Utilization of Glycerol for Glycerol Carbonate Synthesis via Transesterification Reaction over Bio-Char Catalyst prepared from reed plant

Shafaa D. Mohammed  
MSC student  
College of Engineering - University of Baghdad  
shafaadhya@gmail.com

Muthana J. Ahmed  
Asst.prof.  
College of Engineering - University of Baghdad  
muthannaj@yahoo.com

ABSTRACT

Biodiesel production process was attracted more attention recently due to the surplus quantity of glycerol (G) as a byproduct from the process. Glycerol Utilization must take in to consideration to fix this issue also, to ensure biodiesel industry sustainability. Highly amount of Glycerol converted to more benefit material Glycerol carbonate (GC) was one of the most allurement compound derived from glycerol by transesterification of glycerol with dimethyl carbonate (DMC). Various parameters have highly impact on transesterification was investigated like catalyst loading (1-5) %wt., molar ratio of DMC:glycerol (5:1 – 1:1), reaction time (30 - 150) min and temperature (40 – 80) °C. The Optimum glycerol carbonate yield (YGC) and glycerol conversion (XG) was obtained 94.2% and 94.5% respectively at catalyst loading 5% wt., temperature 70°C, DMC:G ratio 5:1 and 120 min. GC has large scale of uses such as liquid membrane in gas separation, surfactants ,detergents , blowing agent , in plastics industry, in Pharmaceutical industry and electrolytes in lithium batteries.

Keywords: Glycerol Carbonate, Glycerol, Transesterification, Biochar.
1. INTRODUCTION

Nowadays, the highly improvement in biodiesel production process which led to surplus quantity of glycerol. Availability and renewability of glycerol raw material was attracted attention of many researchers to convert glycerol and obtain more benefits chemical glycerol carbonate with wide range of uses (Corma, et al., 2007, Gu, et al., 2008, Juben, et al., 2007, Pagliaro, et al., 2007, Je´ ro´me, et al., 2008, Zhou, et al., 2008, Behr, et al., 2008, Lee, et al., 2007). GC is such a substance that has been extensively used in gas-separation membranes, paints, and solvent for therapeutic research and personal care products as of its low flammability, worthy bio-degradability, low toxicity, slight viscosity, high boiling point, and water solubility. Also, GC has strained greatly care in the last few years owing to its possible manufacturing uses in the preparation of polyurethanes (Wang, et al., 2017) For these significant features, it detections many uses in diverse industrial parts, particularly as a glacial great hot solvent or middle in organic synthesises (i.e., synthesis of additional polymeric and polycarbonates constituents in the plastics arena employed in plastics, textile, cosmetics, and pharmaceutical industries), as a forerunner in biomedical uses and as a protection group in carbohydrate chemistry. Transesterification of glycerol with dialkyl carbonate specifically dimethyl carbonate to form glycerol carbonate is one of the most attractive processes to obtain glycerol carbonate (Kim, et al., 2007, Rockiki, et al., 2005, Naik, et al., 2009). Glycerol carbonate can be considered as highly interesting derivatives from glycerol which was gained a big attention over the world due to it's use as a pharmaceutical intermediate also replacing the risky solvents with a safety and environmentally friendly material (Simaˇ o, et al., 2006, Shaikh, and Sivaram, 1999). Synthesis of glycerol carbonate from glycerol and dimethyl carbonate by transesterification reaction can be catalyzed with various homogeneous catalysts like K2CO3 and 1-n-butyl-3-methyl-limidazolium -2-carboxlyate but according to difficult separation of this type of catalyst led to rely on heterogeneous catalysts (Ochoa-Gomez, et al., 2009, Li, et al., 2010, Takagaki, et al., 2010).

Many heterogeneous catalysts were reported in the previous studies to form glycerol carbonate from glycerol and DMC and more of these catalysts give an acceptable GC production (Mori, et al., 2002, Lu, et al., 2013, Khayoon, and Hameed, 2013, Liu, et al., 2013). These catalysts usually either mixed oxide catalyst or alkali metal oxide, For example CaO can be considered as a suitable heterogeneous catalyst which was given a good conception in glycerol carbonate production process, Approximately 95% glycerol carbonate yield was obtained when the transesterification reaction catalyzed with CaO. First of all, the preparation of catalyst must be submissive to environmental safety conditions also take in account the reduction time, from the other side the cost must be minimized (Balakrishnan, et al., 2011). Obviously the researchers destination at the recent time to the easy preparation catalyst method due to its highly applicability in industrial scale. Heterogeneous catalysts with basic catalytic activity can be prepared from natural materials to catalyze basic reactions (Jain, et al., 2012, Khatri, et al., 2010, Li, et al., 2008, Chakraborty, et al., 2010).

Glycerol carbonate is an important multi-functional complex used as additive, solvent, and create a block in substitute chlorine-free procedures (Chiappe, and Rajamani, 2011). As described previously, glycerol can also directly or indirectly be converted to glycerol carbonate via a number of routes reacting with a “CO” source. These sources include, urea,
ethylene carbonate, alkyl carbonates, as well as CO2, alkaline hydrogen carbonate and alkaline carbonate if glycerol is first converted to either epichlorohydrin or 3-chloro-1, 2-propanediol (Stewart, 2015). The shortcomings of making GC from urea and glycerol lead to the formation of great quantities of ammonia and the difficulty in extrication the undesired by-products such as: biuret and isocyanic acid. Though GC may be attained from ethylene carbonate and glycerol via transesterification. A by-product which is ethylene glycol is produced and owing to their high boiling points it makes the separation of products hard. Related with these ways, transesterification of dimethyl carbonate (DMC) with glycerol for GC preparation is reflected as the talented method for industrial use owing to the easy separation, mild reaction circumstances, high GC produce, and simple process (Liu, et al.,2017). In the current study glycerol carbonate produce from transesterification of glycerol by using char from reed plant as a catalyst. The effect of different variables (time, temperature, DMC:G ratio ,catalyst loading and catalyst recovering) were studied.

2. EXPERIMENTAL WORK
2.1 Materials
Glycerol (Kimadia Company , purity 98%), di-methyl carbonate (Kimadia Company , purity 95.5% ), Reed plant was collected from different area in Baghdad/Iraq washed, dried ,cut, crushed, grinded and sieved to achieve (600 Mm and 1.2 mm) particle size . Hydrocloric acid HCl(ACSISO,Reag.ph Eur,Hydrocloric acid fuming 37%).

2.2 Preparation of bio-char catalyst
Catalyst prepared by pyrolysis technique, preparation process started with washing Reed plant twice with deionized water instead of raw water to prevent increasing impurities in pore sites then dried for 6 hr by dryer under (110 ℃) before uses. Then cut, crushed and grind, after grinding the reed plant particles sieved by sieve size (600 and 1200) micrometer to obtain the particle size around (600 – 1200) micrometer .Biochar manufactured through combustion of reed plant particles in closed container by furnace under absence or very low oxygen at 700℃ for 1 hr. The prepared bio-char was immersed within (0.1 M) HCL for 24 hr then washed with deionized water after that drying performed for 5 hr in 110 ℃ .The prepared biochar catalyst used to catalyze transesterification reaction (Abdul-Hameed, et al.,2017).

2.3 Catalyst characterization
2.3.1 FTIR
FTIR analytical test was performed by mixing10 mg from the catalyst sample with 90 mg KBr then pressed to form a disc shap after that the test was done by Fourier Transform Infrared (FTIR) Spectrophotometer (IR- Shimazdu, Japan) using a resolution of 600 - 4000 cm⁻¹.

2.3.2 BET
The surface area (BET test) of the catalyst was performed by using nitrogen adsorbed at 77.3 K . Nitrogen with high purity was used in this test approximately(99.99%).

2.4 Transesterification reaction procedure
The reaction of glycerol and dimethyl carbonate was carried out in a three neck around bottom flask reactor (50 ml) equipped with a condenser, and put it in water bath over hot plate with magnetic stirrer stirring with (150 Rpm), and two thermometer for monitoring temperature one of them in flask and the another one in water bath. The mixture of biochar catalyst and glycerol was heated to reach the reaction temperature and then dimethyl carbonate was added. Various ranges of time (30-150) minutes, temperature (40-80) ℃, DMC:G ratio (1:1-5:1) and bio-char catalyst loading (1-5)%wt. was studied (Sameer, et al.,2016).
2.5 HPLC analysis

After catalyst separation by centrifuge, the sample was analyzing by HPLC (type: Shimadzu, Japan). HPLC system equipped with I.C.S pump and injector of (20 micro litters) injection loop. High capacity cat ion exchange resin C1 column [30 cm long, i.d. 7.8 mm, Touzard and Matignon]. The temperature was fixed at (25°C), the mobile phase was used water/acetonitrile (60:40, v/v) acidifying with 0.01 N sulfuric acid until PH reach to 3.5 to keep the column safe, the mobile phase supplied by the pump was water and acetonitrile [60/40 v/v] acidified with 0.01N sulphuric acid, set the flow rate of mobile phase on 0.6 mL/min. The software used for data Acquisition was (Pic 3).

2.6 Catalyst Recycling

Catalyst reusability was investigated to evaluate the stability and catalytic activity of heterogeneous catalyst for three cycles. After the first batch of reaction, catalyst separated from the reaction mixture by centrifuge then washed with 10 ml of 98% methanol for 1 hr with shaking after that drying was performed at 100°C for 5 hr. The catalyst was collected for recycling in the next cycle, new charge reactants were added to the recycled catalyst and new run was performed to show the effect of catalyst recycling on the yield of glycerol carbonate and conversion of glycerol.

3. RESULTS AND DISCUSSION

3.1 Catalyst characterization

FTIR spectrum of prepared is shown in Fig.1 to evaluate the catalyst qualitatively. For prepared char, the sample assigned to several functional groups which include amines, hydroxyl groups, aldehydes, various unsaturated hydrocarbons, carbonyl compounds (Olivares-Marin, et al.,2005, Phan, et al.,2006, Nabais, et al.,2008). Hydroxyl groups more important in transesterification of glycerol to increase in basic active sites in order to initiate the reaction between the proton of weak acid from one of the two primary hydroxyl group of glycerol with the base catalyst to form glycerol carbonate as described by (Algoufi, and Hameed,2014).

Whereas, the spectrum of prepared bio-char is very simple consisting of considerable number of peaks of functional groups. The broad peak observed at 3005 cm\(^{-1}\) is due to the presence of hydroxyl groups (O – H stretch) on the surface. The peaks observed at 3421 cm\(^{-1}\) is due to the (C – C) bond. The peaks observed at 2947.23 cm\(^{-1}\) is due to the asymmetric and symmetric stretchings (C – H) group. The weak bands observed between 1350 – 1260 cm\(^{-1}\) might be due to the existence of in-plane bending of primary or secondary OH groups. The presence of amine groups are confirmed by the peaks observed in the range 1190 – 1030 cm\(^{-1}\) and are due to C – N stretchings also peaks observed in the range 2200 to 2400 cm\(^{-1}\) was due to triple bond C-C (Coates, J, 2000). The measured BET surface area and total pores volume of prepared char from reed plant particles are 214.1487 m\(^2\)/g, 0.1204 cm\(^3\)/g respectively.
3.2 Parameters influence study

3.2.1 Study effect of time

Trans esterification reaction should be proceed at variant durations of time from 30 min to 150 min with fixing the other conditions, the reaction time is considered a crucial parameter which is control on conversion of glycerol and glycerol carbonate yield. The reaction was performed at 60°C, 3:1 DMC:G ratio, 150 RPM and 3% wt. catalyst loading, all results shown in Fig. 2. Appreciably there is a dramatic increasing in GC yield and G conversion at the first duration time (30 min) the observation of GC yield and G conversion was below 50%. The continuous increasing in time causes a dramatic increase in methanol solvent subsequently with the miscibility between the reactants and catalyst was increased and this can give a continuous increase in glycerol carbonate yield (Algoufi, and Hameed, 2014). Maximum yield and conversion are 93.05% and 94.22% respectively was obtained at time 120 min after that when the trans esterification reaction operated with the time 150 min there was observed decreasing in GC yield until reach to 48.51% but the conversion stay constant 94.41%, the period between 120 min and 150 min GC start in degradation by decomposition to another constituent and this observation can be compared with that one was reported in the previous study performed by (Algoufi, and Hameed, 2014).

3.2.2 Study effect of temperature

In order to evaluate the effect of various temperatures on the transesterification of glycerol with dimethyl carbonate, Variant range of temperature within (40 – 80) °C was studied over 3% wt. from char catalyst and 3:1 DMC:G ratio in 90 min with 150 RPM. Influence of temperature on GC yield and G conversion was illustrated in Fig. 3. When the reaction was operated with 40°C glycerol conversion obtained below 50% also the same behavior for GC yield. After increasing the reaction temperature to 50°C, slightly increasing in glycerol conversion was observed. Uniform increment was observed in glycerol carbonate yield when the temperature was increased from 50°C to 60°C. Maximum GC yield was noticed at 70°C which was reached to (84.99%). These results can give a perfect conception that the energy amount which is responsible for reducing the reactants viscosity led to increasing the miscibility of DMC with glycerol and this was upgrade interaction between reactants molecules (Selva, et al., 2011). When temperature was increased to 80°C, dramatic decreasing in glycerol carbonate yield occur till reach to (31.16%), deprotonating of hydroxyl group in GC molecules on active sites occur and causes opening the rings of glycerol carbonate to form another constituent.
(Selva, et al., 2011), the same observation reported by authors (Algoufi, and Hameed, 2014) (Zheng, et al., 2008, Chakraborty, et al., 2010, Bai, et al., 2013).

3.2.3 Effect of catalyst loading
Evaluation the effect of catalyst amount should be performed to show the influence of increasing catalyst loading on GC yield and G conversion, various catalyst weight percent with the range (1-5) % wt. are investigated under mild conditions 60°C, 150 RPM, 90 min and 3:1 DMC:G ratio. All the results are illustrate in Fig.4, obviously there is a continuous increase in GC yield and G conversion in each presence of catalyst amount, this behavior gave an indication that the increment of catalyst amount attributed in availability of more active sites and this is necessary to increase the activity of transesterification reaction. The highest values obtained of GC yield and G conversion was 92.55%, 93.95% respectively in presence of 5 wt.% of bio-char catalyst (Jose R. Ochoa-Gomez, et al., 2009), give a clarified indication that the increase in catalyst amount causes an increase in basic active sites to initiate the reaction between the proton of weak acid from one of the two primary hydroxyl group of glycerol with the base catalyst to form glyceroxide anion plus also conjugated acid of base (BH), glyceroxide attacks carbonyl carbon in dimethyl carbonate GC with methanol. This observation agrees with that reported by (Algoufi, and Hameed, 2014).

3.2.4 Effect of DMC: G ratio
Trans-esterification reaction of glycerol is a reversible reaction and to shift the reaction from equilibrium state toward glycerol carbonate production increase DMC:G ratio (Wang, and Lu, 2012), various DMC: G ratio (1:1 – 5:1) was investigated to explain the influence of using excess DMC on glycerol carbonate yield and glycerol conversion, with fixing other conditions 60°C, 150 RPM, 90 min and 3% wt. Catalyst, the behavior of transesterification of glycerol with DMC shown in Fig.5. Preliminarily the equimolar ratio achieved GC yield below 50 percent (41.98%), at each increasing in DMC:G ratio found GC yield and G conversion increased dramatically, there is a sparingly increasing in GC yield and G conversion observed when the ratio increased to 2:1 while there was a good improvement in yield at 3:1 DMC:G 67.86%. Highly conversion & yield was obtained at 5:1 DMC:G ratio (73.45%) (84.13%) respectively. Obviously in each ratio increasing there was increment in yield and conversion, excess DMC used to be a reactant and solvent at the same time this is can be regarded as a major reason for increasing the miscibility between the reactant and catalyst and enhancing reaction activity to achieve highly glycerol carbonate yield (Rockiki, et al., 2005), this observation agreed with the results reported in the previous study performed by author (Algoufi, and Hameed, 2014).
3.3 Effect of catalyst recycling

It is important to evaluate the heterogeneous catalyst recycling effect on Transesterification reaction to investigate the stability of the prepared bio-char catalyst also to detect the reusing activity. Catalyst reusability studied for three cycles to explain the influence of bio-char catalyst reusability on GC yield & G conversion under mild conditions (60°C, 90 min, 3:1 DMC:G ratio, 3% wt. catalyst loading). All results clarified in Fig.6. From the figure we can observe a dramatic decreasing in yield and conversion with each catalyst reuse cycle and this is attributed to a continuous deactivation in catalyst causes decreasing in G conversion and GC yield in each run. Approximately there was 50% lowering in GC yield under the third catalyst cycle comparing with the first one; therefore we can regard this observation belong to a continuous reduction in active sites and decrease the amount of catalyst in each reusing also the decreasing reason can be belong to the traces amount of reactant and products which was adhered the catalyst and residue in the pore of sites (Algoufi, and Hameed, 2014).
4. CONCLUSION
Transesterification of glycerol and dimethyl carbonate performed by catalyzing the reaction with biochar as a heterogeneous catalyst. Char catalyst prepared from reed plant as a natural source show a good stability in recovering for three cycles. Optimum glycerol conversion and glycerol carbonate yield was 94.5% and 94.2% respectively. Reaction time 120 min, temperature 70°C, G:DMC ratio 1:5 and catalyst loading 5% wt. regarded as a best conditions which gave the optimum yield and conversion. The pyrolysis process of reed plant for manufacturing char catalyst was considered cost effective method. The activation of transesterification of glycerol by bio-char from natural source to form glycerol carbonate offers excellent chance to consume waste reed plant.

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