



Etherification of Glycerol with Ethanol over Solid Acid Catalysts: Kinetic Study Using Cation Exchange Resin

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Etherification of Glycerol with Ethanol over Solid Acid Catalysts: Kinetic Study Using Cation Exchange Resin

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Abstract: The etherification of glycerol with ethanol is a novel process to utilize low-value by-product (glycerol) of biodiesel industry to produce ethers of glycerol suitable for use as fuel additive or solvent. The etherification of glycerol with ethanol was investigated under liquid phase in a high pressure batch reactor using two different types of commercial solid acid catalyst (zeolites and strongly acidic cation exchange resin (CER)). The CER showed superior catalytic activity over H-beta zeolite. The diethyl ether was

observed as major product at high ethanol-to-glycerol mole ratio. The product selectivity diverted towards ethers of glycerol with decreasing ethanol-to-glycerol mole ratio. Among ethers of glycerol, glycerol monoethyl ether was major product of the reaction. The reaction mechanism for etherification of glycerol with ethanol was delineated based on experimental observations. The reaction rate increased with increasing catalyst loading and temperature without affecting selectivity to the products significantly. The apparent activation energy of glycerol and ethanol were 25.1 and 26.6 kcal/mol respectively. An empirical kinetic model was developed to correlate experimental data at different temperature. The conversion of the reactants calculated from the kinetic model matched reasonably with experimental data.

Key words: Cation exchange resin, Ethanol, Etherification, Glycerol, Kinetic modelling.

INTRODUCTION

The fossil fuel reserves are decreasing continuously to meet growing energy demand of mounting population of the world with improved standard of living. The increasing concentration of harmful and greenhouse gases in the earth atmosphere due to increased usage of fossil fuels are the additional motivations for an alternative carbon neutral source of energy. The biodiesel, fatty acid methyl esters has been emerged as one such promising biofuel to reduce the dependency away from fossil fuels. The by-product, glycerol is produced about 10 wt% of total biodiesel production during the transesterification of vegetable oils with methanol in presence of NaOH [1]. The glycerol is mainly used in surfactant, cosmetics, medicines, sweetening agents, and additives for food industries [2-4]. When mass production of the biodiesel is realized, the novel processes to utilize low-value glycerol must be developed to improve overall economics of the biodiesel industry [5]. The substantial research efforts have thus been made in last decade to utilize glycerol to produce wide range of chemicals, synthesis gas, fuels, and fuel additives in an integrated biorefinery [6-7].

The etherification of glycerol with either alcohols (e.g. ethanol or isobutanol) or alkenes (e.g. isobutylene) and esterification of glycerol with acetic acid or fatty acid are such novel processes to produce oxygenated compounds that have suitable properties for use as fuel additive or solvent. The ethers of glycerol, especially di- and tri-alkyl ethers have good solubility in biodiesel (or conventional diesel) [8] and thus can be used as potential oxygenate additive to diesel to improve cold flow properties of the fuel [9-11] and to reduce emissions of particulate, hydrocarbon, carbon monoxide, and unregulated aldehyde [8]. The ethers and esters of glycerol also have multitude of additional applications as an additive to enhance physical properties of cement [12], extractive distillation agent, and solvent [9], coolant, and fuel additives [11,13]. The triacetyl glycerol are used as additives of fuels; while mono- and diacetyl glycerol are used in cryogenic and as a raw material of biodegradable polyesters [14].

Substantial development has been made in the past on esterification of glycerol with acetic acid and fatty acid using numerous types of heterogeneous solid acid catalyst [14-21]. The etherification of glycerol with isobutylene and tertiary-butanol have also been studied by several authors using various acid catalyst to alleviate disparity of production and demand of isobutylene [13,22-25,26-30]. The glycerol esterification or etherification reactions were performed over several homogeneous acid catalysts such as dodecatungstophosphoric, dodecamolybdo phosphoric acid, tungstophosphoric acid, *p*-toluene sulfonic acid, methane sulfonic acid, silicotungstic acid [11,17,19,31]. The corrosiveness to process equipment, difficulty in separation of products from the reaction mixture, and generation of large amount of acid waste are some of the problems associated with the use of homogeneous acid catalyst. Therefore, there is an increasing tendency to use safer and simpler catalyst preferably in solid state. A number of studies were thus reported using solid acid catalyst such as Amberlyst (15, 35, 36, 39), zeolite (HY, HZSM, H-beta), and sulfonic acid functionalized mesostructured silica (Ar-SO₃H and SBA-15) [5,10-11,24-25,30].

The bio-ethanol has been gaining immense importance throughout the world as a renewable liquid fuel or fuel blend and source of chemicals [6-7]. The etherification of glycerol with ethanol has thus been reported recently in presence of different acid catalysts such as H₂SO₄, Amberlyst (A15 and A35), zeolites (H-ZSM5 and H-Beta), arenesulfonic acid-functionalized mesostructured silica, sulfonic-acid grafted silica, tungstophosphoric acid (HPW), SiO₂-supported HPW, FeCl₃, and AlCl₃ [1,5,32]. However, to the best of our knowledge, comprehensive study on etherification of glycerol with ethanol was not reported until now over strongly acidic cation exchange resin (CER). The present work was therefore commenced on detailed kinetic study of etherification of glycerol with ethanol to divert the selectivity towards ethers of glycerol away from diethyl ether, understand reaction mechanism, and develop a suitable kinetic model.

EXPERIMENTAL

Chemicals

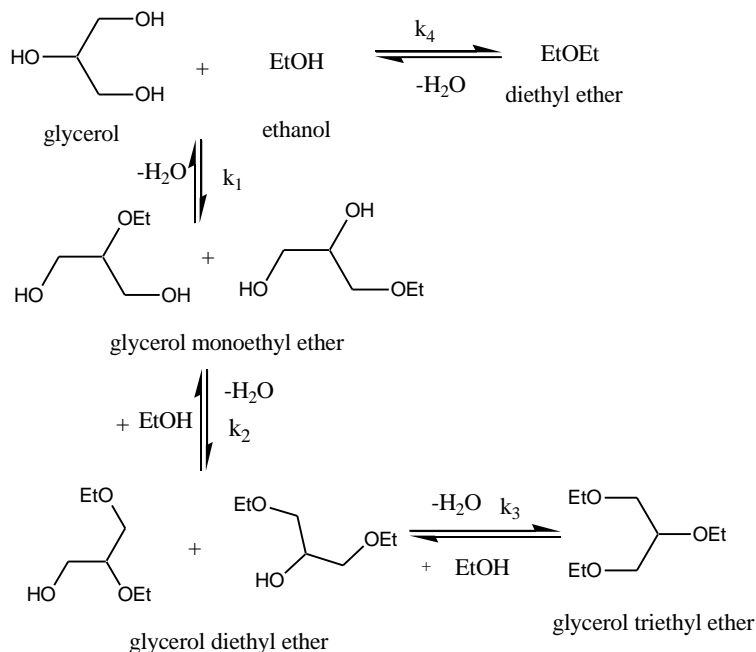
Glycerol (98%) and ethanol (99.9%) were obtained from Merck Specialist Pvt. Ltd., Mumbai, India and Hngzhou Chemical Co. Ltd., China respectively. The CER (Serelite SRC-120, ion exchange capacity = minimum 4.5 meq/g dry resin) in the form of granular gel was purchased from Sisco Research Laboratories Pvt. Ltd., Mumbai, India. NaY and H-Beta zeolite powder were obtained from Sud Chemie India Pvt. Ltd., Baroda, India. The NaX (13X) zeolite was obtained from Sorbead India, Vadodara.

Equipment and Procedure

The experiments were carried out in a mechanically agitated 400 ml stainless steel high pressure autoclave (Amar Equipment Pvt. Ltd., Mumbai, India). The reactor was jacketed with heating coil and the reactor temperature was controlled within ± 1 K of the set point using a PID controller. In all experiments, the reactor was flushed with nitrogen before start of the reaction to avoid unwanted oxidation of ethanol and glycerol by air. In a typical run, a known amount of glycerol, ethanol, and CER were charged simultaneously into the reactor. The reactor was then pressurized to 10 bar using nitrogen gas. The reaction mixture was then agitated at a constant stirring speed and heated to the desired reaction temperature. Once the desired reaction temperature was reached, the stirrer was stopped and first liquid sample was withdrawn from the reactor through liquid sampling valve using a cold trap (to avoid vaporization of volatiles components during sampling). This was considered as the initial condition of the reaction and all subsequent calculations were performed based on this initial condition. The final pressure of about 14.2, 15.0, 16.2, and 18 bar was observed at reaction temperature of 393, 403, 413, and 423 K respectively. About 0.5 cm³ of the sample was withdrawn at a regular interval after stopping the agitation and allowing the catalyst to settle from reaction mixture. The collected samples were first centrifuged to separate the catalyst particles, if any, and stored inside a deep freeze before analysis in a gas chromatograph.

Analysis

All liquid samples were analysed by gas chromatograph (Shimadzu GC-2014) equipped with flame ionization detector (FID) and ZB wax capillary column (30m \times 0.25mm \times 0.25 μ m) using nitrogen as carrier gas. The oven temperature was programmed with an initial temperature of 313 K, increased at a rate of 10 K/min up to 493 K, and maintained at 493 K for 5 min. Injector and detector temperature were kept at 513 K and 523 K respectively. The quantification of the products formed in the reaction was done based on the corresponding FID peak areas. However, the water formed in the reaction cannot be detected by FID. Therefore, the amount of water formed in the reaction was calculated based on stoichiometry of the reactions of [Scheme 1](#). All the products were identified using GC-MS (Shimadzu GC-2010 Plus) using the library. The reaction was stopped at 480 min and gas sample was then collected through gas release valve. The gas samples were subsequently analysed in a gas chromatograph equipped with thermal conductivity detector (TCD) using Porapak-Q packed column (2 meter length and 1/8" diameter) under isothermal condition at 423 K. During the gas analysis, injector and detector temperature were kept at 453 K and 523 K respectively.



Scheme 1. Reactions network for etherification of glycerol with ethanol.

Catalyst Characterization

Specific surface area of calcined H-beta and NaY zeolites were determined from nitrogen adsorption-desorption isotherms recorded at liquid nitrogen temperature, 77 K, using Micromeritics ASAP 2020 physisorption analyser. Specific surface area was determined using multipoint BET equation in the relative pressure range of 0.05 to 0.3. Temperature programmed desorption (TPD) of ammonia was used to measure acidity of calcined zeolite catalysts using Micromeritics AutoChem II 2920 chemisorption analyser. Prior to the analysis, the sample was degassed at 393 K for 3 h under the flow of helium (50 ml/min). Adsorption of ammonia was carried out at 373 K for 1 h followed by purging the sample under the flow of helium at 50 ml/min for 1 h at same temperature. The sample was heated from 373 K to 1073 K using a temperature ramp of 10 K/min and desorbed ammonia was monitored by a TCD. The acidity and surface area of zeolite catalysts are shown in [Table 1](#). The NH_3 -TPD of zeolite catalysts are shown in [Fig. S1](#).

Table 1. Acidity and surface area of the zeolite catalysts.

catalysts	acidity, mmol NH_3/g	surface area, m^2/g
H-beta	0.936	494.5
NaY	0.877	450.6
NaX	0.487	-

RESULTS AND DISCUSSION

The etherification of glycerol with ethanol was carried out in a batch reactor in absence and presence of two different types of solid acid catalyst (CER, H-beta, NaX, and NaY) in the temperature range of 393-443 K. The glycerol monoethyl ether (GME), glycerol diethyl ether (GDE), glycerol triethyl ether (GTE), and diethyl ether (DEE) were observed as the products. A typical GC chromatogram of liquid sample representing peak of reactants and products are shown in [Fig. S2](#). The progress of the reaction measured in terms of conversion of ethanol and glycerol used throughout the article are defined as follows.

$$\text{Conversion, \%} = 100 \times \frac{\text{moles of ethanol or glycerol reacted}}{\text{moles of ethanol or glycerol present initially}} \quad (1)$$

During the course of reaction, the glycerol is converted to three products, GME, GDE, and GTE. Therefore, selectivity to GME, GDE, and GTE with respect to glycerol used throughout the article is defined by following expression.

$$\text{Selectivity to GME, GDE, or GTE, \%} = 100 \times \frac{\text{moles of GME, GDE, or GTE formed}}{\text{moles of glycerol reacted}} \quad (2)$$

The ethanol reacted with itself and glycerol leading to formation of DEE, GME, GDE, and GTE. Therefore, the selectivity to DEE with respect to ethanol is defined as follows.

$$\text{Selectivity to DEE, \%} = 100 \times \frac{2 \times \text{moles of DEE formed}}{\text{moles of ethanol reacted}} \quad (3)$$

Reaction Mechanism

The etherification of glycerol with ethanol proceeds in three consecutive steps. The glycerol first reacts with ethanol forming GME which reacts further with ethanol to form GDE. The GDE then reacts with ethanol to form GTE as shown in [Scheme 1](#). It was observed from an independent reaction study using pure ethanol over CER catalyst that ethanol undergoes dehydration reaction leading to formation of DEE ([Fig. 1](#)) [5]. As observed from the [Fig. 1](#), conversion of ethanol to DEE increased with increasing temperature. Dehydration of ethanol over acidic catalyst to produce DEE (as an alternate motor vehicle fuel) and ethylene (as feedstock of petrochemical industry) has been gaining importance for sustainable production of fuels and chemicals in an integrated bio-refinery [33-34]. It was reported that dehydration reaction is selective towards DEE below about 453 K and ethylene above 523 K.

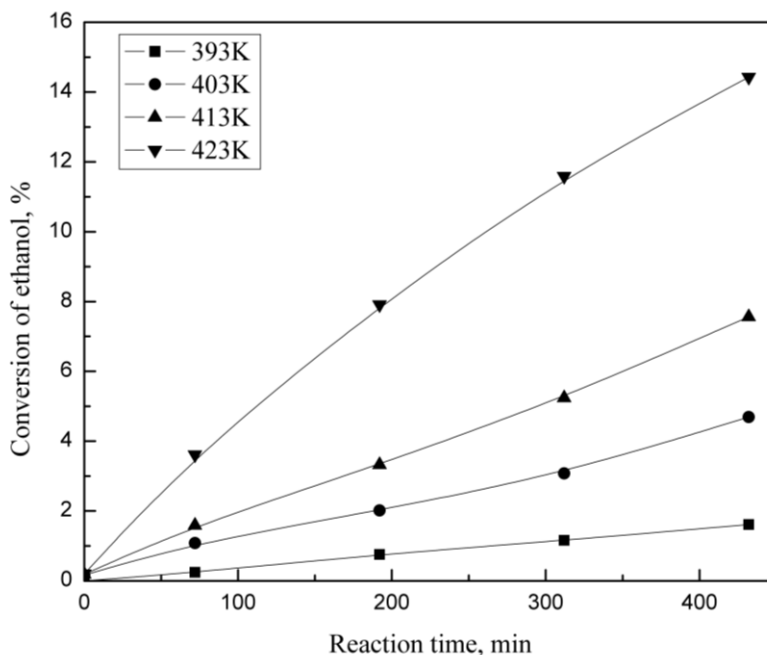


Fig. 1. Dehydration of pure ethanol to DEE at different temperature. Conditions: catalyst = CER; catalyst loading = 1.0 (w/v)%; initial nitrogen pressure = 10 bar; ethanol concentration = 17.2 kmol/m³.

Because of high viscosity of glycerol, the similar experiment with pure glycerol was carried out using a solvent, dimethyl sulfoxide (DMSO) under otherwise similar conditions; but no products were observed under the experimental conditions. From this observation it may be concluded that the dehydration of glycerol is not taking place under the experimental conditions. It has been reported that ethanol also undergoes oxidation to acetaldehyde which further reacts with glycerol leading to formation of 4-(ethoxymethyl)-2-methyl-1,3-dioxolane and 5-ethoxy-2-methyl-1,3-dioxane [32]. In order to confirm formation of those products, an independent reaction of glycerol with ethanol was conducted using externally added acetaldehyde under otherwise similar experimental conditions. However, formations of

those products were not observed even after 8 h of reaction. From this observation it may be concluded that reactants were not degraded to any lighter hydrocarbons.

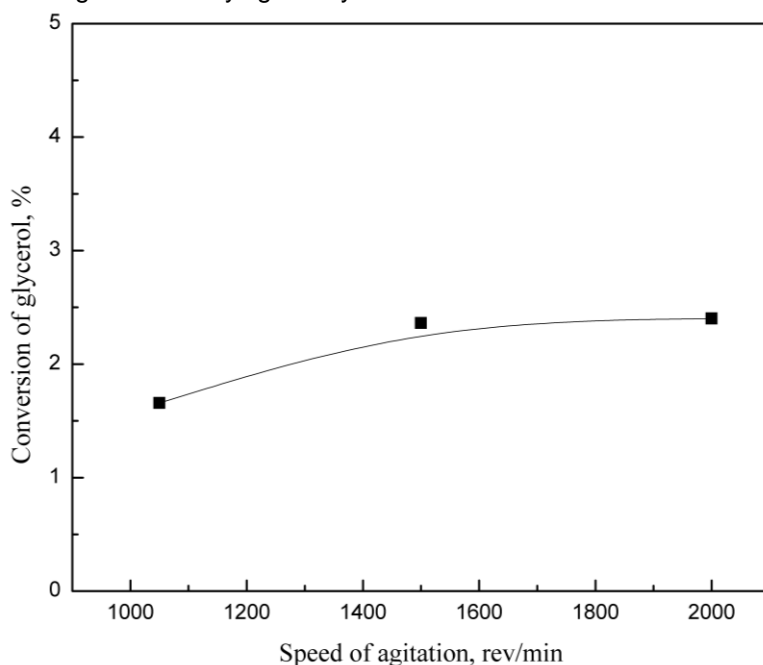


Fig. 2. Effect of speed of agitation on glycerol conversion. Conditions: glycerol concentration = 4.1 kmol/m³; ethanol concentration = 12.0 kmol/m³; temperature = 413 K; catalyst = CER; catalyst loading = 1.0 (w/v)%; matching reaction time = 210 min; initial nitrogen pressure = 10 bar.

Effect of Speed of Agitation

The effect of speed of agitation were studied in the range of 1000-2000 rpm under otherwise identical experimental conditions. The increase of glycerol conversion with speed of agitation was negligibly small as shown in Fig. 2. Therefore, the reaction can be considered as free from external mass transfer resistance. However, internal diffusional resistance could not be evaluated as it requires variation of particle size of granular gel form of CER catalyst. Hence, the kinetic parameters presented in the present article include internal diffusional resistance effect, if any. All subsequent experiments were performed at 1100 rpm to ensure that the reaction was free from external mass transfer resistance.

Table 2. Bubble point pressure of pure ethanol, glycerol, and mixture of glycerol and ethanol.^a

temperature, K	bubble point pressure, bar			
	ethanol	glycerol	diethyl ether	ethanol (67 mol%)+ glycerol (23 mol%)
393	4.3	0.99×10 ⁻³	10.0	3.3
403	5.7	1.8×10 ⁻³	12.2	4.4
413	7.5	3.3×10 ⁻³	14.8	5.8
423	9.8	5.7×10 ⁻³	17.7	7.5

^a The data was generated using Aspen Plus®, Aspen Tech™

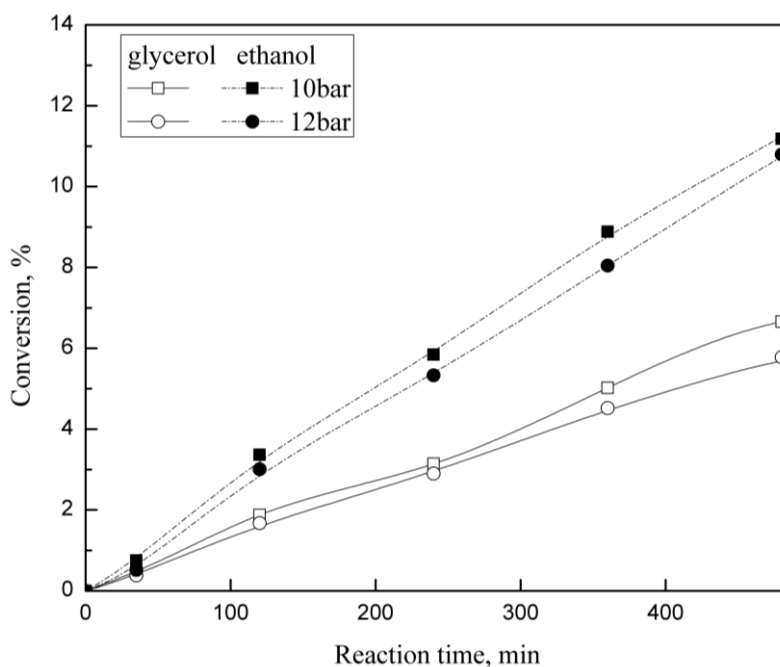


Fig. 3. Effect of pressure on conversion of glycerol and ethanol. Conditions: glycerol concentration = 2.2 kmol/m³; ethanol concentration = 14.4 kmol/m³; temperature = 413 K; catalyst = CER; catalyst loading=1.0 (w/v)%.

Effect of Pressure

The etherification of glycerol with ethanol was studied well above the normal boiling point of the volatile reactant (ethanol) and product (DEE). Therefore, it is essential to study the reaction at high initial pressure to retain ethanol and DEE completely in liquid phase. Moreover, the study of effect of pressure on the reaction is quite meaningful as partial vaporization of ethanol and DEE during the reaction might affect the reaction significantly. The bubble point pressure of pure ethanol, glycerol, DEE, and mixtures of ethanol and glycerol are shown in Table 2. The effect of pressure on the reaction was studied at two different initial nitrogen pressure, 10 and 12 bar, which were well above the bubble point pressure at the reaction temperature. About 16.1 and 17.5 bar of final pressure were observed after reaching 413 K for initial pressure of 10 and 12 bar respectively. The effect of pressure on conversion of glycerol and ethanol are shown in Fig. 3. As observed from the Fig. 3, conversion of reactants decreased slightly with pressure. All subsequent experiments were therefore performed at 10 bar of initial pressure as the variation of conversion with pressure was negligible beyond this pressure.

It was reported in the published literature that no etherification product formed below 433 K during the etherification reaction of glycerol with ethanol under autogenously pressure⁵. This may be due to the fact that the significant fraction of volatile component (ethanol) remained in the vapour phase under autogenously pressure conditions. However, in the present study, the etherification reaction happened at temperature as low as 393 K. This clearly indicates that maintaining an initial pressure above the bubble point pressure of the reaction mixture is essential to keep ethanol in liquid phase and to enhance the reaction rate. No volatile compounds were observed during the analysis of gas sample which further confirmed that the reactants and products remained in the liquid phase.

Types of Catalysts

The catalytic performance of various commercial solid acid catalysts, zeolites (H-beta, NaX, and NaY) and CER was evaluated for etherification of glycerol with ethanol under identical experimental conditions. The CER showed highest catalytic activity followed by H-beta as shown in Table 3. This is quite expected as CER has stronger acidity than H-beta. The NaX and NaY however showed no catalytic activity even after 480 min of reaction because of their weak acidity. From these observations it may be concluded that the acidity of the catalysts plays crucial role in etherification of glycerol with ethanol. From the Table 3, it may be further observed that ethanol dehydration reaction was dominating one over the etherification of glycerol with ethanol leading to very high selectivity to DEE. The selectivity to DEE was significantly higher for H-

beta compared to CER. These results suggest that pore size of the catalysts may also plays an important role in this reaction [10]. The formation of ethers of glycerol especially GTE is difficult because of porous structure of the H-beta zeolite leading to higher selectivity to DEE and lower selectivity to GTE. Since CER is thermally stable only up to 423 K, the study was extended to higher temperature (433 and 443 K) using H-beta zeolite only. The significant improvement in conversion of glycerol and ethanol were observed at higher reaction temperature (Table 3).

Table 3. Effect of different type of catalysts on conversion and products selectivity.¹

catalysts	Temperature, K	conversion, % ^c		selectivity, % ^d			
		glycerol	ethanol	GME	GDE	GTE	DEE
CER ^a	413	6.65	11.18	75.3	16.5	8.2	90.7
H-beta ^b	413	1.02	5.69	77.3	18.9	3.8	98.7
H-beta ^{b,e}	433	8.6	24.09	89.2	6.6	4.2	91.6
H-beta ^{b,e}	443	15.6	36.6	87.4	10.5	2.1	96.6
NaX ^b	413	0.0	0.0	-	-	-	-
NaY ^b	413	0.0	0.0	-	-	-	-

¹ Conditions: glycerol concentration = 2.2 kmol/m³; ethanol concentration = 14.4 kmol/m³; initial pressure = 10 bar. ^acatalyst loading = 1.0 (w/v)%; ^bcatalyst loading = 2.5 (w/v)%; ^cmatching reaction time = 445 min; ^dmatching glycerol conversion = 1%; ^einitial pressure = 15 bar.

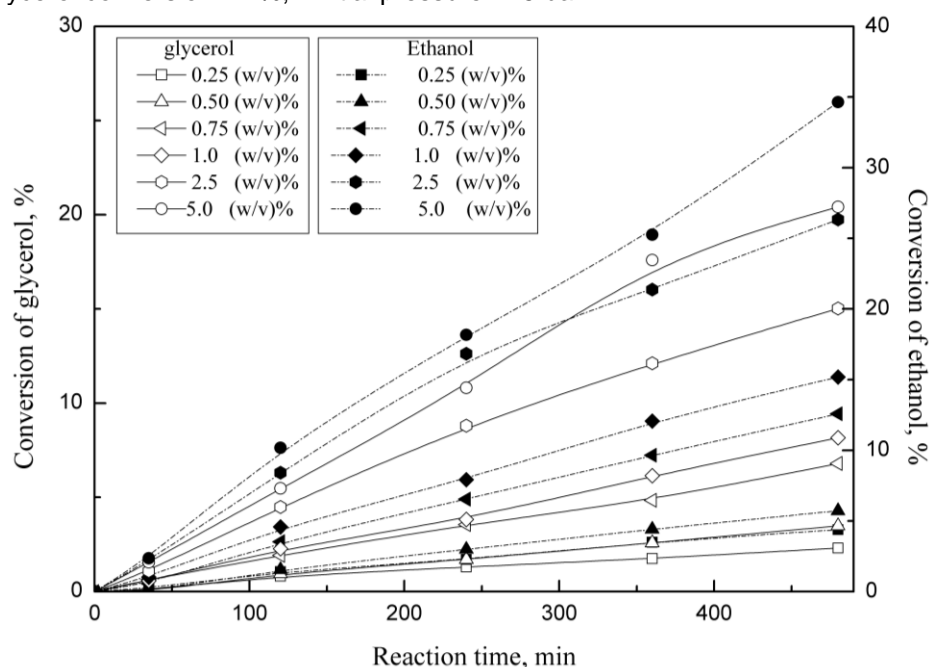


Fig. 4. Effect of catalyst loading on conversion of glycerol and ethanol. Conditions: glycerol concentration = 2.2 kmol/m³; ethanol concentration = 14.4 kmol/m³; temperature = 413 K; catalyst = CER; initial pressure = 10 bar for 0.25-1.0 (w/v)% and 15 bar for 2.5-5.0 (w/v)% of catalyst loading.

Effect of Catalyst Loading

The effect of catalyst loading for etherification of glycerol with ethanol were studied using CER for different catalyst loadings in the range of 0.25-5.0 (w/v)%. The effect of catalyst loading on conversion of glycerol and ethanol are shown in Fig. 4. As observed from the Fig. 4, the conversion of glycerol and ethanol increased with increasing catalyst loading for a fixed reaction time. The maximum conversion of glycerol was about 20.4% for 5.0 (w/v)% of catalyst loading at 480 min of reaction. The study was also conducted in absence of any catalyst under otherwise same experimental conditions. However, no conversion of glycerol and ethanol was observed even after 480 min of the reaction. The effect of catalyst loading on selectivity to different products are shown in Table 4. As observed from the table, the products selectivity remained almost unaffected by catalyst loading. The increase of catalyst loading enhanced the rate of all reactions equally thereby maintaining identical selectivity to products for all catalyst loading.

Table 4. Effect of catalyst loading on products selectivity.^a

catalyst loading, (w/v)%	selectivity, %			
	GME	GDE	GTE	DEE
0.25	84.0	9.6	6.4	86.2
0.5	83.3	9.5	7.2	86.6
0.75	81.9	10.5	7.6	91.7
1.0	83.0	9.7	7.3	91.2
2.5	84.8	11.3	3.9	87.9
5.0	82.3	13.7	4.0	83.3

^a Conditions: matching glycerol conversion = 1%; all other conditions are same as in Fig. 4.

Table 5. Effect of ethanol-to-glycerol mole ratio on products selectivity.^a

ethanol-to-glycerol mole ratio	selectivity, %			
	GME	GDE	GTE	DEE
1.33	97.1	1.6	1.3	75.8
6.51	90.3	5.9	3.8	90.7
8.62	89.3	6.5	4.2	92.4

^a Conditions: matching glycerol conversion = 3%; all other conditions are same as in Fig. 5.

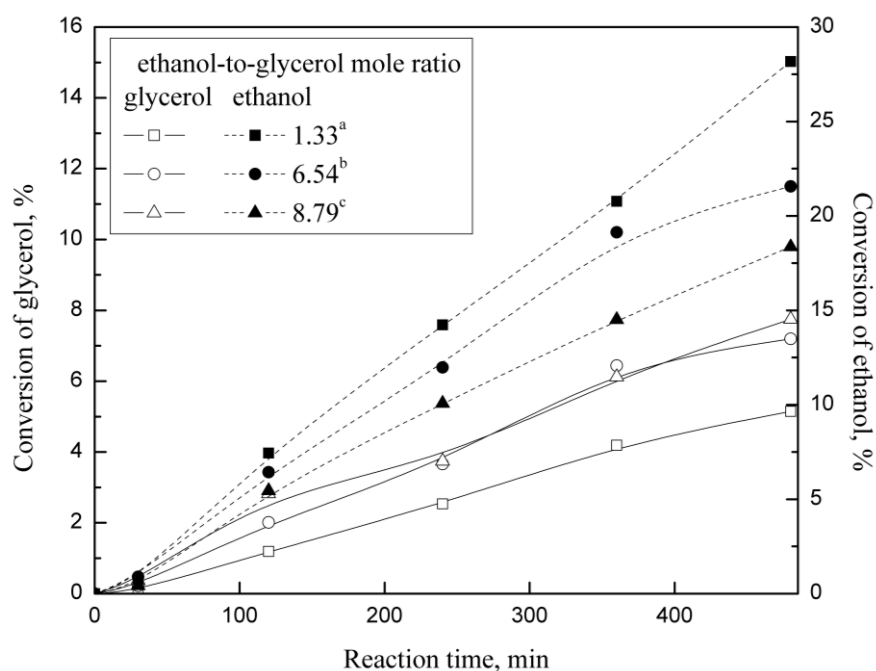


Fig. 5. Effect of ethanol-to-glycerol mole ratio on conversion of glycerol and ethanol. Conditions: temperature = 413 K; catalyst = CER; catalyst loading=1.0 (w/v)%; initial nitrogen pressure = 10 bar; ^aglycerol concentration = 6.63 kmol/m³; ethanol concentration = 8.84 kmol/m³. ^bglycerol concentration = 2.21 kmol/m³; ethanol concentration = 14.38 kmol/m³. ^cglycerol concentration = 1.74 kmol/m³; ethanol concentration = 14.97 kmol/m³.

Effect of Ethanol-to-Glycerol Mole Ratio

The effect of ethanol-to-glycerol mole ratio on conversion of reactants and selectivity to products were studied at three different mole ratios, 1.33, 6.51, and 8.62 keeping total volume of the reaction mixture and all other reaction conditions same. The effect of ethanol-to-glycerol mole ratio on conversion of glycerol and ethanol are shown in Fig. 5. As observed from the Fig. 5, the conversion of glycerol increased and conversion of ethanol decreased with increasing ethanol-to-glycerol mole ratio.

The effect of ethanol-to-glycerol mole ratio on selectivity to different products are shown in Table 5. As observed from the table, the selectivity to undesirable DEE increased with increasing ethanol-to-glycerol mole ratio and minimum selectivity to DEE observed was about 75% for ethanol-to-glycerol mole ratio of

1.33. It is also observed from the table that selectivity to GDE and GTE increased with increasing ethanol-to-glycerol mole ratio. From these results it may be concluded that with decreasing ethanol-to-glycerol mole ratio the concentration of ethanol relative to concentration of glycerol decreased leading to lower selectivity to DEE and higher selectivity to ethyl ethers of glycerol.

The additional enhancement of selectivity to desirable ethyl ethers of glycerol is expected by decreasing the ethanol-to-glycerol mole ratio even further. The study was however not possible to extend to lower ethanol-to-glycerol mole ratio because of difficulty in handling and analysis of highly viscous glycerol rich reaction mixture. In order to demonstrate the effect of low ethanol-to-glycerol mole ratio (lower than 1), the study was extended in presence of a solvent (DMSO) as shown in Table 6. As observed from the table, very low selectivity to DEE can be realized by using low ethanol-to-glycerol mole ratio. The minimum selectivity to DEE was about 16% at ethanol-to-glycerol mole ratio of 0.29.

Table 6. Effect of ethanol-to-glycerol mole ratio in presence of solvent (DMSO) on products selectivity.^a

ethanol-to-glycerol mole ratio	selectivity, %		
	GME	GDE+GTE	DEE
0.29 ^a	67.8	32.2	16.8
0.40 ^b	73.6	26.4	16.8
0.67 ^c	77.1	22.9	27.1

^a Conditions: temperature = 413 K; catalyst = CER; catalyst loading = 1.0 (w/v)%; matching reaction time = 480 min; initial reactor pressure = 10 bar. ^aglycerol concentration = 6.7 kmol/m³; ethanol concentration = 2.0 kmol/m³. ^bglycerol concentration = 6.2 kmol/m³; ethanol concentration = 2.5 kmol/m³. ^cglycerol concentration = 5.3 kmol/m³; ethanol concentration = 3.6 kmol/m³.

Table 7. Reproducibility and reusability of the catalyst.^a

reaction run	conversion, %		selectivity, %			
	glycerol	ethanol	GME	GDE	GTE	DEE
fresh catalyst-I	1.5	2.7	92.7	4.9	2.4	79.5
fresh catalyst-II	1.5	2.6	93.7	4.0	2.3	78.5
reused catalyst	2.3	4.5	96.2	2.0	1.8	81.6

^a Conditions: initial nitrogen pressure = 10 bar; glycerol concentration = 4.1 kmol/m³; ethanol concentration = 12.0 kmol/m³; temperature = 413 K; catalyst = CER; catalyst loading = 1.0 (w/v)%; matching reaction time = 120 min.

Reproducibility and Reusability of the Catalyst

In order to demonstrate the reproducibility, two reaction runs were carried out under same experimental conditions. The result showed that conversion of glycerol and ethanol and selectivity to products were comparable for both runs as shown in Table 7. To study reusability, CER catalyst used in previous runs was first regenerated by filtering under vacuum and washed thoroughly with ethanol for several time. The filtered catalyst was then dried in oven for overnight at 353 K and the dried catalyst was then used for next catalytic run. The comparison of results of fresh catalyst and reused catalyst are shown in Table 7. The reused catalyst showed no loss of catalytic activity. Reusability of catalysts was also reported by several authors for etherification of glycerol with ethanol. The Amberlyst (A15) showed no loss of catalytic activity even after three catalytic runs. However, zeolite (BEA 12.5), HPW/SiO₂, and arenesulfonic acid-functionalized mesostructured silica showed reduced catalytic activity compared to fresh catalysts [1,5,32].

Kinetic Modelling

The etherification of glycerol (G) with ethanol (E) results in the formation of GME, GDE, GTE, DEE, and water (W) as represented by Scheme 1. In this work, an empirical kinetic model was developed considering etherification as overall second order reactions. Accordingly, the rate of formation of glycerol, ethanol, DEE, GME, GDE, GTE, and W are represented by following equations.

Table 8. Effect of temperature on products selectivity.^a

Temperature, K	selectivity, %			
	GME	GDE	GTE	DEE
393	94.7	3.2	2.1	86.0

403	89.3	4.2	6.5	83.7
413	93.5	3.5	3.0	86.2
423	95.0	2.9	2.1	84.9

^a Conditions: matching glycerol conversion = 1%; all other conditions are same as in Fig. 6.

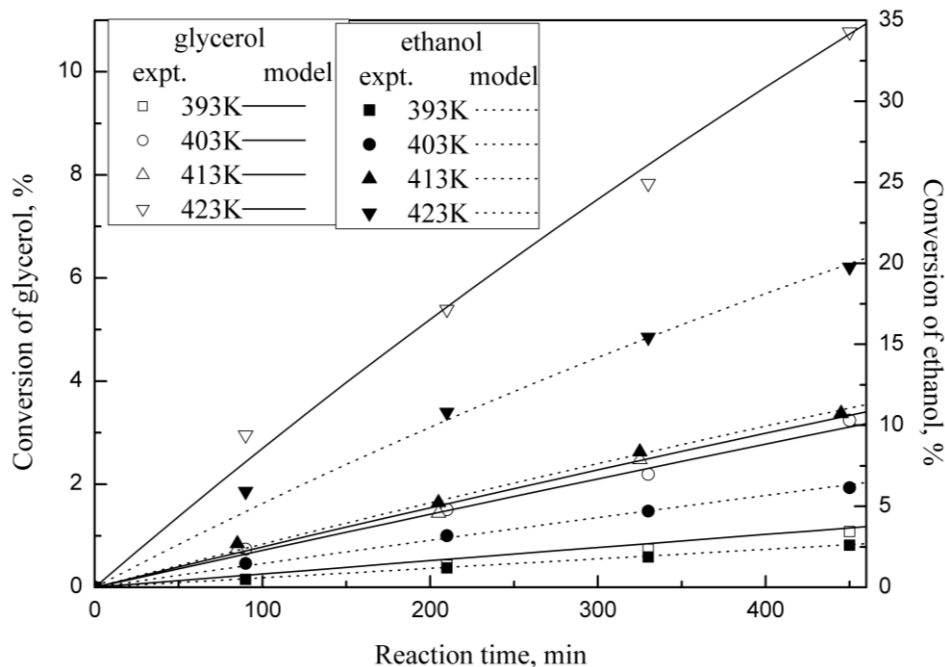


Fig. 6. Comparison of experimental and calculated conversion of glycerol and ethanol at different temperature. Conditions: catalyst = CER; catalyst loading = 1.0 (w/v)%; initial nitrogen pressure = 10 bar; glycerol concentration = 4.1 kmol/m³; ethanol concentration = 12.0 kmol/m³.

$$r_G = -k_1 C_G C_E \quad (4)$$

$$r_E = -k_1 C_G C_E - k_2 C_{GME} C_E - k_3 C_{GDE} C_E - k_4 C_E^2 \quad (5)$$

$$r_{DEE} = \frac{k_4}{2} C_E^2 \quad (6)$$

$$r_{GME} = k_1 C_G C_E - k_2 C_{GME} C_E \quad (7)$$

$$r_{GDE} = k_2 C_{GME} C_E - k_3 C_{GDE} C_E \quad (8)$$

$$r_{GTE} = k_3 C_{GDE} C_E \quad (9)$$

$$r_W = k_1 C_G C_E + k_2 C_{GME} C_E + k_3 C_{GDE} C_E + \frac{k_4}{2} C_E^2 \quad (10)$$

Kinetic Studies

The kinetic studies of etherification of glycerol with ethanol were performed in presence of CER at four different reaction temperature, 393 K, 403 K, 413 K and 423 K under identical experimental conditions. The strongly acidic CER is thermal stable only up to 423K. Therefore, the kinetic study was limited only up to 423 K. The effect of temperature on conversion of reactants and selectivity to different products are shown in Fig. 6 and Table 8 respectively. As observed from the Fig. 6, the conversion of both ethanol and glycerol increased with increasing temperature. The selectivity to different products was almost unaffected by temperature as observed from the table. Based on the experimental results, the initial rate of reaction of both glycerol and ethanol were calculated at different temperature and a plot of $\ln(r_0)$ versus $1/T$ was made. The apparent activation energy of the reaction was then calculated from the slope of the best fitted straight

line as shown in Fig. 7. The apparent activation energies of glycerol and ethanol were found to be 25.1 and 26.6 kcal/mol respectively. The high value of activation energy further confirms that the reaction is kinetically controlled. The rate constants of the developed kinetic model were estimated using the experimental data at four different temperature by non-linear regression algorithm based on modified Levenberg–Marquardt. The objective function, F , of Eq. (11) was minimized.

$$F = \sum_{i=1}^N \left(\frac{C_{G,i}^{\text{expt}} - C_{G,i}^{\text{model}}}{C_{G,i}^{\text{expt}}} \right)^2 + \sum_{i=1}^N \left(\frac{C_{E,i}^{\text{expt}} - C_{E,i}^{\text{model}}}{C_{E,i}^{\text{expt}}} \right)^2 + \sum_{i=1}^N \left(\frac{C_{DEE,i}^{\text{expt}} - C_{DEE,i}^{\text{model}}}{C_{DEE,i}^{\text{expt}}} \right)^2 + \sum_{i=1}^N \left(\frac{C_{GME,i}^{\text{expt}} - C_{GME,i}^{\text{model}}}{C_{GME,i}^{\text{expt}}} \right)^2 + \sum_{i=1}^N \left(\frac{C_{GDE,i}^{\text{expt}} - C_{GDE,i}^{\text{model}}}{C_{GDE,i}^{\text{expt}}} \right)^2 + \sum_{i=1}^N \left(\frac{C_{GTE,i}^{\text{expt}} - C_{GTE,i}^{\text{model}}}{C_{GTE,i}^{\text{expt}}} \right)^2 + \sum_{i=1}^N \left(\frac{C_{W,i}^{\text{expt}} - C_{W,i}^{\text{model}}}{C_{W,i}^{\text{expt}}} \right)^2 \quad (11)$$

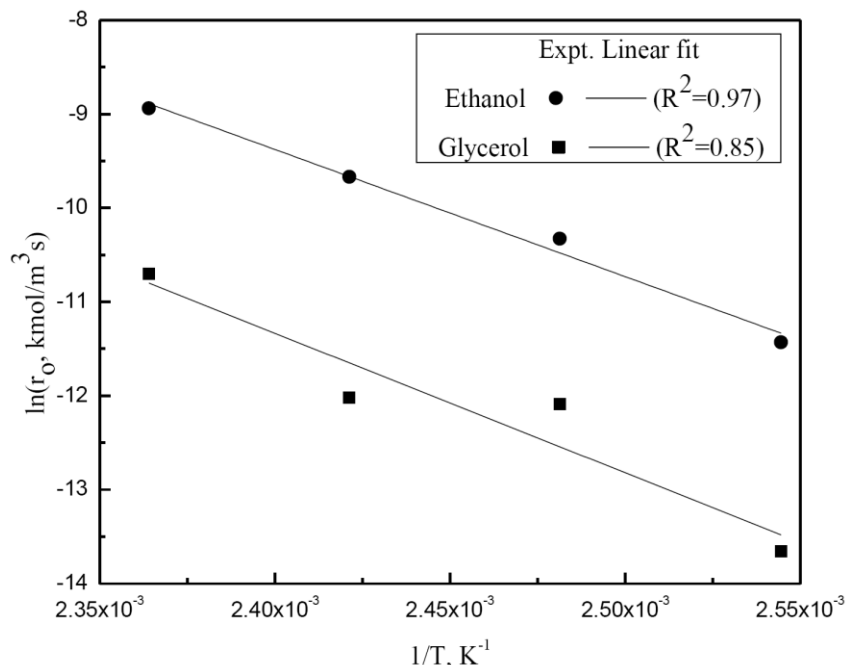


Fig. 7. Apparent activation energy plot of $\ln(r_0)$ versus $1/T$.

Table 9. Rate constants at different temperature and activation energies and pre-exponential factor of the rate constants.

rate constants, m ³ /kmol s	temperature, K				pre-exponential factor, m ³ /kmol s	activation energy, kcal/mol
	393	403	413	423		
k ₁	3.9 × 10 ⁻⁰⁸	1.09 × 10 ⁻⁰⁷	1.23 × 10 ⁻⁰⁷	4.38 × 10 ⁻⁰⁷	1.28 × 10 ⁰⁶	24.27
k ₂	8.9 × 10 ⁻⁰⁸	8.99 × 10 ⁻⁰⁸	9.00 × 10 ⁻⁰⁸	9.04 × 10 ⁻⁰⁸	-	-
k ₃	9.50 × 10 ⁻⁰⁷	1.00 × 10 ⁻⁰⁶	1.50 × 10 ⁻⁰⁶	2.90 × 10 ⁻⁰⁶	-	-
k ₄	3.72 × 10 ⁻⁰⁸	9.44 × 10 ⁻⁰⁸	1.89 × 10 ⁻⁰⁷	3.49 × 10 ⁻⁰⁷	1.76 × 10 ⁰⁶	24.53

The estimated rate constants at different temperature are shown in Table 9. As observed from the table, the value of the rate constants increased with increasing temperature as expected. An Arrhenius plot of $\ln(r_0)$ versus $1/T$ was then made using two significant rate constants (k_1 and k_4) (Fig. S3). The activation energy and pre-exponential factor were obtained from the slope and intercept of the Arrhenius plot respectively as shown in Table 9. The activation energy is comparable with the apparent activation energy. Furthermore, the concentrations of the reactants and products were calculated at various reaction times using the estimated rate constants at different temperature. The experimental and calculated conversion of glycerol and ethanol at different temperature were then compared (Fig. 6) and a fairly decent agreement was observed between calculated and experimental results.

CONCLUSIONS

The etherification of glycerol with ethanol was examined under liquid phase in a high pressure stainless steel batch reactor over two different types of solid acid catalysts (zeolites and CER). The CER showed superior catalytic activity over H-beta zeolite. The detailed kinetic study was performed using CER. The reaction was free from external mass transfer resistance. The high ethanol-to-glycerol mole ratio directed to undesirable DEE as the major product. The selectivity to ethyl ethers of glycerol however enhanced considerably with decreasing ethanol-to-glycerol mole ratio. The conversion of reactants increased with increasing catalyst loading and temperature without affecting the selectivity to products meaningfully. An empirical kinetic model was developed and rate constants of the kinetic model were estimated using the experimental data at different temperature by non-linear least square techniques. The conversion of the reactants calculated based on estimated rate constants were then compared with experimental data and reasonably good agreement between experimental and calculated conversion was observed. The activation energies and frequency factors of the rate constants were then determined from slope and intercept of the Arrhenius plot of $\ln(k)$ versus $1/T$ respectively.

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ABBREVIATION

CER	cation exchange resin
DEE	diethyl ether
GME	glycerol monoethyl ether
GDE	glycerol diethyl ether
GTE	glycerol triethyl ether
k_1 - k_4	rate constants, $(\text{kmol.m}^{-3})^{-1} \text{ s}^{-1}$
W	water

REFERENCES

- [1] Melero, J., Vicente, G., Paniagua, M., Morales, G. and Munoz, P., "Etherification of Biodiesel-Derived Glycerol with Ethanol for Fuel Formulation over Sulfonic Modified Catalysts", *Bioresour. Technol.*, **103(1)**, pp. 142-51 (2012).
- [2] Duane, J.T. and Katherine, T.A., "The Glycerine Glut: Options for the Value-Added Conversion of Crude Glycerol Resulting from Biodiesel Production", *Environ. Prog.*, **26**, pp. 338-48 (2007).
- [3] Gu, Y., Azzouzi, A. and Pouilloux, Y., "Heterogeneously Catalyzed Etherification of Glycerol: New Pathways for Transformation of Glycerol to More Valuable Chemicals", *Green Chem.*, **10**, pp. 164-167 (2008).
- [4] Rahmat, N., Abdullah, Z.A. and Mohamed, R.A., "Recent Progress on Innovative and Potential Technologies for Glycerol Transformation into Fuel Additives: A Critical Review", *Renew. Sust. Energ. Rev.*, **14**, pp. 987-1000 (2010).
- [5] Pariente, S. and Tanchoux, N., "Etherification of Glycerol with Ethanol over Solid Acid Catalysts", *Green Chem.*, **11**, pp. 1256-1261 (2009).
- [6] Maity, S.K., "Opportunities, Recent Trends and Challenges of Integrated Biorefinery: Part I", *Renew. Sust. Energ. Rev.*, **43**, pp. 1427-1445 (2015).
- [7] Maity, S.K., "Opportunities, Recent Trends and Challenges of Integrated Biorefinery: Part II", *Renew. Sust. Energ. Rev.*, **43**, pp. 1446-1466 (2015).
- [8] Kesling, S.H., Karas, J. L. and Liotta, F. J., *U. S. Pat.* **5**, 308, 365 (1994).
- [9] Nouredini, H., *U. S. Pat.* **6**, 174, 501 (2001).
- [10] Klepacova, K., Mravec, D. and Bajus, M., "Butylation of Glycerol Catalysed by Ion-Exchange Resins", *Appl. Catal. A: Gen.*, **294**, pp. 141-147 (2005).
- [11] Karinen, S.R. and Krause, I.O., "New Biocomponents from Glycerol", *Appl. Catal. A: Gen.*, **306**, 128-133 (2006).
- [12] Shawl, T.E. and Kesling, S. H., *U. S. Pat.* **5**, 413, 634 (1995).
- [13] Melero, A.J., Vicente, G., Morales, G., Paniagua, M. and Bustamante, J., "Oxygenated Compounds Derived from Glycerol for Biodiesel Formulation: Influence on EN 14214 Quality Parameters", *Fuel*, **89**, pp. 2011-2018 (2010).

- [14] Goncalves, C.L.V., Pinto, P.B., Silva, C.J. and Mota, A.J.C., "Acetylation of Glycerol Catalyzed by Different Solid Acids", *Catal. Today*, **133**, pp. 673–677 (2008).
- [15] Pouilloux, Y., Abro, S., Vanhove, C. and Barrault, J., "Reaction of Glycerol with Fatty Acids in the Presence of Ion-Exchange Resins Preparation of Monoglycerides", *J. Mol. Catal. A: Chem.*, **149**, pp. 243–254 (1999).
- [16] Melero, A.J., Grieken, V.R., Morales, G. and Paniagua, M., "Acidic Mesoporous Silica for the Acetylation of Glycerol: Synthesis of Bioadditives to Petrol Fuel", *Energ. Fuels*, **21**, pp. 1782-1791 (2007).
- [17] Ferreira, P., Fonseca, M.I., Ramos, M.A., Vital, J. and Castanheiro, E.J., "Environmental Glycerol Acetylation over Dodecatungstophosphoric Acid Immobilized into A Silica Matrix as Catalyst", *Appl. Catal. B: Environ.*, **91**, pp. 416-422 (2009).
- [18] Ferreira, P., Fonseca, M.I., Ramos, M.A., Vital, J. and Castanheiro, E.J., "Esterification of Glycerol with Acetic Acid over Dodecamolybdophosphoric Acid Encaged in USY Zeolite", *Catal. Commun.*, **10**, pp. 481-484 (2009).
- [19] Balaraju, M., Nikhitha, P., Jagadeeswaraiah, K., Srilatha, K., Prasad, S.S.P. and Lingaiah, N., "Acetylation of Glycerol to Synthesize Bioadditives over Niobic Acid Supported Tungstophosphoric Acid Catalysts", *Fuel Process. Technol.*, **91**, pp. 249-253 (2010).
- [20] Jagadeeswaraiah, K., Balaraju, M., Prasad, S.S.P. and Lingaiah, N., "Selective Esterification of Glycerol to Bioadditives over Heteropoly Tungstate Supported on Cs-Containing Zirconia Catalysts", *Appl. Catal. A: Gen.*, **386**, pp. 166-170 (2010).
- [21] Reddy, S.P., Sudarsanam, P., Raju, G. and Reddy, M.B., "Synthesis of Bio-Additives: Acetylation of Glycerol over Zirconia-Based Solid Acid Catalysts", *Catal. Commun.*, **11**, pp. 1224–1228 (2010).
- [22] Xiao, L., Mao, J., Zhou, J., Guo, X. and Zhang, S., "Enhanced Performance of HY Zeolites by Acid Wash for Glycerol Etherification with Isobutene", *Appl. Catal. A: Gen.*, **393**, pp. 88-95 (2011).
- [23] Lee, J.H., Seung, D., Filimonov, N.I. and Kim, H., "Etherification of Glycerol by Isobutylene: Effects of the Density of Acidic Sites in Ion-Exchange Resin on the Distribution of Products", *Korean J. Chem. Eng.*, **28**, pp. 756-762 (2011).
- [24] Lee, J.H., Seung, D., Jung, S.K., Kim, H. and Filimonov, N.I., "Etherification of Glycerol by Isobutylene: Tuning the Product Composition", *Appl. Catal. A: Gen.*, **390**, pp. 235-244 (2010).
- [25] Serio, M.D., Casale, L., Tesser, R. and Santacesaria, E., "New Process for the Production of Glycerol tert-Butyl Ethers", *Energ. Fuels*, **24**, pp. 4668-4672 (2010).
- [26] Ancillotti, F. and Fattore, V., "Oxygenate Fuels: Market Expansion and Catalytic Aspect of Synthesis", *Fuel Process. Technol.*, **57**, pp. 163-194 (1998).
- [27] Liu, J., Yang, B., and Yi, C., "Kinetic Study of Glycerol Etherification with Isobutene", *Ind. Eng. Chem. Res.*, **52**, pp. 3742-3751 (2013).
- [28] Zhou, J., Wang, Y., Guo, X., Mao, J. and Zhang, S., "Etherification of Glycerol with Isobutene on Sulfonated Graphene: Reaction and Separation", *Green Chem.*, **16**, pp. 4669-4679 (2014).
- [29] Singh, J., Kumar, J., Negi, M.S., Bangwal, D., Kaul, S. and Garg, M.O., "Kinetics and Modeling Study on Etherification of Glycerol Using Isobutylene by in Situ Production from tert -Butyl Alcohol", *Ind. Eng. Chem. Res.*, **54**, pp. 5213-5219 (2015).
- [30] Klepacova, K., Mravec, D., Kaszonyi, A. and Bajus, M., "Etherification of Glycerol and Ethylene Glycol by Isobutylene", *Appl. Catal. A: Gen.*, **328**, pp. 1-13 (2007).
- [31] Harmer, A.M. and Sun, Q., "Solid Acid Catalysis using Ion-Exchange Resins", *Appl. Catal. A: Gen.*, **221**, pp. 45-62 (2001).
- [32] Yuan, Z., Xia, S., Chen, P., Hou, Z., and Zheng, X., "Etherification of Biodiesel-Based Glycerol with Bioethanol over Tungstophosphoric Acid to Synthesize Glyceryl Ethers", *Energ. Fuels*, **25**, pp. 3186-3191 (2011).
- [33] Varisli, D., Dogu, T. and Dogu, G., "Ethylene and Diethyl-Ether Production by Dehydration Reaction of Ethanol over Different Heteropolyacid Catalysts", *Chem. Eng. Sci.*, **62**, pp. 5349-5352 (2007).
- [34] Vanoye, L., Zanota, M., Desgranges, A., Reguillon, F.A. and Bellefon, D.C., "Solvent Effects in Liquid-Phase Dehydration Reaction of Ethanol to Diethylether Catalysed by Sulfonic-Acid Catalyst", *Appl. Catal. A: Gen.*, **394**, pp. 276-280 (2011).