Reusable TsOH-H₂SO₄ Mixed Catalysis for Tandem Synthesis of Biodiesel and Oxygenated Fuel Additives, *tert*-Butyl Glycerol Ethers

Natta Rattanapanya¹ and Surachai Pornpakakul^{2*}

¹ Program in Petrochemistry, Faculty of Science, Chulalongkorn University, Pathumwan, Bangkok 10330, THAILAND

² Research Centre for Bioorganic Chemistry, Department of Chemistry, Faculty of Science, Chulalongkorn University, Phayathai Road, Pathumwan, Bangkok 10330, THAILAND

Abstract: A mixture of *p*-toluenesulfonic acid and sulfuric acid (TsOH-H₂SO₄) was used as a catalyst with a good performance in transesterification of palm oil (PO) with methanol and etherification of crude glycerol with isobutylene (tandem synthesis). For TsOH-H₂SO₄ catalyzed biodiesel production, the reaction noticeably ran faster in comparison with TsOH or H₂SO₄ alone and also gave up to 99.9% of the conversion using MeOH/PO molar ratio 9:1 at 80°C, in the period of 4 h. After the whole transesterification process, the crude glycerol phase was separated and then reacted with isobutylene in the etherification process using isobutylene/glycerol molar ratio 9:1 at 80°C, in the period of 5 h reaction time, to give DTBG and TTBG (91.14%). In the case of the etherification in biodiesel, higher selectivity of DTBG and TTBG (99.39%) was obtained in comparison with an absence of biodiesel as the solvent. Furthermore, the catalyst could be reused for 6 cycles of tandem synthesis (transesterification and etherification). The TsOH-H₂SO₄ catalyst showed a good catalytic performance in tandem synthesis similar to TsOH and it could be recovered for reuse while TsOH could not be recovered. This process offers an attractive route for reuse homogeneous catalyst of tandem synthesis, the main by-product of biodiesel, to *tert*-butyl glycerol ethers – a value-added in applications as a valuable fuel additive.

Key words: biodiesel, glycerol, transesterification, etherification, *tert*-butyl glycerol ethers, *p*-toluenesulfonic acid

1 Introduction

Most of the large trucks, buses, and tractors around the world have engines that require diesel fuel. Biomass-based diesel fuels are biofuels made from biomass or biomass-derived materials which include biodiesel and renewable diesel. From the record, the forecast of energy and fuel demand towards a sustainable road transport sector (2016–2035) represented around 27.8% of the total world energy demand¹.

Biodiesel, the methyl esters of fatty acids, is produced by transesterification of triglycerides with short-chain alcohols in the presence of a catalyst. In the transesterification process, glycerol is obtained as a by-product equivalent to approximately 10 wt% of the obtained biodiesel. The amount of glycerol is expected to grow at an annual rate of demand for biodiesel¹. Glycerol is a nontoxic, edible, and biodegradable compound used as a raw material in different industries². Due to it can also be applied to various

uses, including textiles (24%), food and beverages (21%), cosmetics and toiletries (18%), drugs (18%), tobacco (6%), and paper and printing (5%), and others³. However, recovery and purification of the crude glycerol contributes to high production costs and energy consumption. Therefore, direct use of crude glycerol needs to be investigated, and a great deal of research is focused on the conversion of glycerol into value-added products, for example, fuel additive, acrolein, glycerol carbonate, glycerol acetal, etc^{3,4}.

One possible application of glycerol is the etherification of glycerol into mono-, di- and tri-*tert*-butyl glycerol. These ethers, mainly di- and tri-*tert*-butyl glycerol ethers, can be used as additives in diesel fuel, biodiesel, and gasoline⁵. In addition of ethers and esters to the diesel fuel, the reformulated diesel fuel (diesel with oxygenates) has lowered the cloud point and reduced emission of particulate matters⁴. The glycerol ethers are preferably produced via etherification of glycerol and isobutylene. Filiminov *et al.*⁶

*Correspondence to: Surachai Pornpakakul, Research Centre for Bioorganic Chemistry, Department of Chemistry, Faculty of Science, Chulalongkorn University, Phayathai Road, Pathumwan, Bangkok 10330, THAILAND

E-mail: psuracha@chula.ac.th

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studied etherification of glycerol with isobutylene using *p*-toluenesulfonic acid (TsOH), Amberlyst 15, 1-(4-sulfobutyl)-3-hexylimidazolium trifluoromethanesulfonate (IL6) and silicotungstic acid $\text{H}_4\text{SiW}_{12}\text{O}_4$ (HSiW) as catalysts. The optimal condition for etherification process using TsOH (7.5 wt% based on glycerol), 4:1 molar ratio of isobutylene and glycerol, at the condition of 60°C and 5 h reaction time resulted in 99% conversion and 70% of di- and tri-glycerol ether. Klepacova *et al.*⁴⁾ studied etherification of glycerol with isobutylene using Amberlyst types (15 and 35), TsOH and two large-pore zeolite H-Y and H-Beta. The highest glycerol conversion 88.7% was achieved over zeolite H-Y after 8 h. In the presence of TsOH, the etherification (in dioxane) ran faster in comparison with heterogeneous catalyst in a period of 4 h. The glycerol conversion (up to 90%) was achieved and provided better results in di-*tert*-butyl glycerol ether (DTBG) formation. Likewise, di- and triethers can also act as cold flow improvers for biodiesel.

In biodiesel production, base or acid-catalysts are both used for transesterification reactions. Since base-catalysts lead to unexpected soap productions⁷⁾. Unlike base-catalysts, acid-catalysts can avoid saponification, and are suitable for both transesterification reaction of triglycerides and etherification reaction of glycerol as well. In previous research, sulfuric acid (H_2SO_4) and TsOH were also used as a catalyst for the transesterification. Kusakabe *et al.*⁸⁾ studied the transesterification of corn oil with methanol using TsOH, benzenesulfonic acid, H_2SO_4 as catalysts and dimethyl ether (DME) as the co-solvent. The result showed the highest catalytic activity and the yield of fatty acid methyl ester (FAME) reached 97.1% when the reaction in the presence of DME was carried out by using 4 wt% of TsOH based on the oil weight with methanol/oil 10:1 at 80°C for 2 h. In the case of using H_2SO_4 as catalyst, the yield of FAME reached 60.3% in the same condition of TsOH. Freedman *et al.*⁹⁾ reported that the transesterification of soybean with methanol using 1 wt% H_2SO_4 , methanol/oil 30:1, at 65°C for 69 h gave over 99% yield of FAME.

According to the literatures, TsOH and H_2SO_4 were individually used as the catalyst in transesterification of triglycerides and the etherification of glycerol. However, homogeneous catalysts have the main advantage of acting in the same phase of the reaction mixture, so the mass transfer resistance is minimized. Homogeneous acid catalysts cannot be separated from the reaction mixtures, so it cannot be separated from the mixture as it is dissolved in the reaction system, so they are difficult to recycle and leading to the corrode processing. In the purification process, a large amount of water is needed to neutralize and purify the biodiesel, resulting in a large quantity of wastewater and higher production costs²⁾. In this work, we studied on similar catalytic ability of homogeneous acid catalysts in transesterification process and glycerol ether production, and also found reusability of homogeneous

acid catalysts. Herein, we report the performance of TsOH- H_2SO_4 mixed catalyst in transesterification of PO with methanol, etherification of glycerol with isobutylene, tandem synthesis for transesterification of PO and etherification of glycerol and reusability of TsOH- H_2SO_4 homogeneous catalysts, we expected that TsOH- H_2SO_4 could be reused for transesterification and etherification or through tandem synthesis.

2 Material and Methods

2.1 Chemicals and reagents

Palm oil (PO) (Morakot[®]) was purchased from the local market. *p*-Toluenesulfonic acid (TsOH) and standard FAME were purchased from Sigma-Aldrich. Isobutylene was purchased from Linde Thailand. Glycerol (99%), sulfuric acid (H_2SO_4) and methanol (MeOH) were purchased from Merck.

2.2 Synthesis of biodiesel

Transesterification of PO with methanol using TsOH, H_2SO_4 and TsOH- H_2SO_4 as the catalyst was carried out in Parr[®] reactor, equipped with thermocouples. TsOH was dried in oven at 100°C for 24 h and then kept in the desiccator prior to use. PO, desired amounts of methanol, and catalyst were used and the reaction was performed at a temperature ranging from 50°C to 90°C, molar ratios of methanol and PO ranging from 6:1 to 15:1, amount of catalyst ranging from 5 wt% to 15 wt% of PO and a reaction time of 2 to 8 h. The reactions were monitored by the proton nuclear magnetic resonance spectroscopy (¹H NMR). After the reaction, the products were extracted by *n*-hexane, and the *n*-hexane layer (biodiesel layer) was washed with saturated sodium bicarbonate (NaHCO_3) followed by distilled water for thrice. Then, *n*-hexane and the residual trace water were removed by rotary evaporator under reduced pressure before the products were analyzed. The reactions were monitored by ¹H NMR¹⁰⁾ and gas chromatography (GC-MS)¹¹⁾.

2.3 *tert*-butyl glycerol ether process

2.3.1 Etherification of glycerol.

2.3.1A Etherification of commercial glycerol

Etherification of commercial glycerol (99%, analytical grade) with isobutylene was carried out in a Parr[®] reactor, equipped with thermocouples. In typical conditions, 0.125 mole of glycerol, 7.5 wt% TsOH, 6:1 molar ratio of isobutylene and glycerol, reaction temperature 70°C and a reaction time of 4 h were used⁶⁾. GC-MS used to monitor the reactions and the products were interpreted as mono, 1,3-di, 1,2-di, and tri-*tert* butyl glycerol ether, respectively, according to Jamroz *et al.*¹²⁾.

2.3.1B Etherification of crude glycerol from biodiesel production

After the transesterification, the methanol was removed under reduced pressure. The lower phase comprising of glycerol and the catalyst was separated then extracted by *n*-hexane and used as starting material for the etherification. In typical conditions, 6:1 molar ratio of isobutylene and glycerol, reaction temperature 70°C and a reaction time of 5 h were used.

2.3.1C Etherification of crude glycerol in the presence of biodiesel as a solvent

After the removal of methanol from the transesterified product, a residue containing biodiesel, glycerol and catalyst was etherified with isobutylene. The etherification was carried out by using molar ratios of isobutylene and a residual glycerol (estimated by mole of PO) ranging from 6:1 to 12:1, temperature ranging from 60 to 90°C and reaction time ranging from 4 to 6 h in a Parr® reactor.

2.4 Analytical method

The reaction products were identified by GC/MS analysis. Samples were analyzed with GC-MS Agilent using HP-5 column stationary phase polyethylene glycol (column 35 m × 0.32 mm × 0.25 μm). To prepare the sample 10 mg/mL were added into a 10 mL vial. Helium gas was used as carrier gas and the temperature of the injector was set at 290°C. The oven temperature was retained at 50°C for 5 min and increased to 240°C with ramping rate of 20°C/min. Quantitative analysis was based on response factors determined for the components.

3 Results and Discussion

3.1 Transesterification

3.1.1 Effects of TsOH, H₂SO₄ and TsOH-H₂SO₄ as catalyst

Kusakabe and coworker⁸⁾ studied transesterification of corn oil with methanol in the presence of dimethyl ether (DME) as co-solvent. TsOH and H₂SO₄ were used as catalysts. TsOH showed highest catalytic activity. The yield of FAME reached 97.1% when 4 wt% of TsOH base on the oil weight was used at 80°C and reaction time 2 h. Freedman *et al.*⁹⁾ reported that the transesterification of soybean with butanol using 1 wt% H₂SO₄ with butanol/oil 30:1, 117°C at 10 h, high temperature, high ratio of alcohol and high reaction time gave fatty acid methyl ester over 99% yield. In our study, transesterification of PO using 5 wt% of TsOH as catalyst (without co-solvent) and MeOH/oil with different molar ratio (6:1, 9:1, 12:1 and 15:1) at 80°C was carried out. The results (Fig. 1) have shown that 6:1, 9:1, 12:1 and 15:1 molar ratios of MeOH/oil gave the conversion within 8 h for 98.2, 99.7, 99.6 and 99.6%, respectively. In comparison with the previous research^{8,9)}, this study without co-solvent in the process gave the conversion of biodiesel up to 99%

Fig. 1 Conversion of the transesterification at 80°C using 5% TsOH and 5 wt% H₂SO₄ as the catalyst and different MeOH/PO molar ratios.

using amount of TsOH (5 wt%), with methanol/PO 9:1, 80°C at 5 h. Even though this research was used the higher amount of TsOH (5 wt%), it was used less time and temperature. Although the molar ratio of 9:1 or above gave over 99% of conversion within 5 h, molar ratios 12:1 and 15:1 produced some difficulty on separation of the biodiesel and glycerol phase due to the lowered density of the glycerol phase through the high amount of remaining methanol in the glycerol phase. After the transesterification, methanol was thus removed and then 2 phases of the biodiesel and glycerol were appeared. In addition, 5 wt% H₂SO₄ was used for the transesterification at 80°C with the different MeOH/oil ratios 6:1, 9:1, 12:1 and 15:1 yielding the conversion of the transesterification 65.9, 67.1, 67.2 and 67.4%, respectively, within 8 h. Theoretically, a stoichiometric ratio for the transesterification requires three moles of alcohol per mole of triglyceride to yield three moles of fatty acid ester and one mole of glycerol. However, the molar ratio of MeOH/oil used in the transesterification depends on feedstock and catalyst^{8,9,13)}.

Furthermore, the results showed that TsOH, an organic acid, as the catalyst exhibited higher potentiality in transesterification than H₂SO₄, due to its solubility in glycerol as it is more soluble in triglyceride compared to H₂SO₄, an inorganic acid. Thus, TsOH resulted in faster transesterification and higher conversion. After 5 h of reaction at 80°C, the yield of FAME reached 99% when using the TsOH catalyst, while 5% H₂SO₄ resulted around 50%.

Since TsOH and H₂SO₄ alone effected on transesterification, it was speculated whether a mixture of TsOH-H₂SO₄ accelerated this reaction. Thus, the effect of TsOH-H₂SO₄ as a catalyst on transesterification of PO with MeOH (9:1 molar ratio of MeOH:PO) at 80°C was investigated and the results were shown in Fig. 2. When TsOH was kept at 2.5 wt% and H₂SO₄ were varied by 2.5, 5 and 7.5 wt%, sequentially, the results showed that conversion has reached 89.8, 95.0, 95.5 wt%, respectively after 6 h of reaction.

Fig. 2 Effect of amount of the acid catalysts on transesterification using TsOH-H₂SO₄ as a catalyst at 80°C and MeOH/oil molar ratio 9:1.

When TsOH was kept at 5 wt% and H₂SO₄ were varied by 2.5, 5 and 7.5 wt% conversion has reached 92.5, 98.0 and 99.2%, respectively after 4 h and 98.1, 99.6 and 99.8%, sequentially at 6 h. When TsOH was kept at 7.5 wt% and H₂SO₄ were varied by 2.5, 5 and 7.5 wt%, the conversion has reached 92.3, 99.5 and 99.5%, sequentially after 4 h. From the result, the maximum conversion was 99.8% using TsOH-H₂SO₄(7.5:5) as a catalyst in 9:1 molar ratio of MeOH:PO at 80°C for 4 h. Accordingly, the mixture of TsOH-H₂SO₄ accelerated the reaction faster than the single catalyst.

After transesterification (Figs. 3a and 3b), the distribution of the catalyst in the lower phase (glycerol) and the upper phase (biodiesel) was examined by ¹H NMR analysis. In biodiesel phase, chemical shift (δ_H) of TsOH at 2.27, 7.24 and 7.56 ppm indicated that it was presented in glyceride phase and about 20 and 2%mol compared to fatty acyl

moiety for 3 h transesterification using TsOH and TsOH-H₂SO₄, respectively. In Fig. 4, ¹H NMR results of the transesterification indicated the presence of TsOH when it alone was used, while no signal of TsOH was shown in the biodiesel phase when TsOH-H₂SO₄(7.5:5) was used. For the crude glycerol obtained by transesterification using TsOH-H₂SO₄(7.5:5) with >99% conversion, the ¹H NMR (Figs. 4 and 5) showed that a large amount of the acid catalysts was remained. It was obvious that most of catalyst was presented in the crude glycerol and the combined TsOH-H₂SO₄ was dissolved in the glycerol phase better than a single catalyst. Therefore, it was explained that increased solubility of TsOH in glycerol was caused by addition of H₂SO₄.

3.1.2 Effects of reaction temperature

Using TsOH-H₂SO₄(7.5:5) as a catalyst, 9:1 ratio of MeOH-PO, and an 8 h reaction time, a set of temperature experiment (50, 60, 70, 80 and 90°C) were investigated; The conversion (Fig. 5) has reached 80.6, 85.1, 96.5, 99.8 and 99.1 wt%, respectively. The conversion of the reaction at 80 and 90°C were increased up to 99% within 6 h, yet did not result in a significant difference in the conversion. The results indicated that the increase of reaction temperature resulted in the increase of conversion as it is clearly explain the increase of reaction temperature could improve the miscibility of oil and methanol and increase the reaction rate⁶. Therefore, 9:1 ratio of MeOH-PO, TsOH-H₂SO₄(7.5:5) as catalyst at 80°C for 4 h, was the maximum condition (99%) of biodiesel production.

3.2 Etherification

Etherification of commercial glycerol with isobutylene was shown in Fig. 6. When glycerol is etherified with isobutylene, some or all of the hydroxyl groups in the glycerol molecule react. Thus, depending on the extent of etherifi-

Fig. 3 ¹H-NMR spectra of 9:1 MeOH/oil molar ratio, and the product from transesterification at 80°C for 3 h (a) biodiesel using 7.5% TsOH as catalyst (b) biodiesel using TsOH-H₂SO₄(7.5:5) as catalyst.

(a) Crude glycerol in D₃OD

(b) Biodiesel in CDCl₃

Fig. 4 ¹H-NMR spectra of (a) crude glycerol (b) biodiesel production obtained by transesterification using TsOH-H₂SO₄ (7.5:5) with >99% conversion 9:1 MeOH-oil molar ratio at 80°C for 4 h.

Fig. 5 Effect of reaction temperature on transesterification using TsOH-H₂SO₄ (7.5:5) and 9:1 ratio of MeOH-PO.

cation, up to five ether isomers may be formed: two mono-substituted monoethers (3-*tert*-butoxy-1,2-propanediol and 2-*tert*-butoxy-1,3-propanediol; mono-*tert*-butyl glycerol ether (MTBG)), two disubstituted diethers (2,3-di-*tert*-butoxy-1-propanol and 1,3-di-*tert*-butoxy-2-propanol; di-*tert*-butyl glycerol ether (DTBG)) and one trisubstituted triether (1,2,3-tri-*tert*-butoxy propane; tri-*tert*-butyl glycerol ether (TTBG)). Glycerol based additives can effectively improve fuel properties by reducing of harmful exhaust emission when blended with diesel or biodiesel. DTBG and TTBG have been shown as valuable fuel additive to enhance cold properties for biodiesel^{5, 14)}. And two side reactions give rise to the formation of *tert*-butyl alcohol (TBA) and oligomers of isobutylene (mainly dimers – diisobutylene (DIB))⁶⁾.

3.2.1 Etherification of crude glycerol

Selectivity and conversion of ether isomer were verified

Fig. 6 Etherification of glycerol with isobutylene.

Fig. 7 The transesterification product a) the crude glycerol in a presence of biodiesel b) the crude glycerol.

the formation of all these isomers in our experiments. From biodiesel production with >99% conversion was obtained when the $\text{TsOH-H}_2\text{SO}_4$ with 7.5:2.5, 7.5:5 and 7.5:7.5 weight ratios and single TsOH were used. After separation of glycerol from the transesterification production and removal of methanol, the crude glycerol (Fig. 7a) together with remaining catalyst was subjected to etherification. Thus, effect of those catalysts on etherification of the crude glycerol under isobutylene/glycerol molar ratio 6:1 at 70°C for 5 h was investigated. Table 1 showed that the resulted those catalysts in 100% conversion of glycerol and amount of H_2SO_4 in $\text{TsOH-H}_2\text{SO}_4$ had a significant influence on the selectivity of the glycerol ethers. From the result, $\text{TsOH-H}_2\text{SO}_4$ with 7.5:5 and 7.5:2.5 ratios gave the highest yield of (DTBG + TTBG) about 90.6% and MTBG and DTBG yield were increased when H_2SO_4 in $\text{TsOH-H}_2\text{SO}_4$ was increased. On the other hand, TTBG yield was decreased when H_2SO_4 in $\text{TsOH-H}_2\text{SO}_4$ was increased. According to $\text{TsOH-H}_2\text{SO}_4$ with 7.5:5 accelerated the reaction faster than 7.5:2.5 ratios in transesterification production. Therefore, $\text{TsOH-H}_2\text{SO}_4$ with 7.5:5 ratio was selected the optimum cat-

alyst ratio for etherification of crude glycerol in the presence of biodiesel as a solvent. Compared to the previous research using commercial glycerol and fresh catalyst^{4, 6)}, this study using crude glycerol and same catalyst tandem synthesis of biodiesel production and *tert*-butyl glycerol ethers production gave 99% conversion and up to 90% of DTBG and TTBG. Also, the etherification of crude glycerol in the presence of biodiesel as a solvent was studied.

3.2.2 Etherification of crude glycerol in the presence of biodiesel as a solvent

Since etherification in the presence of dioxane and sulfolane as a solvent gave a higher yield of DTBG and TTBG³⁾, we expected that biodiesel itself could be used as a solvent in etherification and the final product could be also used as biodiesel fuel. After transesterification using $\text{TsOH/H}_2\text{SO}_4$ (7.5:5) as a catalyst and removal of MeOH , the crude glycerol in a presence of biodiesel (Fig. 7b) as obtained was etherified with isobutylene.

Furthermore, effect of isobutylene/glycerol molar ratio (4:1, 6:1, 9:1, and 12:1), effect of temperature (60°C , 70°C , 80°C and 90°C) and effect of reaction time (4, 5, 6 and 7

Table 1 Effect of catalyst on conversion of glycerol.

Amount of TsOH-H ₂ SO ₄	Biodiesel, %	Selectivity of glycerol ethers, % ^a				
		M	D	T	D + T	DIB
7.5:0.0	99.0	4.63	48.62	46.64	95.26	0.11
7.5:2.5	99.8	9.23	55.83	34.77	90.60	0.17
7.5:5.0	99.3	9.30	65.62	24.98	90.60	0.10
7.5:7.5	99.2	15.42	67.59	16.84	84.43	0.15

^aAmount of G, M, D and T (%) were calculated from GC-MS chromatogram

G = glycerol; M = MTBG; D = DTBG; T = TTBG, I = isobutylene, DIB = diisobutylene

* wt% TsOH-wt% H₂SO₄ (on the basis of the oi)

Table 2 The effect of isobutylene/glycerol molar ratio and temperature (°C) *tert*-butyl glycerol ethers production.

Feed stock ^a	Temperature, °C	I/G	Reaction time (h)	Selectivity of glycerol ethers ^b , %				
				M	D	T	D + T	DIB
The crude glycerol in a presence of biodiesel	60	6:1	5	11.87	62.96	25.06	88.02	0.11
	70			9.30	66.48	24.08	90.56	0.14
	80			1.20	58.25	40.40	98.65	0.15
	90			4.30	56.62	38.90	95.52	0.18
	80	4:1	5	15.30	57.77	26.86	84.63	0.07
		6:1		1.20	58.25	40.38	98.63	0.14
		9:1		0.46	63.96	35.43	99.39	0.15
		12:1		13.30	56.62	29.92	86.54	0.16
	80	9:1	4	19.26	62.33	18.24	80.57	0.17
			5	0.46	63.96	35.43	99.39	0.15
			6	18.66	62.49	18.68	81.17	0.17
			7	20.79	65.70	13.33	79.03	0.18
Crude glycerol	80	9:1	5	8.43	65.03	26.37	91.14	0.17

^aCrude glycerol was by-product from biodiesel 99%

^bAmount of G, M, D and T (%) were calculated from GC-MS chromatogram and G = glycerol; M = MTBG; D = DTBG; T = TTBG, I = isobutylene, DIB = diisobutylene

* wt% TsOH-wt% H₂SO₄ (on the basis of the oil)

were studied on the TsOH-H₂SO₄ (7.5:5) catalyst. Reaction temperature played a vital role in a rate of reactions. The results (Table 2) indicated that when reaction temperature was increased, the highest amount of DTBG + TTBG (98.65%) was obtained by using 6:1 isobutylene/glycerol ratio at 80°C for 5 h. Continuing increasing the reaction temperature to 90°C showed a slight fluctuation. The decrease in the selectivity above 80°C indicates that the reaction rates of oligomerisation reactions are increasing more rapidly as a function of temperature than the rates of etherification. This means that the activation energies in the oligomerisation reactions are higher than those in etherification reactions. Therefore, 80°C was chosen as the optimum reaction temperature for etherification reaction.

The effect of isobutylene/glycerol molar ratio (4:1, 6:1,

9:1, and 12:1) on etherification for 5 h at 80°C, results (Table 2) showed that the highest amount of DTBG + TTBG (99.39%) when the molar ratio of glycerol and isobutylene was 9:1, the selectivity of glycerol ethers was increased obviously. Higher amount of isobutylene in the reaction system (12:1) led to a slightly decrease of the yield due to dilution of the catalyst and substrates. Therefore, 9:1 was selected as the optimum molar of isobutylene/glycerol for etherification reaction.

Reaction time was one of the most important factors in various reactions. The effect of reaction time on etherification reaction was investigated and was shown in Table 2. As the reaction time was prolonged, the selectivity of glycerol ethers was increased rapidly at first (5 h), and then reached the highest selectivity of glycerol ethers after 5 h.

Continuing prolonging the reaction time led to no further increment of selectivity of glycerol ethers.

On etherification, results showed that maximum selectivity of DTBG + TTBG were obtained by using 9:1 isobutylene/glycerol ratio at 80°C in 99.39% for 5 h. The conversion of crude glycerol, DTBG + TTBG were obtained in 91.14%. It can be observed that better yields and higher selectivity of DTBG and TTBG were obtained when biodiesel was used as the reaction medium. It was probably caused by the addition of biodiesel resulting in a homogeneity of glycerol and isobutylene or better solubility of isobutylene in the reaction mixture. The TsOH-H₂SO₄ catalyst showed a good catalytic performance in the etherification similar to TsOH and it could be recovered for reuse, while TsOH could not be recovered.

Since the crude glycerol could be directly used for the etherification, we expected that TsOH-H₂SO₄ could be reused for transesterification and etherification or through continuous synthesis.

3.3 Reusability of TsOH-H₂SO₄

Reusability of the TsOH-H₂SO₄ catalyst was investigated in the continuous synthesis. After transesterification (9:1 ratio of MeOH-PO, TsOH-H₂SO₄ (7.5:5) as catalyst at 80°C for 4 h.), biodiesel was extracted (thrice) with hexane, and the crude glycerol remained was etherified with isobutylene (9:1 ratio) at 70°C for 8 h followed by extraction with *n*-hexane. The leftover catalyst was used for the next cycle and the process was then repeated. For each cycle of the reaction, biodiesel and selectivity for glycerol ethers were examined.

TsOH was considered as a homogeneous catalyst to organic synthesis. When TsOH was combined with H₂SO₄ through formation of hydrogen bond to produced mixture of TsOH-H₂SO₄ and it would become a “homogeneous” catalyst at the moment. Owing to polarity of TsOH-H₂SO₄, they were not only the catalyst of transesterification reaction, but they were also increased polarity of glycerol. This is because TsOH-H₂SO₄ and glycerol could form a new ternary TsOH-H₂SO₄-glycerol. The ternary TsOH-H₂SO₄-glycerol was easy to separate from the products, making the overall operation convenient, as shown as Fig. 8. According to, the ¹H NMR (Fig. 4) showed that a large amount of the acid catalysts was remained in crude glycerol phase.

The results showed that the catalyst can be reused for at least of 6 cycles until the reaction cannot be resumed and activity of the catalyst was less for 90% after 6 cycles. Moreover, the recyclability experiments of the catalyst were conducted and the results showed that the 6th catalyst recycling run showed a slight reduction in the transesterification yield (78.58%) (>99% for the first run). From acid value test of glycerol phase in 1-6 cycle of catalyst, result showed 3.31, 2.63, 1.47, 1.01, 0.57 and 0.32 g KOH/g of oil, respectively. The above results indicated that TsOH-H₂SO₄ containing the reaction would decrease the activity of the acidic TsOH-H₂SO₄ catalyst in the transesterification process was decreased.

4 Conclusion

In this study, the results showed that the mixture of TsOH-H₂SO₄ could be used in transesterification, etherification of glycerol with isobutylene. For transesterification of PO, 7.5 wt% TsOH and 5 wt% conc. H₂SO₄, 9:1 methanol: PO molar ratios after a reaction period of 4 h at 80°C resulted in up to 99.9% conversion. It was found that the mixture of TsOH and H₂SO₄ could accelerated the reaction noticeably faster than the single catalyst, resulting in the enhancement of the transesterification rate and TsOH-H₂SO₄ as the catalyst for transesterification and etherification in continuous synthesis could be reused for 6 cycles, which produced a reduction in waste and cost. When comparing between crude glycerol and biodiesel with isobutylene as the starting material in the production of *tert*-butyl glycerol ethers, the etherification in biodiesel would result in higher selectivity of DTBG and TTBG (99.39%). The highest amount of DTBG + TTBG was formed etherification in the presence of biodiesel up to 99.39% more than the previous research^{4, 6)}. Higher glycerol ethers (DTBG + TTBG) could be similar as the current commercial oxygenate additives (MTBE, ETBE, TAME applied in gasoline) used as oxygenates to diesel fuel, biodiesel or their mixture.

Fig. 8 Before and after the transesterification process, the distribution of reactants and products.

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Supporting Information

This material is available free of charge via the Internet at doi: 10.5650/jos.ess21001

References

- 1) Gonzalez, L.R.; Bolonio, D.; Mazadiego, L.F.; Silva, N.S.; Segovia, E.K. Long-term forecast of energy and fuels demand towards a sustainable road transport sector in ecuador(2016–2035): A leap model application. *Sustainability* **12**, 472 (2020).
- 2) Ramos, M.; Dias, A.P.S.; Puna, J.F.; Gomes, J.; Borda-do, J.C. Biodiesel production processes and sustainable raw materials. *Energies* **12**, 4408 (2019).
- 3) Amin, T.K.; Amin, N.A.S.; Najaafi, N.; Tarighi, S. A review on the catalytic acetalization of bio-renewable glycerol to fuel additives. *Front Chem.* **6**, 573 (2018).
- 4) Klepacova, K.M.D.; Kaszonyi, A.; Bajus, M. Etherification of glycerol and ethylene glycerol by isobutylene. *Petrol Coal* **45**, 54-57 (2003).
- 5) Rahmat, N.; Abdullah, A.H.; Mohamed, A.R. Recent progress on innovative and potential technologies for glycerol transformation into fuel additives: A critical review. *Renew. Sustain. Energy. Rev.* **14**, 987-1000 (2010).
- 6) Filimonov, L.; Kim, H.; Jung, K.S.; Seung, D.; Lee, H.J. Etherification of glycerol by isobutylene: Tuning the production composition. *Appl. Catal. A* **390**, 235-244 (2010).
- 7) Vicente, G.; Martinez, M.; Aracil, J. Integryield biodiesel production: a comparison of different homogeneous catalysts systems. *Bioresour. Technol.* **92**, 297-305 (2004).
- 8) Kusakabe, K.; Guan, G.; Sakurai, N.; Moriyama, K. Transesterification of vegetable oil to biodiesel fuel using acid catalysts in presence of dimethyl ether. *Fuel* **88**, 81-86 (2009).
- 9) Freedman, B.; Butterfield, R.O.; Pryde, E.H. Transesterification Kinetics of Soybean oil. *J. Am. Oil Chem. Soc.* **63**, 1375-1380 (1986).
- 10) Coen, D. Determination of total FAME and Linolenic acid methyl esters in biodiesel According to EN-14103. *Energy and Fuel* Available from. www.agilent.com.
- 11) Lotero, E.; Liu, Y.; Lopez, D.E.; Suwannakam, K.; Bruce, D.A.; Good, D.A.; Goodwin, Jr, J.G. Synthesis of biodiesel via Acid Catalysis. *Ind. Eng. Chem. Res.* **44**, 5353-5363 (2005).
- 12) Jamroz, M.E.; Jarosz, M.; Jarosz, J.W.; Bednarek, E.; Tecza, W.; Jamroz, M.H.; Dobrowolski, J.C.; Kijenski, J. Mono-, di-, and tri-*tert*-butyl ethers of glycerol A molecular spectroscopic study. *Spectrochim. Acta A* **67**, 980-988 (2007).
- 13) Idris, A.M. The effects of alcohol to oil molar ratios and the type of alcohol on biodiesel production using transesterification process. *Egyp. J. Pet.* **25**, 21-31 (2016).
- 14) Mukhopadhyay, P.; Chakraborty, R. Effect of bioglycerol base fuel additives on diesel fuel property, engine performance and emission quality: A review. *Energy Procedia* **79**, 671-676 (2015).

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