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Synthesis of oxygenated fuel additives via the solventless etherification of glycerol

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ABSTRACT

The synthesis of oxygenated fuel additives via solvent freebase-catalyzed etherification of glycerol is reported. The products of glycerol etherification are diglycerol (DG) and triglycerol (TG) with DG being the favorable one. The catalytic activity of different homogeneous alkali catalysts (LiOH, NaOH, KOH and Na_2CO_3) was investigated during the glycerol etherification process. LiOH exhibited an excellent catalytic activity during this reaction, indicated by the complete glycerol conversion with a corresponding selectivity of 33% toward DG. The best reaction conditions were a reaction temperature of 240 °C, a catalyst/glycerol mass ratio of 0.02 and a reaction time of 6 h. The influences of various reaction variables such as nature of the catalyst, catalyst loading, reaction time and reaction temperature on glycerol etherification were elucidated. Industrially, the findings attained in this study might contribute towards promoting the biodiesel industry through utilization of its by-products.

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1. Introduction

The forecasted decline in the production of petroleum fuels and the growing concern about atmospheric greenhouse gas concentrations have necessitated the search for clean, renewable (sustainable), efficient and affordable alternative fuel. Biodiesel is becoming a key fuel in motor engines if blended in certain portions with petrodiesel (Hasheminejad et al., 2011). It can be readily produced via the transesterification of vegetable oils (edible, non-edible or reused) with low alcohols (methanol or ethanol). Indeed, the inevitable formation of glycerol that accompanies the biodiesel production process is affecting the process economy (Olutoye and Hameed, 2011; Yuan et al., 2010). Moreover, the growth of the biodiesel industry will result in overproduction of glycerol and create a superfluity of this impure product as its production is equivalent to 10% of the total biodiesel produced (Cardona et al., 2007; Khayoon and Hameed, 2011).

Glycerol is an abundant carbon-neutral renewable resource for the production of biomaterials as well as source for a variety of chemical intermediates (Rahmat et al., 2010; García-Sancho et al., 2011). Unfortunately, biodiesel-derived glycerol is not biocompatible due to its contamination with toxic alcohol (methanol or ethanol). Therefore, global research is focused on the effective conversion of glycerol to valuable chemicals to ameliorate the economy of the whole biodiesel production process. Recently, many studies have been dedicated to the transformation of this renewable polyol by various catalytic processes (Rahmat et al., 2010; Melero et al., 2012). This encompasses oxidation process to

obtain dihydroxyacetone, glyceraldehyde, glyceric acid, glycolic acid and hydroxyl pyruvic acid (Liebminger et al., 2009; Augugliaro et al., 2010); fermentation process towards 1,3-propanediol production (Tokumoto and Tanaka, 2011); acetylation process with acetic acid to obtain polyglycerol esters (Gonçalves et al., 2008; Balaraju et al., 2010; Dosuna-Rodríguez et al., 2011; Khayoon and Hameed, 2011) and acetalisation process with ketones to obtain oxygenated acetals and ketals (Umbarkar et al., 2009; Vicente et al., 2010; da Silva and Mota, 2011; Silva et al., 2010).

Glycerol is also an efficient platform for the synthesis of oxygenated components such as polyglycerols and ployglycerol ethers by means of etherification process (Melero et al., 2010, 2012; Yuan et al., 2011). Glycerol ethers (polyglycerols) are produced from catalytic etherification of glycerol with the use of different solvents. Particularly, these components have found colossal potential applications as fuel additives (Rahmat et al., 2010; Martin and Richter, 2011). Polyglycerols, especially diglycerol and triglycerol (called herein later as DG and TG, respectively) are the main products of glycerol etherification. The use of solvent could create some problems in the production process leading to a more complex overall process. In this respect, solventless etherification process could promise several advantages but limited information is currently available on this mode of glycerol etherification process. Venturing into the possibility of such process is a worthwhile research effort.

Glycerol etherification has been extensively investigated with or without the use of organic solvents. For both cases, different homogeneous alkali catalysts like carbonates and hydroxides or heterogeneous catalysts like zeolite, mesoporous silica and metal oxides have been applied (Clacens et al., 2002; Jerome et al., 2008; Martin and Richter, 2011). DG and TG are produced from the consecutive condensation of two or three glycerol molecules,

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respectively. They can be synthesized as linear, branched, or cyclic isomers based on the condensation process which may take place between primary and secondary hydroxyls or even through an intramolecular condensation (Corma et al., 2007). Heterogeneous catalysts show some advantages such as ease of their separation from reaction mixture and the potential for reusability. However, they generally show lower catalytic activity as compared to homogeneous catalysts. Some of them cannot even be applied industrially. Usually, heterogeneous catalysts require relatively higher temperature and longer reaction time than those needed in the case of homogeneous catalysts. In addition, the high cost, difficulty to functionalize, solubility in polar media, leaching of metal clusters from their surfaces, low surface area (in some cases) and their thermal stability are the main disadvantages of some heterogeneous catalysts.

Previously, several bases have been examined as homogeneous catalysts for the conversion of glycerol to polyglycerols. Hydroxides, Carbonates and metal oxides are attractive catalysts for glycerol etherification, being the hydroxides are more active than carbonates due to the stronger base character of the former. Contrary, oxides such as ZnO, MgO and CaO are less active in the aforementioned reaction due to the solubility issue. Nevertheless, these reactions are usually not sufficiently fast (in terms of glycerol conversion) or do not selectively produce DG apart from difficulties in filtration, neutralization and product purification. On the other hand, the need to eliminate the solvents from the homogeneous catalysts is a very challenging task (Clacens et al., 1998). Charles et al. (2003) reported that 96% glycerol conversion with a corresponding selectivity to DG of 24% were achieved using 2% Na₂CO₃ catalyst at 260 °C and 24 h. Alkaline metals impregnated into mesoporous catalysts have been reported to achieve 80% conversion of glycerol with not less than 40% selectivity to DG at 260 °C and a long reaction period of 24 h (Clacens et al., 2002). In 2008, the use of zeolitic catalyst for glycerol etherification was attempted and 80% of glycerol conversion and less than 20% selectivity to DG at 260 °C were achieved (Krisnandi et al., 2008). Recently, glycerol etherification was performed at a lower reaction temperature of 220 °C using Mg Al mixed oxide catalyst. The maximum conversion of 50% was recorded for this mixed oxide catalyst while a high selectivity to DG of ~90% was recorded after 24 h (García-Sancho et al., 2011). It is evident that different catalysts show different activity while at the same time showing different capability to produce the desired product.

Glycerol etherification has been proposed as an equilibrium-limited reaction and the presence of water molecules might enhance the backward reaction. Therefore, the water content in the reaction medium should be diminished either by reactive distillation to displace the co produced water or by employing anhydrous feedstock. On the other hand, the biodiesel derived glycerol cannot be utilized directly in industrial applications due to its being impure and the high water content. Thus, the current work was carried out using anhydrous glycerol to eliminate the undesired byproducts.

In this work, the use of LiOH as an efficient and selective homogeneous catalyst for the solvent free etherification of glycerol has been attempted. This study has been performed to find an applicable, feasible, eco-friendly and cost effective approach to synthesize an oxygenated fuel additive i.e. DG via a controllable homogeneous batch process. The catalytic behaviors of LiOH have been evaluated and compared against those of NaOH, KOH and Na₂CO₃ catalysts.

2. Methods

2.1. Materials

Anhydrous glycerol of high purity (>99%) was purchased from R&M Chemicals, Ltd., Malaysia while lithium hydroxide (99.9%)

was supplied by BDH, UK. Potassium hydroxide (85%), sodium carbonate (>99%) and sodium hydroxide (>98%) were obtained from Sigma–Aldrich, Malaysia. Meanwhile, glycerol (99%) from Sigma–Aldrich, diglycerol (>90%) from Solvay Chemicals and triglycerol (>90%) from Sigma–Aldrich were used as GC standards. All these chemicals were used without any further treatment.

2.2. Reaction procedure

The catalytic activity of the homogeneous catalysts was studied based on the solvent free etherification of glycerol at atmospheric pressure in temperature range of 180–260 °C using 2 wt% of catalyst (based on glycerol weight). A three-neck glass reactor vessel (250 mL) that was used to carry out glycerol etherification was placed on stirring-heating mantle equipped with a PID temperature controller. To avoid glycerol oxidation, the reaction was performed under inert environment using continuous flow of nitrogen gas. In this set up, the forward reaction was promoted by displacing and collecting the formed water using a Dean–Stark apparatus attached to the reactor vessel. In a typical experimental run, the reactor was charged with 50 g of anhydrous glycerol and 1.0 g of catalyst was then added to it and then heated up to the desired reaction temperature.

2.3. Analysis of reaction products

The reaction samples were collected at 2 h intervals (0–8 h) and qualitatively analyzed using a GC/MS Perkin Elmer system (Clarus 600 gas chromatograph attached to a Clarus 600T mass spectrometer) equipped with a DB-5 column. Prior to GC quantitative analysis, silylation pretreatment according to the method reported by Sweeley and coworkers (1963) was performed on the samples. A known mass of reaction sample (50 mg) was first mixed with carefully dried pyridine (1.5 mL) in a screw-capped septum vial (4 mL). After dissolution, 0.2 mL of hexamethyldisilazane (HMDS) and 0.1 mL of trimethylchlorosilane (TMCS) were gently added and the resulting mixture was heated up to 70 °C for 1 h. An aliquot of the solution (0.05 mL) was then diluted in dried toluene (2 mL). Finally, 1 µL of the liquid was injected into a capillary polar GC column DB-HT5 (15 m × 0.32 mm × 0.10 µm) mounted in a gas chromatograph GCD 7820A system (Agilent Technologies, USA). The analysis was performed in a temperature-programmed mode from 60 to 250 °C with a ramping rate of 10 °C/min. The typical retention times (t_R) of the silylated components were to 3.2, 8.6 and 13.1 min for glycerol, DG and TG, respectively. The calibration curves of glycerol, DG and TG were obtained by injecting their respective standard reagents. Glycerol conversion (%), DG yield (%) and DG selectivity (%) were calculated using the following equations;

$$\text{Glycerol conversion(\%)} = \frac{\text{moles of glycerol reacted}}{\text{moles of glycerol taken}} \times 100\% \quad (1)$$

$$\text{DG yield(\%)} = \frac{\text{moles of DG produced}}{\text{moles of glycerol taken}} \times 100\% \quad (2)$$

$$\text{DG selectivity(\%)} = \frac{\text{Moles of DG produced}}{\text{Total moles of products}} \times 100\% \quad (3)$$

3. Results and discussion

3.1. Etherification reaction

Selective etherification of glycerol to polyglycerol using either homogenous or heterogeneous catalysts is an attractive pathway

for organic chemists as it directly gives access to value-added chemicals. The products of glycerol etherification are DG, TG and tetraglycerol. Among these products, DG is the most favorable one due to its characters as a moisturizer in cosmetics and pharmaceutical industries and more recently as a biodiesel additive. The reaction involves the conversion of glycerol to DG by removing one water molecule, and subsequent removal leads to the formation of TG and tetraglycerol.

The catalytic activity of the investigated catalysts was measured based on glycerol conversion and corresponding selectivity to DG during the solventless etherification of glycerol. The reaction was carried out at 240 °C for up to 8 h. In some cases, leaching of the active phase into the reaction medium and the formation of acrolein at high reaction temperature are the two main drawbacks of heterogeneous catalysts. On the other hand, the use of organic solvents for glycerol etherification in the presence of homogeneous catalysts might complicate their separation after the reaction to consequently affect the process economy and products purity. Therefore, the current study addressed a solvent free process in the presence of alkali metals. The effects of different reaction variables were particularly investigated. The reproducibility of the obtained results were checked by repeating some experiments and no more than 7% error was observed which might be attributable to experimental aspects or analytical dissimilarity.

3.2. Performance of different catalysts

Fig. 1 presents the performance of 2 wt% of four different catalysts used for selective glycerol conversion to DG via etherification at 240 °C. The highest conversion of glycerol (~100%) was achieved after 6 h in the presence LiOH and NaOH catalysts. However, the application of 2 wt% of NaOH resulted in slightly lower glycerol conversion and DG selectivity than those obtained using 2 wt% LiOH catalyst. This difference became significant after 2 h of reaction, explaining the key role of Li ions in promoting glycerol conversion and enhancing DG formation. The catalytic activities of NaOH, KOH and Na₂CO₃ were also examined, and the results revealed that significant glycerol conversion with palpable DG selectivity were achieved. However, their catalytic activities were found to be lower than that of LiOH. It was also observed that Na₂CO₃, which was used as reference catalyst, presented poor glycerol conversion and DG selectivity compared to those attained using LiOH. Na₂CO₃ might possess higher catalytic activity, than that recorded in this study if applied at reaction temperature higher than 240 °C or longer reaction period than 12 h (Clacens et al., 2002). However,

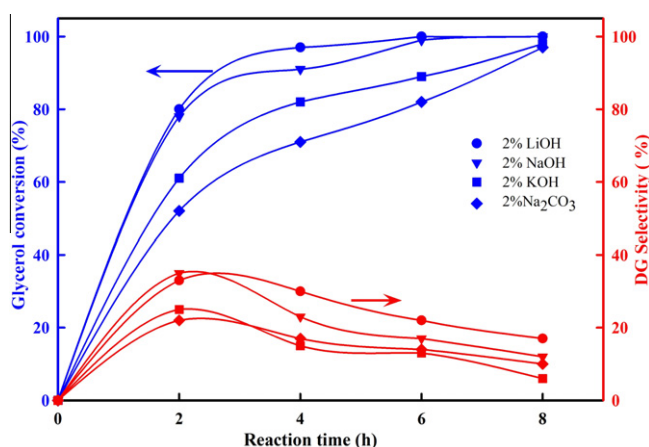


Fig. 1. Performance of different catalysts in the etherification process measured in terms of DG yield% (Reaction temperature: 240 °C, catalyst loading: 2 wt.%).

such extreme conditions were not used in this work to avoid significant degradation reactions on the reactants, intermediates and products.

Fig. 2 provides the measured original pH values of glycerol and the mixtures of different alkali catalysts with glycerol. It is obvious that different catalysts resulted in different pH value after mixing with glycerol. The pH value increased in the order of: LiOH + glycerol > NaOH + glycerol > KOH + glycerol > Na₂CO₃ + glycerol. This observation suggested that a mixture with higher pH value performed better during the solvent free glycerol etherification. LiOH was the most active catalyst during the selective glycerol conversion to DG and it might be attributable to its highest alkalinity in the reaction mixture. Li has smaller ionic size and higher atomic electronegativity than other metals used in this study. Higher nuclear charge enabled it to make stronger attraction for electrons or protons during the etherification reaction. This might interpret the relationship between the atomic characteristics of the metals with their catalytic performance in glycerol etherification reaction. After this preliminary screening test, LiOH was selected for further study on the effects of several important reaction variables.

3.3. Effect of catalyst loading

Effect of LiOH catalyst loading was studied using the same reaction conditions as those mentioned in Section 3.2. The catalyst concentration in the reaction medium was varied in the range of 10.4–83.5 mmole while the other reaction variables were kept constant. It was observed that different catalyst loadings resulted in indifferent reaction profiles (expressed by glycerol conversion and DG yield) with nonlinear relationship as shown in Fig. 3(a) and (b). The conversion of glycerol attained its maximum level of 100% after 6 h as the amount of LiOH was increased from 2 to 4 wt%. The highest DG selectivity of about 30% was achieved after 4 h with 2 wt% of LiOH. The conversion of glycerol and DG selectivity were found to gradually increase as the LiOH amount was increased from 0.5 to 2 wt%. However, further increase beyond 2 wt% resulted in decreasing trends observed in both glycerol conversion and DG selectivity. The same trend of DG yield was observed and the maximum DG yield achieved was 29%. It was a level at which the highest reaction rate was achieved. Further increase did not bring about the desired effect as the reaction could have been limited by the mass transfer during the reaction. Based on Fig. 3(a) and (b), the selectivity and yield of DG at 4 wt.% of LiOH loading suddenly decreased after 2 h of reaction and came close to zero value after 6 h. Bearing in mind nearly complete glycerol conversion was obtained at the same point, low selectivity and yield for DG indicated the subsequent etherification reaction beyond DG to form TG and other oligomers.

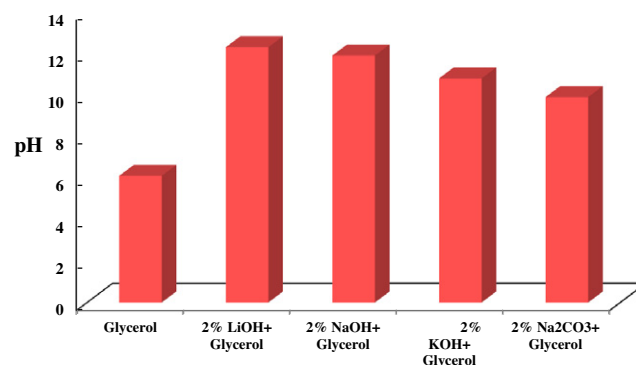


Fig. 2. Measured pH value of glycerol in the presence of different catalysts prior to glycerol etherification reactions.

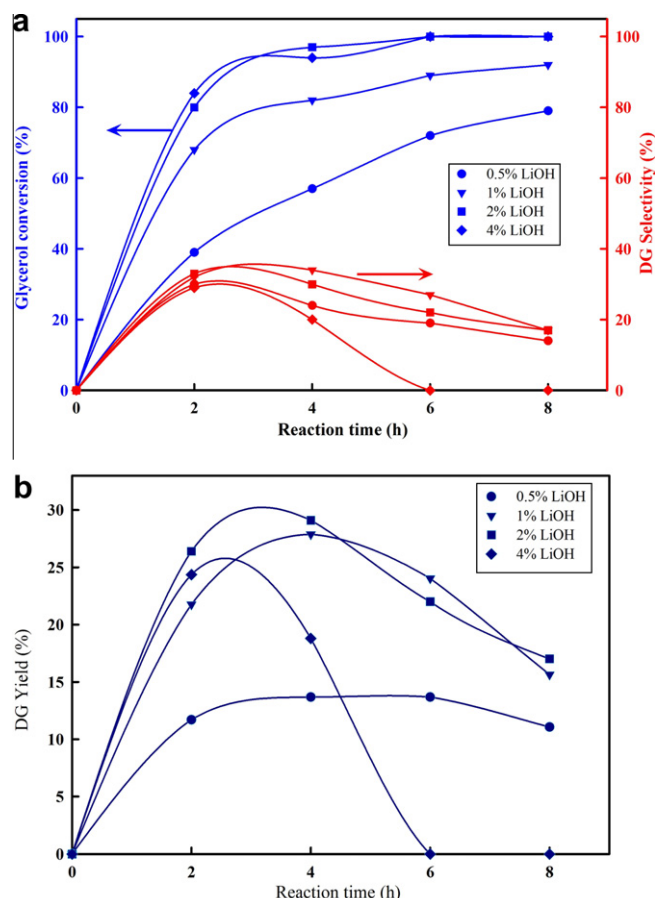


Fig. 3. Influence of LiOH catalyst loading on (a) glycerol conversion and corresponding DG selectivity and, (b) DG yield% (Reaction temperature: 240 °C).

Expectedly, increasing LiOH amount from 0.5 to 2 wt% resulted in improving conversion of glycerol molecules to polymerize into DG molecule by dehydration. Besides promoting over-polymerization reaction, increasing LiOH amount further to 4 wt.% under these reaction conditions could also result in back-scission of DG to glycerol. Martin and Richter (2011) reported that the interaction between the B–OH base with glycerol could weaken one of the glycerol OH bonds and enhanced the nucleophilic character of the hydroxyl oxygen. Attack on this polarized glycerol molecule by the hydroxyl group of a second glycerol molecule would simultaneous split off of water molecule resulting in DG formation. As 2 wt% of LiOH catalyst showed the best DG yield during the reactions, this loading was selected for the subsequent research work.

3.4. Effect of reaction time

The influence of reaction time on reaction profiles (glycerol conversion, DG selectivity and DG yield) was evaluated using 2 wt% LiOH catalyst at 240 °C and the results are also shown in Fig. 3(a) and (b). It was observed that after 2 h of reaction, the selectivity toward DG attained its highest value of ~30%, but decreased as the reaction was further prolonged to 8 h. Whilst, glycerol conversion was found to linearly increase with reaction time to 8 h, the DG yield was 29% after 4 h and behaved like the selectivity of DG. Nevertheless, increasing reaction time further resulted in a decrease in DG yield for all the catalysts used, except for 4 wt% LiOH which showed decreasing DG yield after 2 h.

Indeed, as the etherification reaction was prolonged, more glycerol molecules underwent dehydration or any other form of

reaction which resulted in an increase in the conversion of glycerol. Unfortunately, during this conversion, the cleavage of glycerol molecules might not exactly result in polyglycerol form, but in some other forms of by-products such as acrolein due to the double dehydration of glycerol. These by-products are not desirable in the polymerization etherification reaction and might lead to unfavorable products (Clacens et al., 2002). Subsequently, the DG molecules that formed might be converted into higher glycerol ethers under uncontrolled reaction conditions. This may also happen, in some cases due to the weak formation of two polymerized glycerol molecules (DG isomers) which might not be highly stable under given reaction conditions. Therefore, the selectivity and yield of DG gradually started to decrease after 2 h of reaction time.

3.5. Effect of reaction temperature

It has been well established that chemical reaction rate is strongly influenced by reaction temperature. Therefore, the influence of reaction temperature in the range of 180–260 °C on glycerol etherification was investigated. As shown in Fig. 4, the maximum glycerol conversion after 6 h was 100% and it was achieved in the presence of 2 wt% LiOH at 240 °C. However, the selectivity to DG at this point was not high (<20%) and was decreasing with increasing temperature and reaction time. Meanwhile, etherification reaction rate was lower at a lower reaction temperature of 220 °C, achieving a glycerol conversion of 23% (after 8 h) and a DG selectivity of lower than 5%.

Fig. 4 shows that glycerol conversion increased uniformly with increasing reaction temperature from 240 to 260 °C. On the contrary, DG selectivity decreased with increasing reaction temperature beyond 240 °C. The observation suggested that reaction temperatures higher than 240 °C might have speeded up the conversion of the remaining glycerol and enhanced the consecutive etherification reaction of DG to higher glycerol oligomers to consequently result in decreasing DG yield. These observations were in good agreement with earlier reported results (Clacens et al., 1998; Charles et al., 2003).

Overall, Table 1 presents a detailed comparison with those reported in previous studies implemented using different homogeneous catalysts. This study investigated the catalytic glycerol etherification using alkaline metals catalysts (LiOH, NaOH, KOH and Na₂CO₃) at comparable reaction temperature of 240 °C and very short reaction time that is maximum of 8 h. More specifically, this work focused on exploring the catalytic potential of different alkaline metals as an example of eco-friendly catalysts.

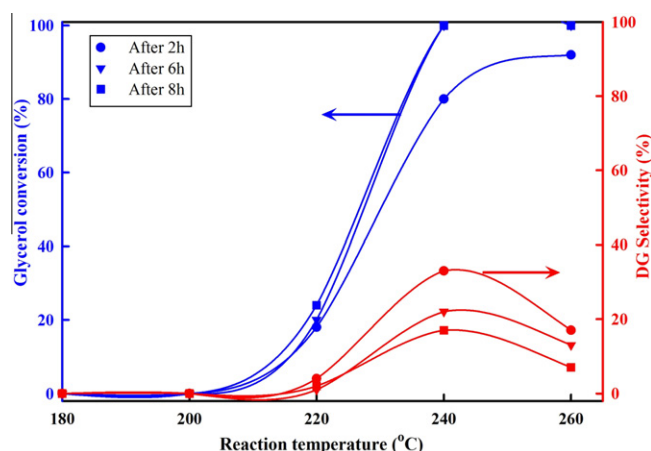


Fig. 4. Effect of reaction temperature on glycerol conversion and corresponding DG selectivity. (Catalyst loading: 2 wt.% of LiOH).

Table 1

Comparison of the catalytic activity (expressed by glycerol conversion and products selectivity) of different homogenous catalysts in the glycerol etherification process.

Catalyst	T (°C)	Xg [*]	Selectivity (%) after 8 h				Ref.
			DG	TG	Tetra-	Other	
Na ₂ CO ₃	240	76	46	34	13	75	Cottin et al. (1998)
Na ₂ CO ₃	260	96	24	35	22	75	Charles et al. (2003)
Na ₂ CO ₃	260	94	27	31	21	–	Barrault et al. (2004)
Na ₂ CO ₃	260	80	31	28	17	–	Calatayud et al. (2009)
Na ₂ CO ₃	220	80	45	36	–	75	Ruppert et al. (2008)
NaOH	240	63	60	32	7	–	Cottin et al. (1998)
NaHCO ₃	260	75	27	12	0	30	Krisnandi et al. (2008)
CsHCO ₃	260	64	23	9.5	2.5	75	Richter et al. (2008)
Cs ₂ CO ₃	–	71	39	19	6	75	Richter et al. (2008)
CsOH	260	74	32	21	5	75	Richter et al. (2008)

^{*} Xg: Glycerol conversion (%).

4. Conclusions

In this work, solventless etherification of glycerol to DG using various alkaline metal precursors was successfully investigated and the obtained results were compared with those obtained with Na₂CO₃ as a reference catalyst. LiOH catalyst showed unique activity for glycerol etherification, achieving complete glycerol conversion with a corresponding 33% selectivity toward DG as the desired product. The best reaction conditions were 240 °C of reaction temperature, 2 wt% of catalyst loading and 6 h. Glycerol conversion and DG selectivity were found to be influenced by the alkalinity of the metal catalyst as well as the reaction conditions.

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