

# Viable Glycerol Carbonate Synthesis Through Direct Crude Glycerol Utilization from Biodiesel Industry

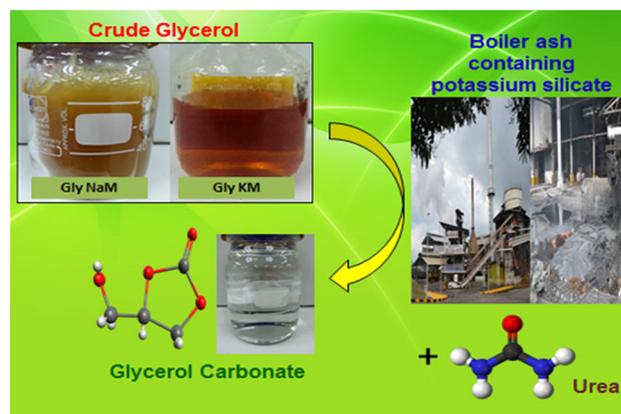
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**Abstract** Synthesis of organic carbonates specifically glycerol carbonate has become a major concern among researchers due to its interesting chemical properties. In this study, we report the direct utilization of two different sources of crude glycerol in glycerolysis reaction with urea for the synthesis of glycerol carbonate using potassium silicate containing boiler ash as a catalyst. The level of interference of moisture and methanol content in crude glycerol was studied by mimicking conditions in pure glycerol and it was found that moisture at 10 wt% significantly effects the conversion of glycerol while methanol at 5 wt% affects the selectivity towards glycerol carbonate. However, due to the low moisture and methanol content in crude glycerol, comparable yield % of glycerol carbonate with commercial pure glycerol as starting feedstock was noted. Besides, the study also found that the potassium methylate and sodium methylate used as catalysts for the commercial production of biodiesel can be also used as an effective catalyst for the synthesis of glycerol carbonate. The current approach is a near approach for a greener

environment which proposes use of both catalyst and glycerol derived from waste sources.

## Graphical Abstract



**Keywords** Crude glycerol · Glycerol carbonate · Boiler ash · Impurities · Potassium silicate · Industrial waste

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## Introduction

Globally, the production of biodiesel as an alternative energy source is growing due to demand from depletion of fossil fuel [1]. Biodiesel is a product from transesterification of vegetable oils or animal fats using methanol catalyzed by potassium hydroxide or sodium hydroxide [2, 3]. Crude glycerol is the major by-product formed from biodiesel production [4]. It is believed that for every 100 wt% of biodiesel produced 10 wt% of glycerol is produced as the by-product [5, 6]. In recent times, synthesis of glycerol carbonate from glycerol has interest

many researchers across the world. This scenario is due to the surplus of by-product formation of glycerol from the growing biodiesel industries [6]. Glycerol carbonate has variety of interesting applications in industries such as in the polymer, pharmaceuticals, chemicals and agricultural industries [7].

The root of glycerol carbonate production involved the use of phosgene a toxic chemical as a carbonate source which was later replaced with other safer carbonate sources such as ethylene carbonate, propylene carbonate, dimethyl carbonate and diethyl carbonate due to hazard issues associated with the phosgenation reaction [8, 9]. In this study we report the possibility of directly converting crude glycerol into glycerol carbonate without any prior purification treatment on crude glycerol. Most of the available works on synthesis of glycerol carbonate either utilized commercial glycerol as a starting feedstock or uses crude glycerol after purification process in glycerolysis reaction with synthetic catalyst [10–12]. In addition, review by Galadima and Muraza [13] suggests that purification of glycerol is necessary before being utilized in transcarnation reaction. One of the main reason hindered the direct use of crude glycerol is due to presence of impurities such as soap, moisture, methanol, oils, ash and MONG [14, 15] which is expected to affect transformation of glycerol into value added chemicals. Therefore, to introduce an economical synthesis approach for the current scenario, boiler ash from palm oil industry introduced in our previous study was used as catalyst along with commercial potassium silicate in direct glycerolysis reaction with crude glycerol as well as urea [16, 17]. Even though, there are a few studies that has reported production of glycerol carbonate through use of direct crude glycerol as feedstock, these studies suggested use of different synthesis route such as microwave assisted technique, different carbonate sources such as DMC and use of catalyst derived synthetically [18, 19]. In addition, the reaction involving glycerolysis of crude glycerol involves purification through separation of soap before actually being transformed into glycerol carbonate [19]. Hence, the use of bio-renewable feedstock crude glycerol directly without purification and urea along with catalyst derived from boiler ash from oil palm industry is expected to pave through a new economical and nearer approach to green synthesis. On the other hand, potassium methylate and sodium methylate catalysts used in biodiesel industry were also used as catalysts to study the possibility of using the same catalyst concurrently for both biodiesel production and glycerol carbonate production.

## Experimental

### Materials

Crude glycerol, potassium methylate and sodium methylate was obtained from Biodiesel Production Plant, Selangor, Malaysia. Glycerol (99.5 %) and Urea (AR Grade) was purchased from Friendemann Schmidt Chemical. Waste boiler ash used as the catalyst was collected from a palm oil mill located in Lepar Hilir, Pahang, Malaysia. The boiler ash used is the ash obtained from incineration of palm fruits, palm kernel, palm shells and palm fiber. Potassium Silicate ( $K_2SiO_3$ )  $\geq 99.9$  % used was purchased from Sigma-Aldrich. Methanol ACS Reagent,  $\geq 99.8$  % was purchased from Sigma Aldrich.

### Catalyst Preparation and Characterization

Boiler ash collected from local palm oil industry located in Lepar Hilir, Pahang Malaysia was dried at 110 °C and sieved using 200  $\mu$ m size sieves. The catalyst was later calcined at 900 °C for 4 h and labelled as BA 900. The active sites and element responsible for the catalytic behaviour of waste boiler ash were studied and reported in our previous work using a series of catalyst characterisation technique which involves use of Fourier Transform Infrared Spectroscopy (FTIR), Hammett test, Temperature Programmed Desorption-Carbon Dioxide (TPD- $CO_2$ ), X-Ray Diffraction (XRD), Inductively Couple Plasma-Mass Spectroscopy (ICP-MS), Brunauer Emmett Teller (BET), Thermogravimetry (TGA) and Field Emission Scanning Microscopy-Energy Dispersive X-ray (FESEM-EDX) [16]. Potassium silicate purchased from Sigma Aldrich was used directly in this study without any prior pretreatment. Sodium methylate and potassium methylate obtained from biodiesel industry were also directly used with any pretreatment. The Hammett test were carried out on potassium methylate and sodium methylate where phenolphthalein, 2,4-dinitroaniline, 4-nitroaniline and methyl red were used as indicators to determine the qualitative acidic as well as basic properties of the catalyst. 25 mg of catalysts were weighed and prepared in three batches and 5 mL of methanol was added to the catalyst. Then, 1 mL of the indicator was added to 4 mL of methanol with the final volume of 5 mL indicators were added separately to the catalysts weighed in batches. The mixture was then let to equilibrate for 2 h and the colour changes were observed and noted.

### Catalytic Testing of Crude Glycerol

The experiment was conducted using a three-neck 100 mL round bottom flask attached to a cycle condenser with continuous flow of water. Typically, 150 mmol of crude glycerol was allowed to heat up to 150 °C for under the flow of nitrogen gas for 20 min. The molar ratio of crude glycerol to urea used was (1:1.5). Sampling was done from 0 to 10 h (typical or otherwise mentioned) with the time interval of 1 h. 50 µL of sample was transferred in 1450 µL of deionized water. Blank reaction was conducted in absence of catalyst with similar parameter. The experiment was repeated three times for repeatability study.

### Catalytic Testing of Simulated Glycerol

Simulated crude glycerol study is required in order to assess the possible effect of major impurities available in crude glycerol which influences the overall catalytic activity. The reaction was conducted as the method described in the procedure of catalytic testing of crude glycerol. Typically, 150 mmol of pure glycerol simulated with maximum 10 wt% of water, 5 wt% of methanol, mixture of water and methanol at 10 and 5 wt% as well as 3.15 and 0.8 wt% respectively in accordance to the obtained certificate of analysis. Other simulations also include 1.6 wt% of sodium methylate and 1.6 wt% potassium methylate in 150 mmol glycerol respectively. The molar ratio of glycerol to urea used was (1:1.5). Sampling was done from 0 to 10 h (typical or otherwise mentioned) with the time interval of 1 h. 50 µL of sample was transferred in 1450 µL of deionized water. The experiment was repeated three times for repeatability study.

### Moisture Analysis of Pure Glycerol Simulated with 10 wt% Water

The moisture analysis of glycerol simulated with 10 wt% deionized water was carried using 870 KF Tritino Plus. The sample was analyzed based on the method of Mehtrohm Moisture Analyzer. When the drift value is below 20 and without fluctuation, the 870 KF Titrino Plus was set as ready for sample injection. The weighing spoon was tarred to zero, and then 2 mL of sample was introduced by sample addition. The instrument measures the sample weight and sample weight was keyed in. The sample solution was then titrated until the end point was reach and result was shown on the screen in %. The analysis was repeated three times using the same procedure for repeatable results.

### Product Analysis

Gas Chromatography-Flame Ionized Detector (GC-FID) Agilent Technologies 7890A equipped with Varian Capillary Column, CP-PoraBOND Q (25 m, 0.53 mm, 10 µm) was used to analyze the liquid product of reaction. The temperature of the injector and the detector were 225 and 250 °C, respectively. The temperature of the column was programmed to have a 2 min initial hold at 80 °C, then 10 °C/min ramp from 80 to 250 and 15 °C/min ramp from 250 to 300 °C with 3 min hold time. The split ratio was 1:10 and injection volume was 1 µL. ATR-FTIR Perkin Elmer USA was used to study the functional group present in the time online analysis of the product from 0 min to 10 h, which could attribute to the product and by-product that is also present in the reaction mixture as a validation. A single drop of reaction mixture was placed on the liquid holder and the transmission data were collected in the range of 4000–700 cm<sup>-1</sup>. NMR, BRUKER Ultra Shield Plus 500 MHz was also used to study the <sup>13</sup>C NMR of the products formed.

## Results and Discussion

### Analysis of Crude Glycerol

In this study, two different sources of crude glycerol were obtained from the commercial biodiesel plant located in Selangor, Malaysia. The crude glycerol was classified based on the different type of catalysts used for the biodiesel transesterification process. The catalysts were sodium methylate, (crude glycerol denoted as Gly NaM) and potassium methylate (crude glycerol denoted as Gly KM). Scheme 1, illustrates the biodiesel synthesis route of the stated commercial biodiesel plant. The crude glycerol typically contained several compounds and impurities which originated from the parent feedstock used such as refined bleached deodorized palm oil, methanol and catalyst (sodium methylate or potassium methylate) in the biodiesel production process. Thus, an analysis carried out on that particular crude glycerol was necessary. The information should be obtained before any meaningful catalytic testing can be carried out.

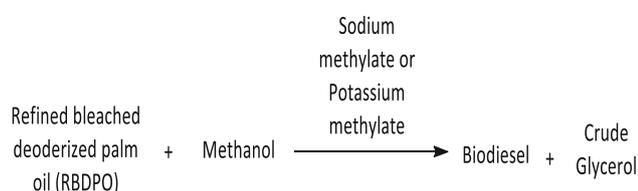
The detailed analysis results involving total glycerol content, moisture, soap, methanol, ester, ash and matter of organic content non-glycerol (MONG) was carried out and summarized in (Table 1). It was also found that the catalyst present in both crudes were 1.6 wt% respectively for both Gly NaM and Gly KM based on the initial loading of catalyst to produce biodiesel fuels.

## Catalytic Synthesis of Glycerol Carbonates Using Different Sources of Crude Glycerol

The development of catalytic system whereby the direct utilization of industrial crude glycerol without any pre-treatment step will significantly contribute to a more economical process and subsequently reduce the total production cost of glycerol carbonate. For that purpose, two different sources of crude glycerol obtained from the commercial biodiesel plant were tested as a feedstock for the production of glycerol carbonate as the target product. For the record, potassium methylate and sodium methylate is the key catalysts used in the current biodiesel industry in which the sample of crude glycerol is collected. Therefore, studying the effect of both methylate catalysts presence in the respective crude glycerol is crucial in order to investigate their catalytic effect towards glycerol carbonate yield. Besides, it is worthy to note that that very limited studies have been reported to directly use crude glycerol for the synthesis of glycerol carbonate [20]. Nguyen and Demirel, in 2011 reported that crude glycerol eluted in the biodiesel plant can be converted into value added glycerol carbonate using glycerolysis reaction with urea. However, the study suggested use of non-economical catalyst such as  $\text{La}_2\text{O}_3$  calcined at 600 °C and under reduced pressure. On the other hand, Teng et al. [18], reviewed that the use of microwave assisted glycerolysis gives prominent results with crude glycerol. However, fundamentally the application has not been used in industry yet due to the limitations of microwave technology that cannot penetrate through larger volume of samples as reported by Strum et al. [21]. In this case, we introduced the utilization of BA 900 containing  $\text{K}_2\text{SiO}_3$  and commercial  $\text{K}_2\text{SiO}_3$  as catalysts in glycerolysis reaction of direct crude glycerol with urea. Besides, the simulated blank reaction without presence of any of the aforementioned catalysts was carried out to establish the baseline reaction data.

### Synthesis of Glycerol Carbonate Using Crude Glycerol (Gly NaM)

Figure 1a illustrates the time online analysis (TOL) of crude glycerol (Gly NaM) in blank reaction without presence of any catalyst compared with the study of blank with



**Scheme 1** Feedstock and catalysts used for synthesis of biodiesel in Artistic Support Sdn. Bhd

**Table 1** Certificate of analysis (COA) of crude glycerol

Test	Specification (%) <sup>a</sup>	Result (%)
Glycerol content	75 Min	81.0
Moisture	10 Max	3.15
Soap content	25 Max	22.0
Methanol	5 Max	0.80
Oil (as ester)	5 Max	0.29
Ash content	15 Max	4.0
MONG <sup>b</sup>	15 Max	13.0

The results show the real average value obtained through analysis of both crude glycerol Gly NaM and Gly KM

<sup>a</sup> *Min* minimum and *Max* maximum represent the specification of the allowable limit on the content of glycerol and impurities

<sup>b</sup> MONG analyzed includes [sucrose, fructose, free fatty acids (myristic, palmitic, stearic, oleic and linoleic), diglycerides as well as triglycerides]

commercial pure glycerol. From the analysis, it was found that blank reaction of crude glycerol (Gly NaM) with urea showed maximum conversion of glycerol at  $88.3 \pm 0.5 \%$ , selectivity of glycerol carbonate at  $40.2 \pm 0.7 \%$ , and yield of glycerol carbonate at  $35.5 \pm 0.9 \%$  within 4 h of reaction time. In contrast, similar reaction with purified commercial glycerol (99.5 % purity) showed lower glycerol conversion and glycerol carbonate yield. The value of conversion of commercial glycerol was  $78.7 \pm 0.6 \%$ , selectivity and yield of glycerol carbonate was  $32.8 \pm 0.9 \%$  as well as  $25.8 \pm 0.7$ . It is believed that the sodium methylate contained in the crude glycerol NaM might have contributed to the reactions to have higher conversion, selectivity and yields. Sodium methylate contained in the crude glycerol can provide suitable active sites to catalyze the reaction to produce glycerol carbonate. Moreover, there is no available published works reported for the non-catalyzed reaction with crude glycerol as feedstock to synthesize glycerol carbonate through glycerolysis reaction with urea.

Figure 1b, c, clearly showed the significant role of BA 900 and  $\text{K}_2\text{SiO}_3$  catalysts in improving the glycerol conversion and yield of glycerol carbonate. On top of that, it was found that crude Gly NaM with BA 900 and  $\text{K}_2\text{SiO}_3$  showed almost similar catalytic data and TOL pattern, thus further confirmed the previously reported findings [16, 17] in which the catalytic activity and selectivity of boiler ash is mainly influenced by potassium silicate as active material. However, the results of selectivity and yield reported are lower than catalyst testing conducted using commercial glycerol. The presence of other substances in crude glycerol as summarized in Table 1 might contribute to the inferior catalytic data.

## Synthesis of Glycerol Carbonate Using Crude Glycerol (Gly KM)

Figure 1d illustrates the time online analysis of crude glycerol (Gly KM) without presence any catalyst. From the analysis it was found that blank reaction of crude glycerol (Gly KM) with urea showed maximum conversion of glycerol at  $84.3 \pm 0.6$  %, selectivity of glycerol carbonate at  $68.1 \pm 0.3$ , and yield of glycerol carbonate at  $57.5 \pm 0.5$  with 4 h reaction time. These results of selectivity and yield were comparably higher than analogue reaction with crude Gly NaM. It is believed that potassium methylate expresses better catalytic activity compared to sodium methylate. Potassium has an electron further from the nucleus compared to sodium. Therefore, the electron is easily lost to form  $K^+$  which acts as weak Lewis acid to catalyze the reaction. Besides, the strength of bond between potassium and methoxy group is also relatively weaker than sodium. Therefore, the higher ability of potassium ion to delocalize in the homogeneous reaction gives better conversion, yield and selectivity. Moreover, in previous study it was found that potassium ion in any form along with its conjugated basic site can essentially catalyze the glycerolysis reaction with urea to form glycerol carbonate [16]. As discussed earlier, both BA 900 and  $K_2SiO_3$  show beneficial effect on enhancing the productivity of glycerol carbonate from crude glycerol (Gly NaM) and urea (Fig. 1e, f). Similar effect and TOL trend were also observed with utilization of Gly KM. However, glycerol conversion and glycerol carbonate yield for Gly KM as a starting feedstock are 20 % higher than as observed with Gly NaM. This phenomenon is likely due to the similar activity of the potassium ion contained in the crude Gly KM as discussed earlier. However, the results of selectivity and yield reported are still lower than the previous catalyst testing using commercial pure glycerol.

### Simulated Crude Glycerol Analysis

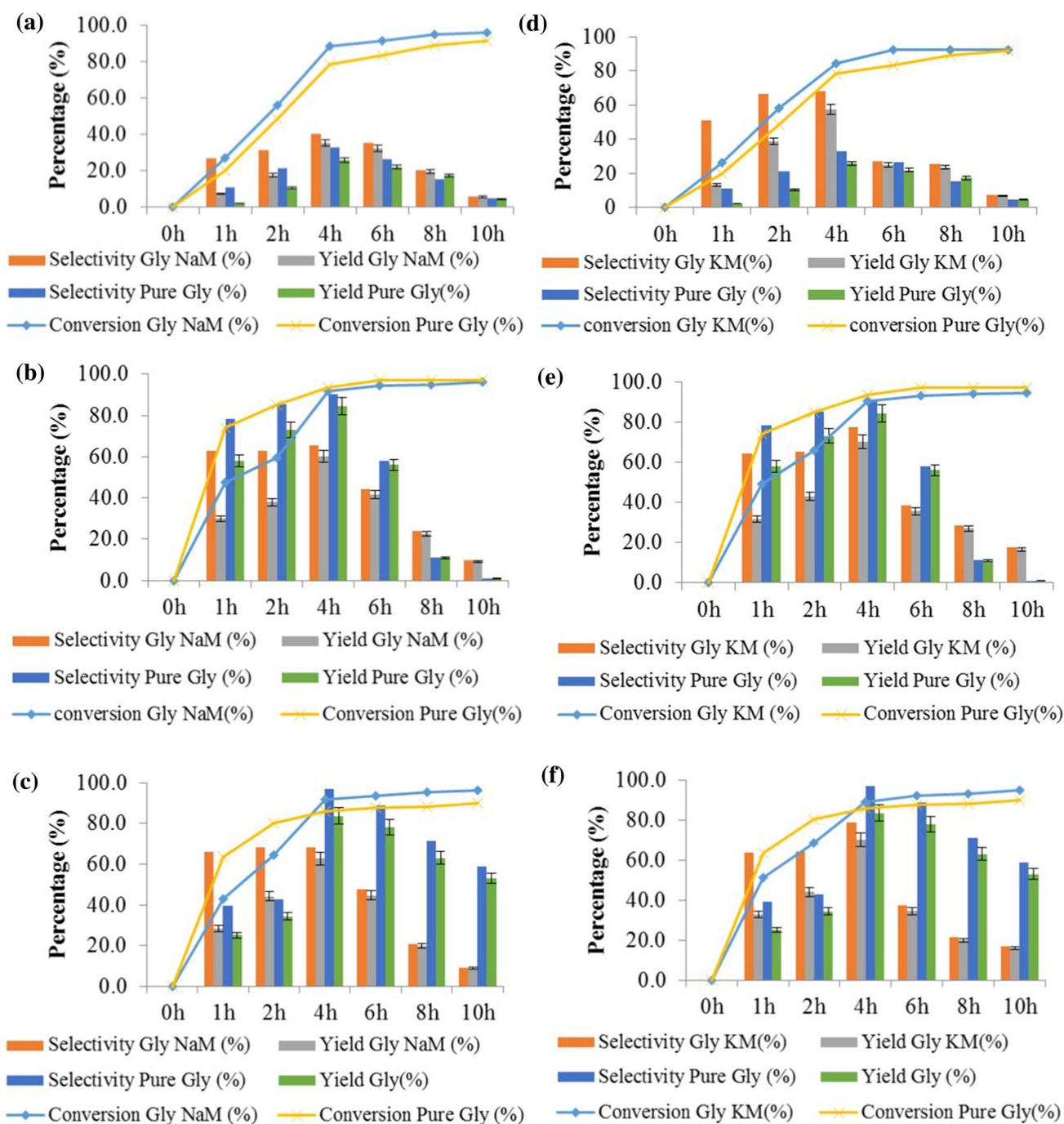
In order to figure out the effect of impurities in crude glycerol, further works were carried out to simulated the crude glycerol either by the introduce single or mixed as identified impurities into commercial glycerol solution. In details, these steps involved mimicking pure glycerol with 10 wt% of moisture (water), 5 wt% of methanol, 1.6 wt% of potassium methylate and 1.6 wt% of sodium methylate. The values of mimicking conditions for moisture and methanol content were extracted from certificate of analysis (COA) as listed in Table 1.

### Glycerol Simulated with 10 wt% of Water

It is evident from Fig. 2a that the presence of 10 wt% water influences the catalytic reaction whereby the conversion of glycerol was effected by almost 50 % drop comparing with the pure glycerol. Figure 2a illustrates the selectivity towards glycerol carbonate increased from 0 to 3 h. However, the poor conversion of glycerol causes the selectivity towards glycerol carbonate to decline after 3 h due to decomposition of glycerol carbonate into glycerol. Therefore, the yield of glycerol was affected by drop in conversion in which the reaction occurs reversibly in the presence of water. Similar observation were also reported by previous researchers [22, 23] This phenomenon can be explained through the stability of glycerol carbonate which is affected by water content. Glycerol carbonate containing water at prolonged time will transform into glycerol. This is clearly proven by the qualitative stability analysis of glycerol carbonate carried out using GC-FID (Fig. ESM 1). From the analysis, 0.4 M of glycerol carbonate containing in water transformed to glycerol after 1 week in storage at 8 °C. Besides, it is also reported that presence of water can cause equilibrium shift in the glycerol carbonate reaction due to hydrolysis [24]. Even though, the reaction is conducted at temperature higher than 100 °C, presence of water is still detected at 10 h as analyzed using Mehtrohm Moisture Analyzer (Table 2). Therefore, it can be expected that there is no complete loss of moisture. However, moisture content in both crude glycerol were reported to be 3.15 wt% only. Hence, this lower amount of moisture could be a pertinent factor which could have attributed to the conversion of glycerol to be higher in both crudes tested. In contrast, the presence of water at lower amount may have resulted in the slight drop in yield of glycerol carbonate synthesized using crude glycerol as reviewed by Teng et al. in 2014. Based on the ATR-FTIR analysis conducted (Fig. ESM 2), the moisture band –OH observed at 10 wt% of  $H_2O$  gradually decreases as duration of reaction increase from 0 to 10 h. Note that 0 h reading is taken after flowing nitrogen gas for 20 min at 150 °C. Thus, the loss of –OH band at range of ( $3200\text{--}3400\text{ cm}^{-1}$ ) due to loss of moisture is clearly evident. However, the formation of glycerol carbonate ( $1790\text{ cm}^{-1}$ ) was not clearly evident due to the poor conversion of glycerol inhibited by moisture in the sample.

### Glycerol Simulated with 5 wt% of Methanol

Figure 2b illustrates the effect of methanol content towards synthesis of glycerol carbonate. 5 wt% of pure methanol

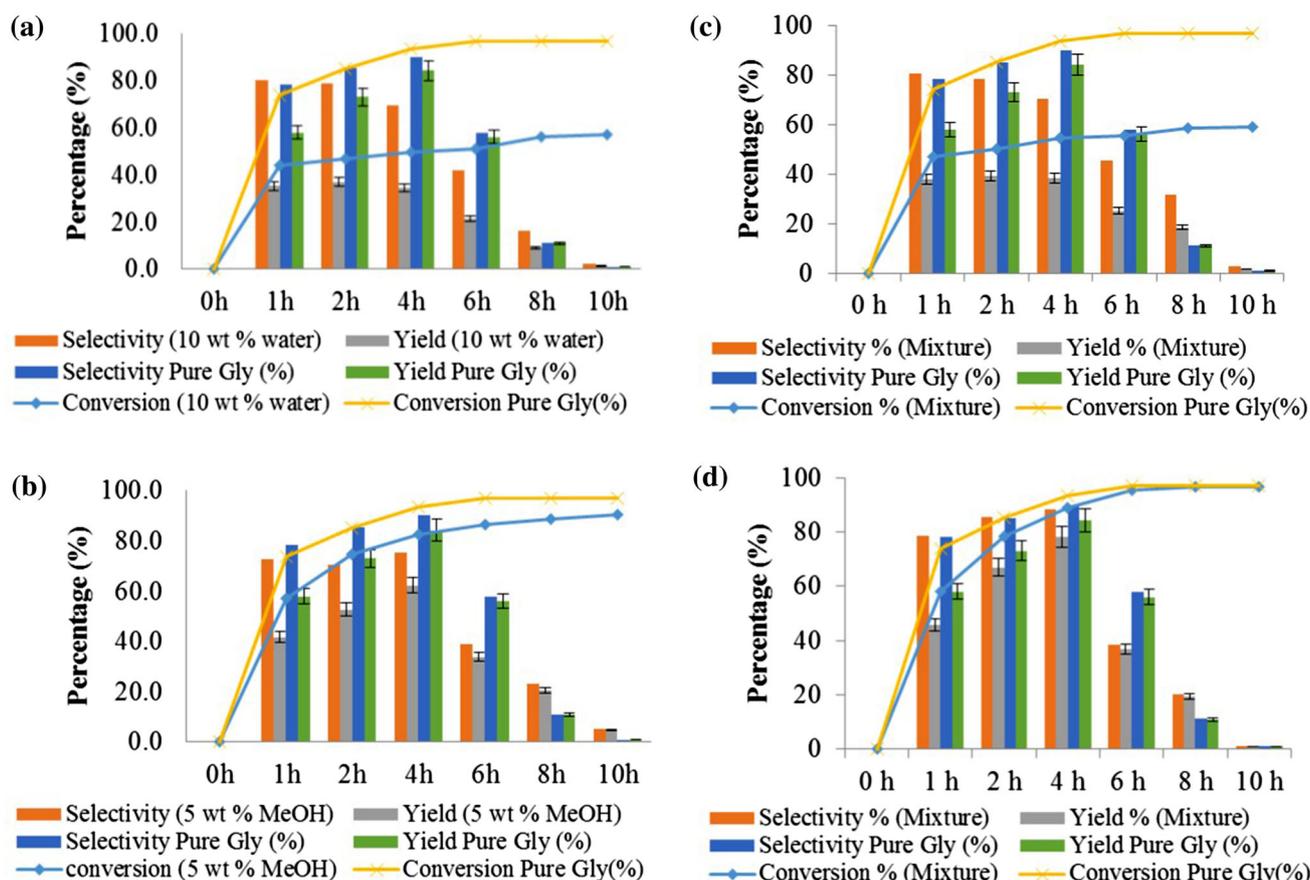


**Fig. 1** Time online analysis (TOL) of glycerol conversion (%), glycerol carbonate selectivity (%) and glycerol carbonate yield (%) of **a** crude Gly NaM blank and commercial pure glycerol (Pure Gly) blank; **b** crude Gly NaM and commercial pure glycerol (Pure Gly) with BA 900; **c** crude Gly NaM and commercial pure glycerol (Pure Gly) with  $K_2SiO_3$ ; **d** crude Gly KM blank and pure glycerol (Pure

Gly) blank; **e** crude Gly KM and commercial pure glycerol (Pure Gly) with BA900; **f** crude Gly NaM and commercial pure glycerol (Pure Gly) with  $K_2SiO_3$ . Reaction conditions: Temperature, 150 °C; Gas, Nitrogen; Glycerol: Urea, 1:1.5 (Molar ratio); Standard stirring rate, 340 rpm

was simulated in pure glycerol following specification of COA in Table 1. The 5 wt% methanol content in glycerol alters selectivity of glycerol carbonate as depicted in Fig. 2b but does not affect conversion of glycerol in the

overall process. Maximum selectivity of glycerol carbonate found was  $75.4 \pm 0.4$  % at 4 h reaction time. Based on the review by Teng et al. [7], presence of methanol can cause decomposition of glycerol carbonate into glycidol. Besides,



**Fig. 2** Time online analysis (TOL) of glycerol conversion (%), glycerol carbonate selectivity (%) and glycerol carbonate yield (%) of **a** glycerol mimic with 10 wt% water compared with the pure glycerol results; **b** glycerol mimic with 5 wt% methanol compared with pure glycerol results; **c** glycerol mimic with 10 wt% moisture and 5 wt%

methanol compared with pure glycerol results; **d** glycerol mimic with 3.15 wt% moisture and 0.8 wt% methanol compared with pure glycerol results. Reaction conditions: Temperature, 150 °C; Gas, Nitrogen; Glycerol: Urea, 1:1.5 (Molar ratio); Catalyst mass, 0.25 g of BA 900; Standard stirring rate, 340 rpm

study by González et al. [25], peak of epoxide belonging to glycidol should be observed at  $1254\text{ cm}^{-1}$ , stretching of C–O of oxirane group at  $909\text{ cm}^{-1}$  and stretching of C–O–C of oxirane group at  $846\text{ cm}^{-1}$ . In analysis of simulated glycerol with 5 wt% of methanol using ATR–FTIR, the formation of glycidol was detected at 10 h but with weak peak absorptions (Fig. 3). Therefore, it can be expected that only minimal level of glycidol could be present in the glycerol simulated with 5 wt% methanol. The formation of glycidol is as depicted in (Scheme 2). Moreover, in ATR–FTIR analysis using direct crude glycerol the formation of glycidol was not detected (Fig. 4). This is due to the very minimal amount of methanol (0.8 wt%) present in both crudes. Thus, the formation of glycidol from decarboxylation of glycerol carbonate is not possible when very low amount of methanol is present. However, the reduction in glycerol carbonate selectivity could have been effected by the increased formation of the other by-products similar to those reported in our previous work [16, 26].

**Table 2** Moisture content analysis

Sample	Percentage of moisture (%)
10 wt% H <sub>2</sub> O	10.0 ± 0.01
0 h	9.2 ± 0.2
10 h	5.6 ± 0.07

Analyzed using mehtrohm moisture analyzer

### Glycerol Simulated with 10 wt% Moisture and 5 wt% Methanol

In order to understand the level of interference of the mixture of moisture and methanol, these substances were simulated in glycerol at 10 and 5 wt% respectively. From the analysis it was found that conversion of glycerol to glycerol carbonate was significantly affected which directly reduced yield of desired product (Fig. 2c). The effect of the data obtained was influenced by the stability of glycerol carbonate in moisture and formation of by-product

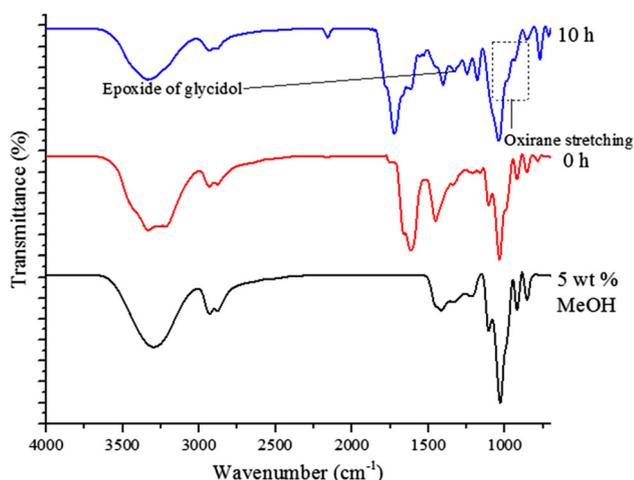
glycidol which was evident in the ATR-FTIR analysis depicted in (Fig. ESM 3).

### Glycerol Simulated with 3.15 wt% Moisture and 0.8 wt% Methanol

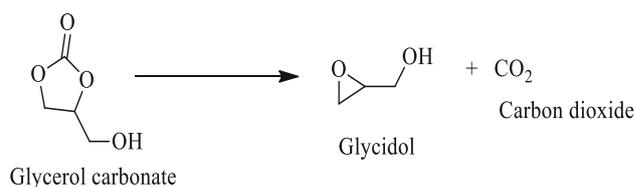
As illustrated in Fig. 2d, it was found that the catalytic data of glycerol simulated with mixture of moisture and methanol at 3.15 and 0.8 wt% does not have a significant impact towards glycerol carbonate yield. Only slight drop in conversion, selectivity and yield was noted. However, mixing of moisture and methanol at higher amount directly effects the conversion, selectivity and yield drastically as depicted in Fig. 2c. About 78.3 % yield glycerol carbonate was found to be present in this study in which the result of simulated mixture dropped to about 6 % from the yield percentage when compared with the pure glycerol reaction with BA 900. Therefore, the crude containing moisture and methanol at lower amounts as shown in the certificate of analysis does not show major interference on the glycerol carbonate formation.

### Glycerol Simulated with 1.6 wt% of Potassium Methylate

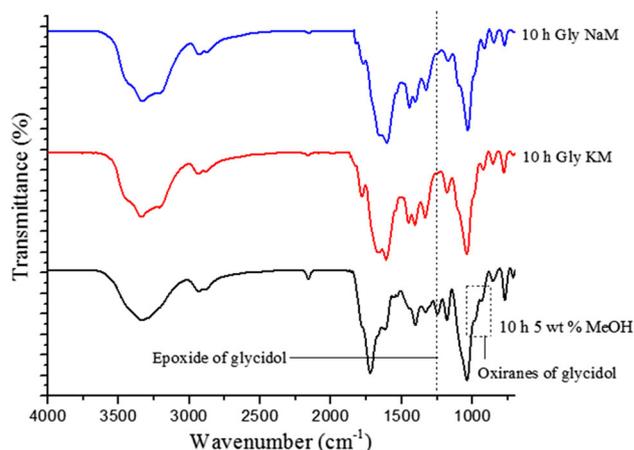
As introduced earlier, there are two different source of crude glycerol obtained from commercial biodiesel production plant which is based on the two different catalyst used (potassium methylate and sodium methylate). According to the process, about 1.6 wt% of these catalysts is loaded respectively into different processing tanks to obtain biodiesel at similar conditions and amount. The final glycerol extracted along with other impurities contains the initial catalyst loaded. Therefore, the effect of the catalyst loaded towards glycerol carbonate synthesis was also



**Fig. 3** ATR-FTIR spectrum analysis of 5 wt% MeOH, 0 and 10 h



**Scheme 2** Decarboxylation of glycerol carbonate to glycidol



**Fig. 4** ATR-FTIR spectrum analysis of 10 h 5 wt% MeOH, 10 h Crude Gly NaM and 10 h Crude Gly KM

investigated. Pure glycerol was simulated with 1.6 wt% of potassium methylate. From Fig. 5a, maximum selectivity and yield of glycerol carbonate was observed at 4 h with  $95.5 \pm 0.6$  and  $86.4 \pm 1.1$  % respectively. The conversion of the glycerol was  $95.4 \pm 0.6$  %. From this study it was found that potassium ion attached to any form of conjugate basic site is highly active for glycerolysis of urea. Besides, potassium methylate showed higher yield and selectivity compared to crude glycerol simulated with sodium methylate.

The Hammett test also indicates that potassium methylate and sodium methylate is basic in nature which is relatively similar to the property of boiler ash as previously reported [16] (Table 3). To add on, all catalyst containing potassium exhibited comparable results with one another. From Fig. 6a, the ATR-FTIR time online analysis of glycerol simulated with 1.6 wt% potassium methylate shows the decomposition pattern of urea from 0 to 10 h and formation of glycerol carbonate along with other by-products. Similarly like synthesis of glycerol carbonate using boiler ash (BA 900) as catalyst [16], the formation of glycerol carbonate in this study also occurred from rapid decomposition of intermediate glycerol carbamate into glycerol carbonate. Therefore, this study also proposes an effective use of potassium methylate for the synthesis of both biodiesel and glycerol carbonate in the biodiesel industry concurrently.

### Glycerol Simulated with 1.6 wt% of Sodium Methylate

Figure 5b illustrates the time online analysis (TOL) of glycerol simulated with 1.6 wt% sodium methylate. At 4 h of reaction time, maximum selectivity and yield of glycerol carbonate observed were  $82.5 \pm 0.7$  and  $79.0 \pm 0.7$  %, respectively. The conversion of glycerol was  $95.7 \pm 0.2$  %. Even though, the selectivity and yield of glycerol carbonate is reported to be lower than using potassium methylate as catalyst, sodium methylate also can act as suitable catalyst for the synthesis of glycerol carbonate.

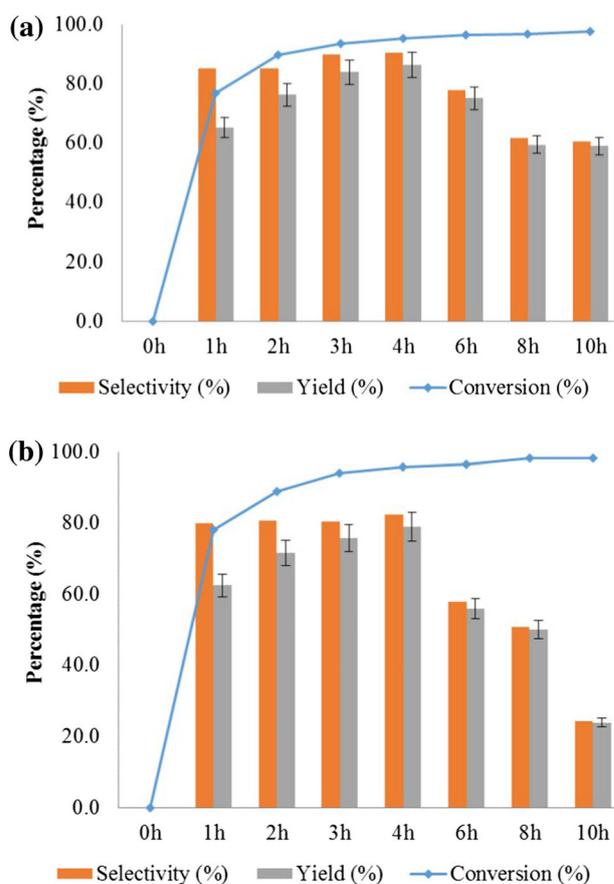
Property of sodium methylate which is found to be basic from the Hammett test (Table 3) allows revealed sodium to act as a Lewis acid to activate the carbonyl group of urea while the methoxy group activates the  $-OH$  group of glycerol to form glycerol carbonate. Even though sodium methylate is less active than potassium methylate, the pattern of TOL from Fig. 6b suggests that it still follows accelerated decomposition of glycerol carbamate into glycerol carbonate. The Lewis acidity of potassium is theoretically expected to be higher than sodium which may be a relevant reason to the current scenario.

### Blank Reaction of Pure Glycerol Stimulated with Moisture and Methanol

The blank reaction with maximum amount of methanol (5 wt%) and moisture (10 wt%) significantly decreased the glycerol carbonate yield. However, for the case of additives introduced in pure glycerol with similar amount as identified from crude glycerol (3.15 wt% moisture and 0.8 wt% methanol), insignificant differences were observed as compared to the analogue blank reaction without presence of any impurities. Thus, this scenario signifies that the actual amount of impurities present in the glycerol plays an important role in determining the yield of glycerol carbonate.

### Summary

In short it was found that moisture at 10 wt% significantly effects the conversion of glycerol due to instability of glycerol carbonate in water. On the other hand, methanol at 5 wt% influences catalyst basicity in selectivity of glycerol carbonate. Nevertheless, the current findings suggest that the crude glycerol can be used directly without purification using boiler ash as catalyst. Even though, optimum yield of glycerol carbonate cannot be achieved, crude glycerol Gly KM achieved promising yield of  $70.1 \pm 0.9$  %. Thus,



**Fig. 5** Time online analysis (TOL) of glycerol conversion (%), glycerol carbonate selectivity (%) and glycerol carbonate yield (%) of **a** glycerol simulated with 1.6 wt% potassium methylate and **b** glycerol simulated with 1.6 wt% sodium methylate. Reaction conditions: Temperature, 150 °C; Gas, Nitrogen; Glycerol: Urea, 1:1.5 (Molar ratio); Catalyst mass, 0.25 g; Standard stirring rate, 340 rpm

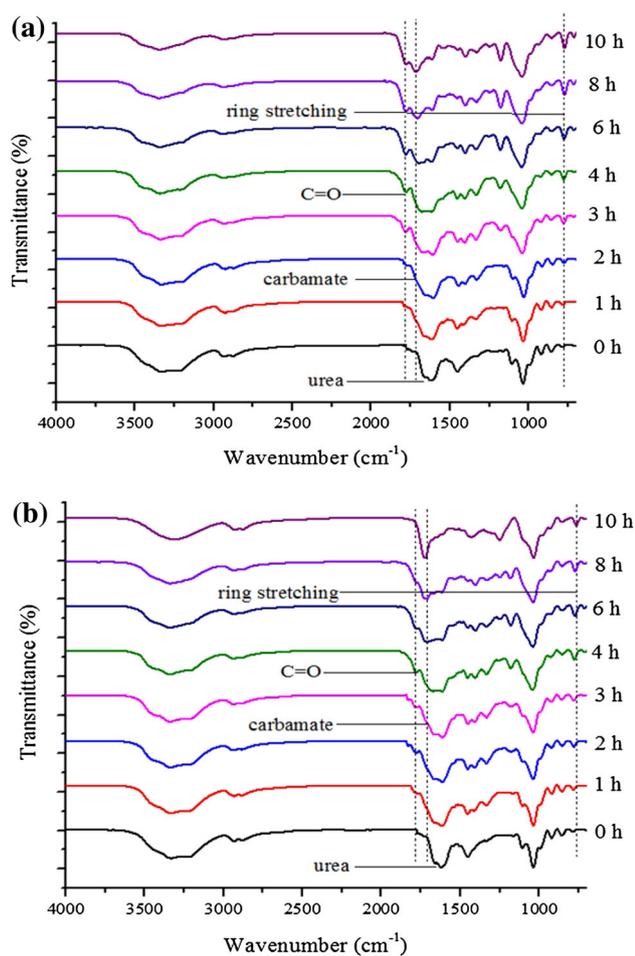
purification of the crude before use may not be susceptible as it will only increase yield by 14 % approximation when compared to our previous study using pure glycerol [16]. The overall study suggests that both potassium methylate and sodium methylate used in the biodiesel industry as catalysts for biodiesel production can also be used as catalysts for the glycerolysis reaction with urea. However, potassium methylate was found to be more effective than sodium methylate.

### Conclusions

In concise, it can be summarized that the activity of crude glycerol is influenced by the presence of moisture and methanol content. However, in this study the lower content of moisture and methanol in crude glycerol allowed transformation of direct crude glycerol into glycerol carbonate. It was also found that moisture at 10 wt%

**Table 3** Hammett test

Catalyst	Methyl red ( $H_- = 4.8$ )	Phenolphthalein ( $H_- = 8.2$ )	2,4-Dinitroaniline ( $H_- = 15$ )	4-Nitroaniline ( $H_- = 18.4$ )
Potassium methylate	No changes	Colourless to pink solution	No changes	No changes
Sodium methylate	No changes	Colourless to pink solution	No changes	No changes



**Fig. 6** ATR–FTIR spectrum for time online analysis of **a** 1.6 wt% potassium methylate mimic reaction 1–10 h and **b** 1.6 wt% sodium methylate mimic reaction 1–10 h

significantly effects the conversion of glycerol due to instability of glycerol carbonate in water. On the other hand, methanol at 5 wt% interferes with selectivity of glycerol carbonate. The studies suggest that both potassium methylate and sodium methylate used in the biodiesel industry as catalysts for biodiesel production can also be used as catalysts for the glycerolysis reaction with glycerol as well as urea. Hence, the study can be categorized as a benchmark near to a complete green synthesis approach.

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