_{176}$ tains several peaks at 575 cm⁻¹, 526 cm⁻¹, and 421 177 cm^{-1}

178 Figure 2B presents the XRD pattern of the beta 360 179 zeolite. The XRD pattern showed two main peaks at $_{180}$ 2 θ values of 7.9° and 22.6°, indicating the presence of 181 the crystallized structure of the beta zeolite. This find-182 ing agrees with the JCPDS 48–0074 standard and with

a previous study¹⁶. Moreover, the NH₃-TPD profile 183 confirmed the existence of acid sites on the Beta 360 184 zeolite with two peaks at ~ 350 °C and ~ 600 °C in 185 the temperature program desorption of NH₃, and the 186 total acid density was 294 µmol NH₃/g catalyst (Fig- 187 ure 3). 188

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Glycerol etherification studies

Glycerol conversion increased with an increase in the 190 TBA/G ratio from 3:1 to 12:1 and decreased thereafter 191 (Figure 4A). Glycerol conversion reached its highest 192 value of 81.35% at a TBA/G ratio of 12:1, and at this 193 TBA/G ratio, the selectivity for diether production 194 also peaked at 32.44%, indicating that the yield of diether was 26.39%. This phenomenon can be explained 196 by the reaction mechanism^{17,18}. An increase in the ¹⁹⁷ tert-butyl alcohol to glycerol (TBA/G) ratio increases 198 the amount of $[(CH_3)_3C^+]$ species, enhancing the reaction between glycerol and [(CH₃)₃C⁺] species and 200 thus increasing glycerol conversion. However, at a 201 higher TBA/G ratio (15:1), the high concentration of 202 TBA decreases the glycerol concentration, reducing 203 the interaction of glycerol with the limited reactive 204 surface area of the catalyst 19,20 and resulting in de- 205 creased glycerol conversion. 206

In terms of reaction time, an increase in reaction time 207 enhances glycerol conversion from 2 hours to 6 hours 208 and decreases it after 8 hours of reaction (Figure 4B). 209 An increased reaction time promoted the reaction be- 210 tween glycerol and tert-butyl alcohol, leading to in- 211 creased glycerol conversion. However, at longer reac- 212 tion times (8 h), tert-butyl alcohol possibly tends to 213 dehydrate to form iso-butylene, followed by the poly- 214 merization of iso-butylene⁷, which reduces the cat- 215 alytic activity and selectivity for diether production. 216 In terms of reaction temperature, both glycerol con- 217 version and diether selectivity increased as the tem- 218 perature increased from 60 to 80 °C (Figure 4C). 219 However, at 90 °C, both glycerol conversion and di- 220 ether selectivity decreased. Indeed, the increase in 221 temperature accelerated the collision between TBA 222 and glycerol, enhancing the catalytic activity. How- 223 ever, at 90 °C, side reactions such as ether hydration 224 and TBA dehydration can occur, leading to decreased 225 catalytic conversion ^{7,19}. Ethers produced from the 226 etherification of glycerol with tert-butyl alcohol can 227 react with the water produced to regenerate glycerol 228 and tert-butyl alcohol. Additionally, tert-butyl alco- 229 hol can dehydrate to form iso-butylene, reducing the 230 amount of TBA relative to glycerol. Consequently, the 231 catalytic activity decreases at higher temperatures (90 232 °C). 233



Figure 1: GC–MS data of glycerol etherified with tert-butyl alcohol over beta 360 zeolite. The data show the presence of mono-tert-butyl-glycerol ethers (monoethers) and di-tert-butyl-glycerol ethers).

234

235 In addition to the effect of the reactant molar ratio, 236 temperature, and reaction time, the amount of catalyst loading can also affect the conversion and se-237 lectivity of the products. Figure 4D shows that the 238 highest glycerol conversion was achieved with 0.15 g 239 of the beta 360 catalyst. The glycerol conversion in-240 creased from 0.045 g of beta 360 catalyst to 0.15 g of 241 beta 360 catalyst and then decreased from 0.15 g to 242 0.45 g of catalyst (Figure 4D). Moreover, the selectiv-243 ity of diether reached its peak with 0.15 g of catalyst 244 and remained relatively constant when 0.15 g to 0.45 g of catalyst was used. An increase in catalyst loading 246 (0.045 g to 0.15 g of catalyst) meant that an increase in 247 acid density enhanced the formation of [(CH₃)₃C⁺] 248 249 species from tert-butyl alcohol, thereby improving the catalytic activity and product distribution. However, 250 a higher catalyst loading (0.3 g to 0.45 g) leads to too 251 252 high an acid density, which tends to dehydrate TBA, causing a decrease in the TBA/G ratio ^{7,19} and, conse-253 quently, a decrease in glycerol conversion. 254

255 DISCUSSION

²⁵⁶ The characteristics of the catalyst were confirmed by
²⁵⁷ IR spectroscopy and XRD, which demonstrated that
²⁵⁸ the catalyst used for this study was a beta zeolite (Fig²⁵⁹ ure 2). The results also showed that the beta 360
²⁶⁰ zeolite contains acid sites, as proven by NH₃-TPD

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analysis (Figure 3), making it suitable for glycerol 261 etherification with tert-butyl alcohol^{17,18}. Indeed, 262 $[(CH_3)_3C^+]$ species were formed on the surface of 263 the acid sites of beta 360 zeolite ¹⁷. Then, an intermediate will be formed between the $[(CH_3)_3C^+]$ cation 265 species and glycerol, followed by the liberation of acid 266 sites to create a monoether ¹⁷. The diether and triether ₂₆₇ can be formed in the same manner as the interaction 268 between the $[(CH_3)_3C^+]$ species and the monoether 269 and diether, respectively, on the surface of acid sites. 270 This indicated that the acid sites of the beta zeolite 271 were important active sites for the glycerol etherifi- 272 cation reaction with tert-butyl alcohol. However, the 273 type of acid sites on the catalyst can be explored by 274 pyridine adsorption using IR spectroscopy. The reac- 275 tion conditions for achieving the highest glycerol con- 276 version and diether yield were 80 °C, TBA/G = 12:1, 277 6 h of reaction time, and 0.15 g of catalyst. Temper- 278 ature is one of the key factors for glycerol etherifica- 279 tion with tert-butyl alcohol. Higher temperatures en- 280 hanced the catalytic activity, but tert-butyl alcohol can 281 dehydrate at very high temperatures, leading to a de- 282 crease in the TBA/G ratio followed by a decrease in 283 glycerol conversion. The TBA/G ratio and reaction 284 time have strong impacts on glycerol conversion (Fig- 285 ure 4). The appropriate amount of tert-butyl alcohol 286 used to react with glycerol was 12:1, and the reaction 287



Figure 2: (A) FT-IR spectrum of beta 360 zeolite; (B) XRD pattern of beta 360 zeolite with two main peaks at 2θ values of 7.9° and 22.6°.

288 time was 6 hours. A prolonged temperature will en-²⁸⁹ hance glycerol conversion, but ethers can decompose or transform into other products over a longer time. 290 In addition, the amount of catalyst can also affect the 291 catalytic activity and product selectivity. The amount 292 of catalyst is relative to the amount of acid sites that 293 294 catalyze tert-butyl alcohol. An appropriate amount of catalyst (0.15 g) resulted in the highest glycerol con-295 version. The glycerol conversion decreased when the 296 amount of catalyst was too high (> 0.15 g) because side 297 298 reactions could occur. These conditions can be fur-299 ther optimized through the use of experimental de-300 sign to maximize glycerol conversion and diether selectivity. The diether yield (26.39%) in this study using beta 360 zeolite is comparable to the results obtained using beta zeolite with intermediate Si/Al ratios, such as h-Beta with Si/Al = 27.7 (di+triether yield = 26% at 75 °C and 4 h)²¹ and H-BETA with Si/Al = 25 (yield = 25.4% at 95 °C and 6 h)²², and lower than the di- and triether yields (68.4% at 90 °C and 6 h) obtained using Nano-Beta zeolite²³. However, the results of this study are promising when using beta zeolite with a very high Si/Al ratio at 80 °C. Additionally, the goal of the etherification of glycerol with tertare diesel additives. However, monoether and diether



Figure 3: NH₃-TPD profile of the beta 360 zeolite shows the presence of acid sites with two main peaks at ~ 350 °C and ~ 600 °C.

were produced in this study. To produce triether with
a large molecule, the pore size of beta zeolite may need
to be increased to obtain both diether and triether.

317 CONCLUSIONS

This study investigated the effect of reaction condi-318 tions on glycerol etherification with tert-butyl alcohol 319 over beta zeolites (SiO₂/Al₂O₃ = 360). This work re-320 vealed that glycerol conversion and product selectiv-321 ity depend on the reaction conditions. The glycerol 322 conversion and diether selectivity increased with in-323 creasing reaction temperature from 60 to 80 °C and 324 decreased at 90 °C. Similarly, they increased with an 325 increase in the tert-butyl alcohol/glycerol molar ratio 326 from 3:1 to 12:1 and decreased at a 15:1 ratio. The 327 reaction time also affected glycerol conversion and 328 product selectivity, with glycerol conversion and di-329 ether selectivity increasing from 2 hours to 6 hours of 330 reaction time and decreasing at 8 hours of reaction. In 331 332 addition, glycerol conversion and diether selectivity ³³³ increased with increasing catalyst loading up to 0.15 334 g of catalyst and decreased at higher catalyst loadings $_{335}$ (> 0.15 g). The highest glycerol conversion (81.35%) 336 and diether selectivity (32.44%)/yield (26.39%) were $_{337}$ obtained at 80 °C, TBA/G = 12:1, 6 h of reaction time, and 0.15 g of catalyst. This study can be further extended to produce both di-tert-butyl-glycerol 339 ethers (diethers) and tri-tert-butylglycerol (triether), 340 which can be used as diesel additives. Additionally, 341 this study provides a background for research on the 342 use of etherification to produce diesel additives under 343 mild conditions. 344

LIST OF ABBREVIATIONS 345

ATR-FT-IR: Attenuated total reflectance - Fourier	346
transform infrared spectroscopy	347
G: Glycerol	348
GTBEs: Glycerol tert-butyl ethers	349
TBA: Tert-butyl alcohol	350
TBA/G: Tert-butyl alcohol to glycerol molar ratio	351
COMPETING INTERESTS	352
The author(s) declare that they have no competing in-	353
terests.	354
ACKNOWLEDGMENT	355

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Figure 4: The conversion of glycerol and selectivity of monoether and diether in the etherification glycerol with tert-butyl alcohol as a function of (A) the tert-butyl alcohol/glycerol molar ratio. Reaction conditions: 0.45 g glycerol, 0.15 g catalyst, 80 °C, 6 h; (B) reaction time. Reaction conditions: 0.45 g glycerol, 0.15 g catalyst, 80 °C, 6 h; (B) reaction conditions: 0.45 g glycerol, 0.15 g catalyst, 80 °C, 7 BA/G = 12:1; (C) reaction temperature. Reaction conditions: 0.45 g glycerol, 0.15 g catalyst, 6 h, TBA/G = 12:1; (D) amount of catalyst loading. Reaction conditions: 0.45 g glycerol, 80 °C, 6 h, TBA/G = 12:1

358 AUTHOR CONTRIBUTIONS

- 359 Hong-Gam Thi Nguyen: Writing original draft, data
- 360 curation and formal analysis
- ³⁶¹ Phuc Hoang Dang: Data curation and formal analysis,
- 362 Thanh Ngoc Nguyen: Formal analysis
- 363 Thanh Khoa Phung: investigation, supervision, writ-
- ³⁶⁴ ing review & editing
- 365 Tai Chiem Do: Funding acquisition, project adminis-
- ³⁶⁶ tration, investigation, supervision, writing review &
 ³⁶⁷ editing

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