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RESEARCH ARTICLE

GREEN CATALYTIC SYNTHESIS OF POLYGLYCEROL OVER GREEN CARBON

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ABSTRACT

The conventional risks in the production of petrochemical products are higher than that of the bio-based products. Glycerol is the major byproduct of biodiesel industry. Due to the increased environmental awareness and cost effectiveness, we have developed an eco-friendly catalyst for effective utilization of glycerol by converting it into polyglycerol. The heterogeneous catalytic polymerization of glycerol was investigated with the influence of green carbon as a catalyst. The catalyst is characterized by various spectroscopic techniques. The FT-IR analysis of the catalyst reveals the absence of OH group. The XRD analysis reveals that the green carbon synthesized has a modified graphite structure. SEM and EDX analysis gives details of the surface morphology and the percentage of carbon present in the green carbon. Experiments were carried out in a batch reactor containing 1.26 wt% of glycerol, 0.01 wt% of catalysts at 300°C and 3 hr duration which proved to be the optimum conditions for maximum conversion of glycerol. The resultant biocompatible lower molecular weight polyglycerol were characterized by FT-IR, ^{1}H NMR and MALDI-TOF techniques. The results obtained reveal the synthesized green carbon as a promising low cost material for the production of polyglycerol.

INTRODUCTION

Biodiesel is currently used as a valuable fuel for diesel engines. Biodiesel is a mixture of methyl esters of fatty acids. It is synthesized by the transesterification reaction of vegetable oil with methanol in the presence of a basic catalyst (Frusteri, *et al.*, 2009). The demand of biodiesel has been increased in the recent years. In the context of biodiesel market, glycerol (1, 2 & 3 - propanetriol) plays a very important role since it is the major by-product in the methanolysis of vegetable oil. About 1kilogram (10%) of glycerol is obtained for each 10 kilograms of biodiesel produced (Olga Guerrero-Pérez, *et al.*, 2009). With a sharp rise in biodiesel production, an oversupply of glycerol has been created, causing its price to decline substantially. As a consequence, new applications for glycerol are being investigated, because it can be considered a promising building block for bio-refineries (Maraisa Goncalves, *et al.*, 2013). A large set of reaction pathways for catalytic conversion of glycerol is available, including selective oxidation, dehydration to acrolein, pyrolysis, polymerization of glycerol etc. Catalytic processes are widely employed in the manufacture of bulk as well as fine chemicals. There are several processes in the fine chemical industry which employ catalytic routes in order to make them eco-friendly and cost effective (Weiqin Zhao, *et al.*, 2010; Xia Ge, *et al.*, 2005; Somaieh Salehpour, *et al.*, 2012). The current reactions for the manufacture of polyglycerols are based on homogeneous acid catalyzed reactions (Kenar, 2007; Bozell, *et al.*, 2010; Valter, *et al.*, 2008; Somaieh Salehpour *et al.*, 2012). In homogeneous catalytic systems, the reactions can be efficiently carried out with high yields, but lengthy purification procedures are inevitable and generally the expensive catalysts are quite difficult to recover and recycle (Yanlong Gu, *et al.*, 2008; Zuliani, *et al.*, 2008; Kamal Iaych, *et al.*, 2011).

In the present work, the catalyst is developed for effective utilization of glycerol by converting it into polyglycerol. The glycerol polymerization reaction reported in the previous literature needed many toxic solvents and catalysts which led to environmental pollution and corrosion (Carlos Ma, *et al.*, 2004; Clacen, *et al.*, 2002). In the present investigation, solvent free glycerol polymerization was studied in the presence of eco-friendly Green Carbon (GC) as a catalyst.

MATERIALS AND METHODS

Catalyst Preparation

The polymerization of glycerol was studied by using the catalyst, Green Carbon. The carbon prepared from cellulose-based material by thermal method without using any chemicals is known as green carbon (GC). High temperature reactor is used for the preparation of green carbon. The wood pieces are packed in a reactor by supporting on either side by asbestos wool. This reactor is kept inside a tubular furnace. The furnace temperature is controlled by a digital temperature controller. The reactor temperature was increased upto 250°C and the

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same temperature was maintained for 3hrs in the absence of air. The reactor is continuously evacuated during the carbonization reaction to remove volatile organic content and moisture.

Catalytic Reaction

The green chemistry approach for the polymerization of glycerol was carried out over green carbon as a catalyst without solvent. The catalyst and the monomer are taken in a two necked 100ml round-bottom flask. The central neck of the flask is fitted with a condenser and a thermometer, the side neck is provided with a mercury well. The flask is gently heated on a heating mantle with controlled temperature. The contents are refluxed at various temperatures. The polyglycerol and monomer are separated by distillation.

Material Characterization

The surface chemistry of the catalyst was determined by Fourier transform infrared (FT-IR) analyzer using JASCO-410 FT-IR Spectrometer. This analysis was performed by mixing dried carbon sample with potassium bromide (KBr). The spectra were acquired in the range of 400-4000 cm^{-1}. X-ray diffraction (XRD) samples were recorded on a Rich Siefert 3000 diffractometer using a monochromated Cu Kα radiation wavelength of 1.5405Á. The peak position (2 Theta) was obtained between 10^{o} and 80^{o}. The morphology was determined by scanning electron microscopy (SEM). The percentage of green carbon was determined by energy dispersive X-ray spectrometry (EDS). Analysis was made on a JEOL JSM 6360 field emission scanning electron microscope. To find out the structure and molecular weight; the polyglycerol was characterized by FT-IR, ^{1}HNMR and MALDI-TOF. The ^{1}H NMR (500MHz) spectra were recorded with a Bruker DRX500 spectrometer and MALDI-TOF measurement was recorded by Shimadzu Biotech Axima CFR.

RESULTS AND DISCUSSION

FTIR analysis

The FT-IR absorption spectrum of green carbon is shown in Figure 1. In FT-IR spectra, the peak in the region of 1698 cm^{-1} is attributed to the stretching vibration of C=O in green carbon and the peak at about 1605 cm^{-1} belongs to C=C stretching vibration. The peak appeared at about 1215 cm^{-1} is due to C-O-C asymmetric stretching. Absence of OH stretching in the FT-IR spectrum proved that all the glucose units present in cellulose are cracked to produce carbon. Since this carbon is produced without any chemicals, it is called green carbon (Kannan, *et al*., 2009).

X-Ray diffraction analysis

The synthesized green carbon is also characterized by XRD to find out the crystallinity and phase purity. The XRD pattern is presented in Figure 2. The diffraction peaks at 14.9^{o} (100), 24.3^{o} (110), 34.1^{o} (200) and 38.2^{o} (211) are observed in the XRD diffraction of green carbon. From the data, unit cell values a, b and c are calculated and it is observed that $a = b \neq c$. This result proves that the green carbon has hexagonal morphology similar to graphite structure (Wenhen Li, *et al.*, 2003).

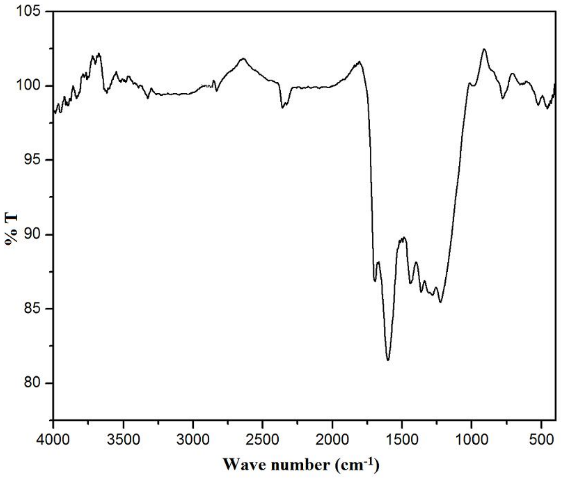


Figure 1. FT-IR spectrum of the green carbon

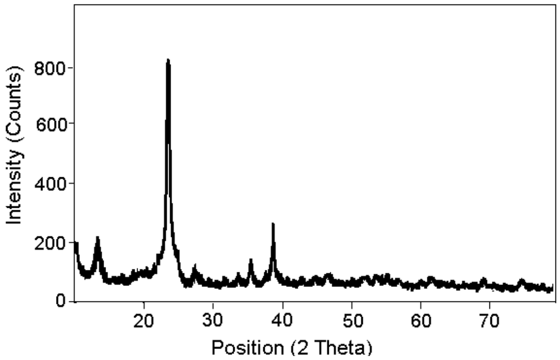
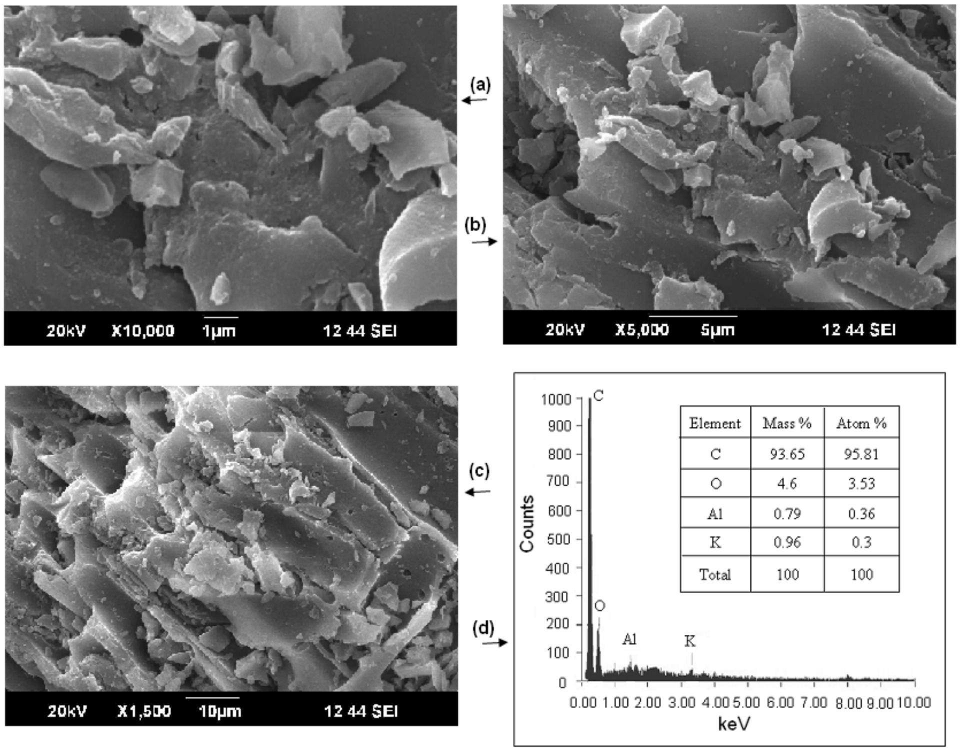


Figure 2. XRD pattern of green carbon

Scanning Electron Microscopy- Energy Dispersive X-ray (SEM-EDX) Analysis

Scanning the surface morphology of electron micrograph of green carbon is presented in Figure 3a – 3c. It shows the expanded graphite flakes which consist of several layers of graphite sheets (Asma Yasmin, *et al*., 2006). Most of the graphite flakes are strongly deformed due to thermal cracking of wood material which also creates many pores in the graphite structure of green carbon, which is clearly visible in the SEM image.

Energy Dispersive X-ray spectroscopy (EDX) analysis is made to find out the elements present in the green carbon. EDX spectrum of green carbon is shown in Figure 3d. The elemental analysis of green carbon reveals that large amount of carbon (93.65%) and trace amount of Oxygen (4.6%), Aluminium (0.79%) and Potassium (0.96%) are present in this green carbon. The major composition of carbon present in the material proves that the cellulose polymer (wood) is completely converted into carbon.



Element	Mass %	Atom %
C	93.65	95.81
O	4.6	3.53
Al	0.79	0.36
K	0.96	0.3
Total	100	100

Figure 3. Surface images of green carbon (a), (b) & (c) and EDX (d)

Polymerization of glycerol

Effect of time

The influence of reaction time on the glycerol polymerization was studied at various time intervals using the same green carbon loading 0.01 wt % and monomer dosage 1.26 wt% by reaction experiments at 300°C and the results are shown in Figure 4. Referring the same, the percentage of conversion is increased with the increase of time and found that the conversion of glycerol is rapidly increased in the first 2 hours and the maximum conversion (81%) is reached slowly in duration of 3 hours. There is no effective conversion after 3 hours duration.

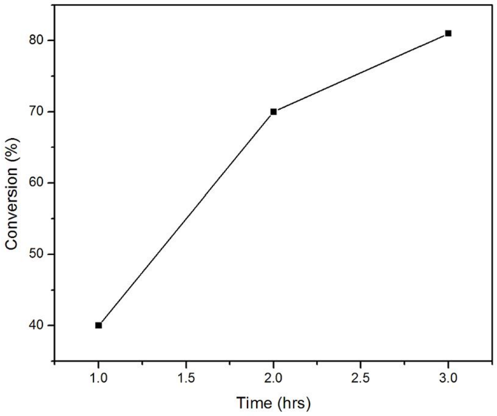


Figure 4. Effect of contact time on glycerol conversion over GC

Effect of temperature

The glycerol polymerization in pursuance of temperature was studied from 100° to 300°C. In this study, the green carbon loading 0.01 wt %, monomer dosage 1.26 wt% and 3 hours duration is maintained throughout the reaction and the results are plotted in a graph (Figure 5). The conversion of glycerol is slowly increased with the increase of temperature from 100° to 200°C. There is a rapid increase in conversion after 200°C and the maximum is attained at 300°C. It is found that the activity of green carbon increases with the increase of temperature.

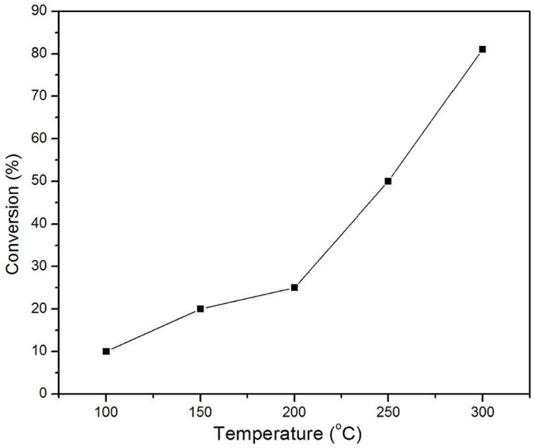


Figure 5. Effect of temperature on glycerol conversion over GC

Effect of glycerol dosage

The glycerol polymerization in relation to glycerol dosage was studied from1.26 to 12.6 wt%. In this study, the green carbon loading 0.01 wt%, temperature at 300^{o}C and 3 hours duration is maintained throughout the reaction and the results are plotted in a graph (Figure 6).

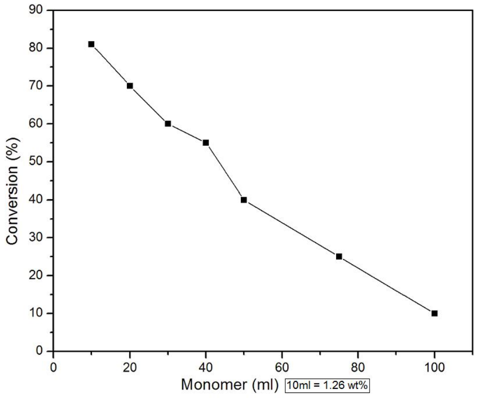


Figure 6. Effect of monomer dosage on glycerol conversion over GC

It is observed that the conversion of glycerol at maximum of 1.26 wt% and it slowly decreases with increased glycerol dosage. This is due to the active sites and pores created in the green carbon framework during carbonization reaction at high temperature. It proves that the catalyst green carbon is very active during glycerol conversion.

Effect of catalyst dosage

The glycerol polymerization in pursuance of catalyst green carbon dosage was studied from 0.002 to 0.01wt %. In this study, the glycerol dosage loading 1.26 wt %, temperature at 300^{o}C and 3 hours duration is maintained throughout the reaction and the results are plotted in a graph (Figure 7). It is found that there is a linear relationship between the active sites of the catalyst and glycerol conversion. In this we find that, the percentage of conversion of glycerol is increased with the increase of catalyst amount. If the catalyst amount is increased, the active sites and surface area of catalyst are also increased.

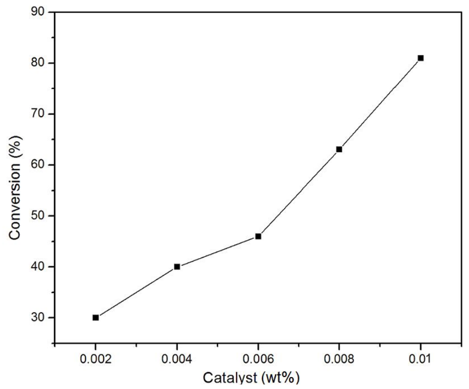


Figure 7. Effect of catalyst dosage on glycerol conversion over GC

Characterization of polyglycerol

FT-IR characterization of Polyglycerol

The synthesized polyglycerol by using green carbon in the liquid phase is characterized by FT-IR spectrum to confirm the polymer structure. The FT-IR spectrum of polyglycerol is shown in Figure 8. The ether group vibration is observed from 1000 to 1150 cm^{-1} due to C-O-C stretching, CH stretching mode is observed from 2840 to 2980 cm^{-1}, CH$_2$ stretching mode is observed from 1212 to 1332 cm^{-1}. The hydroxyl group bands are observed from 3000 to 3650 cm^{-1} (Marc Dube, *et al.*, 2012). The CH$_2$, CH, ether and hydroxyl group vibration are observed from the FT-IR spectrum indicating the formation of polyglycerol in liquid phase reaction over green carbon.

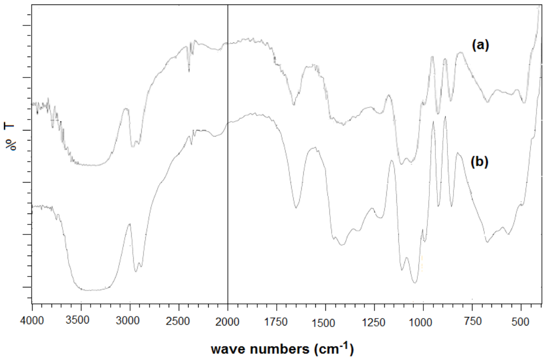


Figure 8. FT-IR spectra for; (a) Polyglycerol & (b) Glycerol

^{1}H-NMR characterization studies of Polyglycerol

The synthesized polyglycerol from green carbon in the liquid phase is characterized by ^{1}H-NMR to confirm the polymer structure. The ^{1}H-NMR spectrum of polyglycerol is shown in Figure 9. In ^{1}H-NMR spectrum, the CH$_2$ and CH protons of polymer signals appear as a multiplet pattern between 3 and 4 ppm and hydroxyl proton signals are observed around 4.5 to 5 ppm as a multiplet (Kim, *et al.*, 1998). The CH$_2$, CH and hydroxyl peaks are observed from the ^{1}HNMR spectrum proving the formation of polyglycerol in liquid phase polymerization reaction in the presence of green carbon.

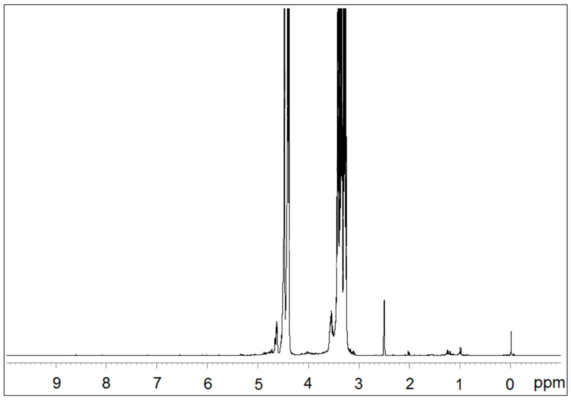


Figure 9: ^{1}H NMR of polyglycerol

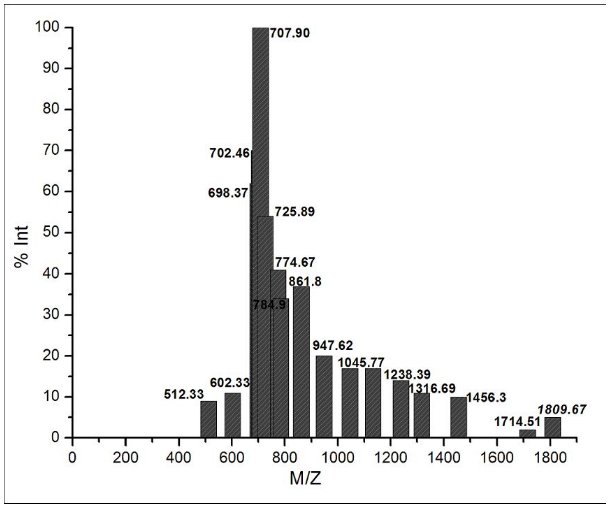


Figure10. MALDI-TOF of polyglycerol

MALDI-TOF characterization of Polyglycerol

MALDI–TOF is one of the most powerful tools for mass analysis of high molecular weight compounds. MALDI-TOF spectrum for polyglycerol synthesized by using green carbon is shown in Figure 10. It is observed that the molecular weight distribution is of a broad pattern for the polyglycerol synthesized over green carbon. The maximum molecular weight (Mn) distribution of polyglycerol obtained over green carbon catalyst is 707 to 861. This molecular weight polyglycerol has various applications i.e., used as drug carriers, molecular labels or probe moieties, hydrogels etc.

Conclusion

The heterogeneous catalytic polymerization of glycerol has been studied in the presence of green carbon in liquid phase. All characterizations have proved that the green carbon structure is similar to a graphite structure but have many number of pores. Green carbon is highly active for this reaction and it has strong active sites; which are probably created due to thermal cracking during carbonization of wood material. This reaction is a solvent free reaction and the catalyst is eco-friendly and reusable. Since this reaction is a green process, this polymer is useful for application as drug carriers, hydrogels, etc.

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