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Enhanced conversion of Glycerol to Glycerol carbonate on modified Bio-Char from reed plant

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Abstract

The surplus glycerol produced from biodiesel production process as a by-product with high quantity can be considered as a good source to prepare glycerol carbonate (GC) whereas with each 1000 kg from biodiesel obtains 100 kg from glycerol. The aim of this paper is studying the possibility of converting the glycerol to glycerol carbonate using the bio-char prepared from reed plant as a catalyst. The catalyst was prepared at different temperatures ranging from 400-800°C. The results show that the bio- char prepared at 700 ^{O}C gives a best one among the others types of bio-char, but the yield was increased to 67.80% using prepared bio-char and when the catalyst promoted by sodium hydroxide, the obtained yield reached to 98.3% and complete conversion. In this study, the complete conversion was achieved at optimum conditions which were 60^{O}C, 90 min, 3:1 DMC:G , 3%wt. catalyst loading and using bio-char modified with 3 molar NaOH .

Keywords: Glycerol Carbonate, Glycerol, Pyrolysis, Trans esterification reaction, Biochar

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1- Introduction

Biodiesel has involved significant consideration as an alternative to the fossil fuel resources. U.S. government and European Union have broadcast obligatory rules for the use of biodiesel in transportation on-road diesel and fuel.

Though, production of biodiesel by plant oil methanolysis produces large quantity of glycerol (about 10 wt. %) as an inevitable by-product that has to be valorized to progress the monetary attractiveness of biodiesel. Consequently, transformation of glycerol into valuable products is of excessive significance. So far, numerous routes for glycerol translation have been stated like: reduction, selective oxidation, esterification, etherification, transesterification, and polymerization [1].

Biodiesel is a harmless fuel with great biodegradability, better lubrication, and combustion efficiency. It can be formed from animal fats, oils, algal, and plant [2]. Usually, 1 mol of triglyceride containing fats and oils reacted with 3 mol of alcohol particularly methanol to provide 3 mol of fatty acid methyl ester fame that is named biodiesel, and 1 mol of glycerol result [3].

Therefore, the creation of every 1000 kg of biodiesel yields by-product of glycerol around 100 kg [4]. Biodiesel production in 2016 reached 37 billion gallons as indicated by Oil World's gauge. So, around 4 billion gallons of glycerol will be delivered that year [5]. It is usually recognized that glycerol has an extensive diversity of applications and usages like: pharmaceutical, perfumery, food, cosmetic, and coating [6].

Furthermore, glycerol itself is very inexpensive and most use needs added refining process. Later, the glycerol transformation to other important synthetic substances like esters of glycerol, glycerol carbonate, propane diols, glyceric acid, and acrolein will create included an incentive for glycerol, yet additionally advance biodiesel generation [5] [7] [8].

Glycerol is a non-flammable, non-toxic, readily biodegradable, water-soluble viscous liquid which is produced in the modern oleo chemical industry as a coproduct via a variety of processes including alcoholysis, saponification, as well as dedicated synthesis processes from propene and fermentation of sugars [9],[10]. Lately, scientists have changed Glycerol into a multitude of high valuable substances like propanediols, ethers, glycerol carbonate (GC), and bulk chemicals [11]. (GC) is an important multi-functional complex used as additive, solvent, and creates a block in substitute chlorine-free procedures [12].

GC is such a substance that has been extensively used in gas-separation membranes, paints, and solvent for therapeutic research and personal care products due to its low flammability, worthy bio-degradability, low toxicity, slight viscosity, high boiling point, and water solubility.

Also, GC has strained greatly care in the few last year’s owing to its possible manufacturing uses in the preparation of polyurethanes [13].

For these significant features, it detections many uses in diverse industrial parts, particularly as a glacial great hot solvent or middle in organic syntheses (i.e., synthesis of additional polymeric and polycarbonates constituents in

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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.

It is also used as a constituent in membranes for instead of ethylene, in the synthesis of polyurethanes, gas separation, and in the production of surfactants, propylene carbonates. Finally, glycerol carbonate and its derivatives it reflected to be a green extra for significant petro-derivative compounds (propylene carbonate or ethylene carbonate) [14].

As described previously in the previous studies, 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 [10].

The drawbacks of formation GC from *urea* and glycerol achieved by creation great quantities of ammonia and the difficulty in extrication the undesired by-products such as: biuret and isocyanic acid. Glycerol carbonate may be produced from ethylene carbonate and glycerol via transesterification reaction but the high boiling points of ethylene glycol as a by-product which makes the separation of products hard. Comparison with these ways, transesterification of dimethyl carbonate (DMC) with glycerol for GC preparation is reflected as the talented and most preferable method for industrial use due to the easy separation of byproduct, mild reaction conditions, high GC produce, and simple process [1].

A wide range of catalytic systems have demonstrated effective synthesis of glycerol carbonate, including both heterogeneous and homogeneous catalysts as well as enzymatic processes. The development of heterogeneous catalysts with worthy strength and high action is extremely wanted [15]. Between the probable catalysts which can be used, bio-char achieve high performance for valorization, prepared by pyrolysis method from utilization of renewable source (reed plant) was used to catalyze transesterification reaction and it can be considered a highly efficient heterogeneous catalyst easy to separate and recycle.

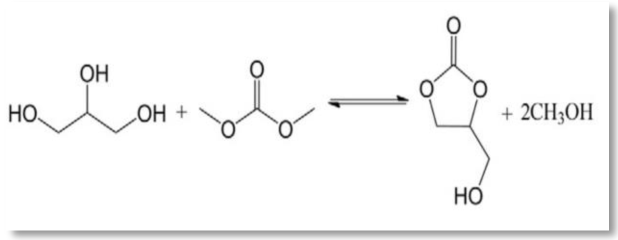

Fig. 1. Transesterification reaction to produce glycerol carbonate

2- Experimental Work

2.1. Char Manufacturing

Catalyst produced depending on pyrolysis technique, char was used to activate the reaction which was manufactured from reed plant as raw material.

Firstly, Reed plant was washed twice with deionized water instead of raw water to prevent increasing impurities in pore sites then dried for 6 hr by dryer under (110 ˚C) before uses. Then it was 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, bio-char prepared by pyrolysis process under different temperature from 400 - 800 ˚C for 1 hr in absence or very low oxygen .
Grinding and sieving to size (600 and 1200*)* micrometer biochar (400-800) ^{O}C

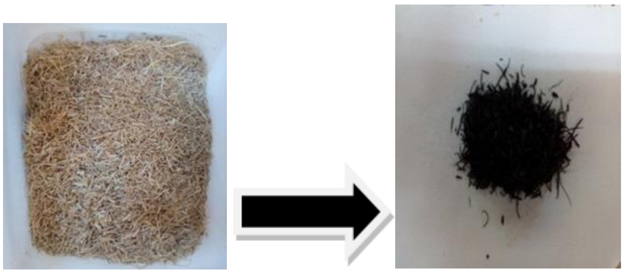

Fig. 2. Reed plant particles and prepared bio-char

2.2. Characterization

a. BET and pore volume

The surface area and pore volume measurement were performed by the Ministry of Oil, Petroleum R and D center by using ASTM D1993 accelerated surface area and porosimetry system. The knowledge of the specific surface, is of great importance in the characterization of a powder or a solid (extruded or beads), regardless of the areas of application. It helps to improve the control of the reactivity of a sample when it is in the presence of other materials.

In the BET measurement, the mixture of nitrogen with helium will pass through a channel for thermal conductivity detector, the detector to sample flow through a glass cell and then pass into analytical channel that is a thermal conductivity detector. Sign of detector was indicated by microprocessor control board, and then saved in a memory file.

The procedure of test began when degassing the sample by a carrier gas at a programming temperature. During the drying of operator transfer the holder of the sample to the analytical port and then fitted them with specified place by basis quick fit connectors.

Turning on the bottom should raise the nitrogen flask carriage will initiate the analysis. Desorption and adsorption of the gas measured with a highly sensitive thermal conductivity detector. High sensitivity will be used for a low surface area begin from 0.1 m2/g.

If the sample with the large surface area, then the thermal conductivity detector give wide range of signal response.

2.3. Glycerol Carbonate Production Procedure

The reaction of glycerol and dimethyl carbonate was performed in a three neck around bottom flask reactor (of 50 ml) equipped with a condenser, and established in a 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. Char prepared at various pyrolysis temperatures used to catalyze the reaction. The mixture of biochar catalyst and glycerol was heated to reach the reaction temperature and then added dimethyl carbonate.

The reaction performed at conditions 3:1 DMC :G ratio,60 ˚C ,90 min ,150 rpm and 3% weight percent catalyst loading ,these conditions selected as a mid-points in the studied variables 5:1 DMC :G ratio, (40 - 80) ˚C , (30 -150) min , (1 – 5)% weight percent catalyst loading and 150 rpm. HPLC (high performance liquid chromatography) was used for analyzing purpose.

Fig. 3. Photographic picture of Experimental work for GC synthesis

2.4. Catalyst Modification Procedure

Modification of catalyst was required in case of want to meet complete conversion and highly yield due to enhance the surface area of active sites.

It is important to investigate the effect of base molar concentration on improvement the catalyst activity [16] to give high glycerol carbonate yield, different molar concentration (1, 2 and 3) M from NaOH was used in char modification. Bio-char was modified as described in [16] by immersing (1.0 g) of bio-char in 20 mL of different molar concentration (1 - 3) Molarity sodium hydroxide solution, then was shaked for 24 hr at 120 rpm. Filtration was performed for solid separation from liquid, after that washed with deionized water till neutral pH was obtained and dried for 24 hr at 110 °C.

The modified bio-char used in the study with operating condition (3:1 ratio DMC: Glycerol, 60˚C, 90 min, 150 rpm and 3% weight per cent catalyst) these conditions selected as a mid-points in the studied variables 5:1 DMC :G ratio, (40 - 80) ˚C , (30 -150) min , (1 – 5)% weight percent catalyst loading and 150 rpm to investigate which molar concentration of NaOH have more effect increase the catalytic activity of bio-char.

3- Results and discussion

3.1. Effect of Pyrolysis Temperature on Bio-Char Yield%

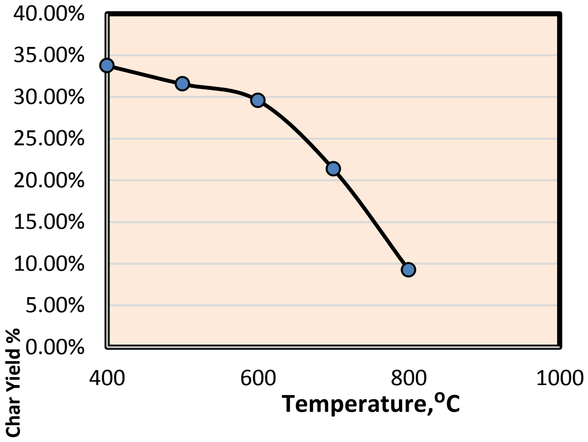

Fig. 4. Effect of pyrolysis temperature on bio-char yield%

Preliminarily the influence of pyrolysis temperature on the yield of bio-char must be investigated by study effect of different temperatures on prepared char from reed plant. Fig. **4** shows the results of the present study and show the effect of difference in pyrolysis temperature on 2 g of reed particles, obviously there is a continuous reduction in the weight of char and this is observed at each 100° C which was increased.

When the reed particles combusted at pyrolysis temperature 400° C the char yield gained 33.75% and when the pyrolysis temperature increased to 500° C and the yield obtained which decreased dramatically to 31.55%. This gives an indication that when the pyrolysis temperature increased the volatile element like hydrogen, nitrogen decreased also the water content will decrease with temperature increasing.

When the pyrolysis temperature became 600°C the char yield slightly decreased to 29.59%, In temperature 700°C and 800°C the yield obtained was 21.36% ,9.27% respectively, so approximately the char yield reached to the quarter yield of char which was prepared at 400°C. Increasing in pyrolysis temperature causes a in rise the ash and fixed C contents, also lowering of volatile materials content (hydrogen and oxygen) readily due to the weaker bonds in the volatile constituents [17].

Optimum bio char yield obtained in this study at the lower pyrolysis temperature 400° C.

Bio-char yield%

The yield of char used for indication the process efficiency for the chemical activation process. The char yield was calculated as the weight percentage of the manufactured char divided by the weight of the grinded reed.

$Yield\% = wei/weig \times 100$

wei (g) is weight of char

$weig$ (g) is weight of raw material

3.2. Effect of Prepared Char at Various Pyrolysis Temperatures on GC Yield% and G Conversion%

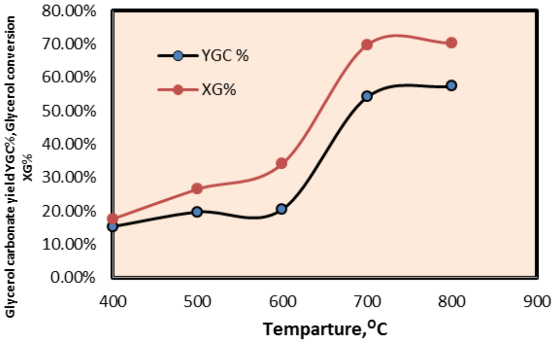

Fig. 5. Effect of prepared char at various pyrolysis temperatures on GC yield% and G conversion%

After preparation of char at different pyrolysis temperature from 400°C to 800°C, the catalytic activity of the prepared char was investigated by transesterification process of glycerol with dimethyl carbonate and to show the influence of prepared bio-char on glycerol carbonate yield and glycerol conversion.

The reaction was carried out under mild conditions temperature 60° C, 3:1 DMC: G ratio, 150 rpm and 3% wt. catalyst loading in time of 90 min ,all results illustrate in Fig. **5**. When the char was manufactured at 400 °C , the obtained GC yield and G conversion was very low (below 20%),after that char was prepared with 500°C used in catalyze the reaction to make a slight increasing in GC yield (19.683%) and G conversion (26.53%). GC yield and G conversion was obtained from catalyze the reaction with char prepared at pyrolysis temperature 600°C were 20.48%, 34.17% respectively.

The prepared char at 700°C has been shown a dramatic increasing in yield and conversion until reach 54.16%, 69.81% respectively.

In each increasing in bio-char preparation temperature causes dramatic increase in GC yield an G conversion this can belong to increasing the active sites numbers and catalytic surface area of bio-char catalyst causes increment in GC yield an G conversion .

The Highest values for yield and conversion were obtained when the reaction catalyze with bio-char prepared with 800 °C pyrolysis temperature but the difference in values of GC yield and G conversion between the two bio-char prepared at temperature (700 °C and 800 °C) is very slight and to reduce in energy and cost , the bio-char prepared at 700°C used for catalyzing transesterification reaction .Finally to enhance the char activity ,the selected bio-char immersed in (0.1 M) HCL for 24 hr to remove impurities from char pores after that washed with deionized water for neutralization purpose to be ready for catalyzing glycerol transesterification reaction then found a good increasing in GC yield happened reach it to 67.8% and G conversion reached to 76.3%, the increment in GC yield and G conversion belonged to clearance the active sites from impurities when the char washed with (0.1 M) HCL.

3.3. Effect of Modified Bio-Char by Different NaOH Molar Concentration on GC Yield% and G Conversion%

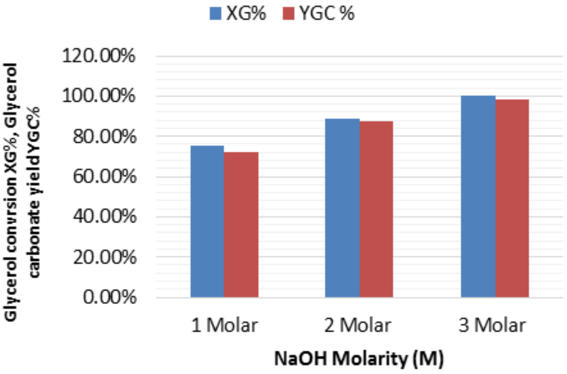

Fig. 6. Effect of different NaOH molar concentration on catalytic activity

Fig. **6** explain all results of glycerol carbonate yield and glycerol conversion at different molar concentrations of NaOH under time 90 min , temperature 60 °C, Dimethyl Carbonate : Glycerol ratio 3:1 DMC:G ratio and 3%wt. used from catalyst loading.

From the figure observed that each increasing in NaOH concentration which was used for catalyst modification there was increasing in GC yield and G conversion. complete conversion of glycerol was achieved by enhancing the catalyst with 3 M NaOH also high yield of GC obtained 98.32%,the increment in yield belonged to enhancing the activity of catalyst when modified with sodium hydroxide base by increasing the number of hydroxyl group OH as described in [18] and this was regarded as a major reason to initiate the reaction between the proton of weak acid from one of the two primary hydroxyl group of glycerol with the base catalyst ,this is mean in each increasing in NaOH concentration the hydrouxyl groups number increment and the GC yield and G conversion also increased .

3.4. Surface Area and Pore Volume

The obtained BET surface area and total pores volume of prepared bio-char from reed plant particles are 214.1487 m^2/g and 0.1204 cm^3/g respectively, so the results show good surface characterization for transesterification process .The surface area and pore volume of char produced from different feedstock clarified in the table below:

Table 1. Specifications of char from different feedstock

Feedstock	Surface Area **m^2/g**	Pore Volume **cm^3/g**	References
Cotton stalk	224	0.070	[19]
Pine wood	209.6	0.009	[20]
Bamboo	351	0.130	[21]

4- Conclusion

Reaction of glycerol with dimethyl carbonate is performed by catalyzing the reaction with bio-char as a heterogeneous catalyst. Char catalyst prepared from reed plant as a natural source by pyrolysis technique under different temperatures from 400°C to 800°C, in each increasing in pyrolysis temperatures the yield of char decrease.

The Highest values for GC yield and G conversion were obtained when the reaction catalyze with bio-char prepared at 800 ^{O}C pyrolysis temperature but the difference in values of GC yield and G conversion between the two prepared bio-char at temperatures (700 ^{O}C and 800 ^{O}C) is very slight also to reduce the energy cost select bio-char prepared at 700^{O}C. The char prepared at 700^{O}C give 54.16 % GC yield and 69.81% G conversion. when the selected catalyst immersed in (0.1 M) HCL for 24 hr and washed with deionized water for neutralization purpose found a good increasing in GC yield happened reach it to 67.8% and conversion reached to 76.3%.

The catalyst modification with 3 M NaOH shows enhance in catalyst activity to give high yield of GC reached to 98.32% and complete conversion achieved, all the reactions carried out under conditions 90 min, 60 ^{O}C, 3:1 DMC:G ratio and 3%wt. used from catalyst loading.

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تحسين تحويل الكليسرول الى كليسرول كاربونيت بأستخدام الفحم الحيوي المحسن والمنتج من نبات القصب

شفاء ضياء و مثنى جبار

جامعة بغداد–كلية الهندسة–قسم الهندسة الكيمياوية

الخلاصة

يعد الكليسرول الفائض من عمليات انتاج البايوديزل كمنتج ثانوي بكميات هائله مصدر جيد لانتاج مادة الكليسرول كاربونيت حيث ان كل 1000 كيلوغرام من البايوديزل يصاحبها تقريبا 100 كيلوغرام من الكليسرول.

الهدف من هذا البحث هو دراسة احتمالية تحويل الكليسرول الى كليسرول كاربونيت بأستخدام الفحم الحيوي المحضر من نبات القصب .يتم تحضير العامل المساعد بحرارات مختلفه من 400الى800°درجة مئوية وقد اظهرت النتائج ان الفحم المحضر بالدرجه الحراريه 700° درجة مئوية يعد الافضل من بين انواع الفحم المحضره .لكن الانتاجية زادت الى 80, 67 % بأستخدام الفحم الحيوي المحضر وعندما تم تحسين العامل المساعد باستخدام هيدروكسيد الصوديوم فأن الانتاجية وصلت الى 98.3% وتحول تام .في هذه الدراسة يتم تحقيق تحول تام بظروف 60°درجة مئوية، 90 دقيقة، 3:1 نسبة الكليسرول:الداي مثيل كاربونيت ,3% نسبة تحميل العامل المساعد واستخدام الفحم الحيوي المحسن ب 3 مولاري من هيدروكسيد الصوديوم.

الكلمات الدالة: كليسرول كاربونيت, كليسرول, التحلل الحراري, الفحم الحيوي.