



Synthesis and characterization of carbon cryogel microspheres from lignin–furfural mixtures for biodiesel production



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HIGHLIGHTS

- Carbon cryogel has been synthesized from lignin and furfural.
- The carbon cryogel produced has microspheres structure.
- High total acidity and large surface area of hydrophobic amorphous carbon cryogel.
- Carbon cryogel exhibits potential for catalyzing oleic acid esterification.

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ABSTRACT

The aim of this work was to study the potential of biofuel and biomass processing industry side-products as acid catalyst. The synthesis of carbon cryogel from lignin–furfural mixture, prepared via sol–gel polycondensation at 90 °C for 0.5 h, has been investigated for biodiesel production. The effect of lignin to furfural (L/F) ratios, lignin to water (L/W) ratios and acid concentration on carbon cryogel synthesis was studied. The carbon cryogels were characterized and tested for oleic acid conversion. The thermally stable amorphous spherical carbon cryogel has a large total surface area with high acidity. Experimental results revealed the optimum FAME yield and oleic acid conversion of 91.3 wt.% and 98.1 wt.%, respectively were attained at 65 °C for 5 h with 5 wt.% catalyst loading and 20:1 methanol to oleic acid molar ratio. Therefore, carbon cryogel is highly potential for heterogeneous esterification of free fatty acid to biodiesel.

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1. Introduction

The more common applications of carbon include as catalyst supports and adsorbents. The carbon could be prepared by drying and carbonizing synthesized organic gels. Carbon gel is a type of carbon similar to activated carbon, carbon composite, and carbon film. Different drying methods such as supercritical, freeze and evaporative would produce aerogels, cryogels, and xerogels, respectively. Carbon cryogel is one type of carbons with good properties, characteristics and much potential due to its unique structure. Among its applications are for column packing material in high performance liquid chromatography (HPLC) (Yamamoto et al., 2002), anode material (Chao et al., 2008) and support catalyst (Mukai et al., 2005).

In previous studies, phenol has been commonly used with formaldehyde to produce gels (Mukai et al., 2005; Poljanšek and

Krajnc, 2005; Scherdel and Reichenauer, 2009). Instead of using phenol and formaldehyde, gels could be synthesized by using the derivatives of phenol and formaldehyde, depending on the synthesis process. The synthesis of organic gels via phenol derivatives with higher aldehyde compounds may give different properties and reactivity. Lignin (Çetin and Özmen, 2002; Tejado et al., 2007; Vázquez et al., 1995), tannin (Grishechko et al., 2013b; Szczurek et al., 2011), and resorcinol (Babić et al., 2004; Czakkal et al., 2005; Tamon et al., 1997) have been used to produce organic gels as another alternative to substitute and reduce phenol usage. In addition, formaldehyde derivatives such as paraformaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, glyoxal, trioxane, furfural, and furfural have been tested to produce phenolic resins (Fink, 2005a). For example, substituted phenol and formaldehyde derivatives such as the usage of tannin with furfural (Kraiwattawong et al., 2007) and phenolic polymer with furfural (Pekala et al., 1995) have produced organic gels.

The polymeric organic gel can be synthesized using either basic or acidic catalyst. Previously, gels produced from phenol or

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resorcinol with formaldehyde were synthesized in the presence of basic catalyst (Job et al., 2005; Pekala, 1989; Scherdel and Reichenauer, 2009; Tamon et al., 1999). Lignin–furfural mixture could be used in synthesizing furan resin via poly-condensation reaction in the presence of acid catalyst, which resulted in linear oligomers through the furan rings linkage by methylene and methylene-ether bridges (Fink, 2005b). The reaction between lignin and furfural could form complex resin. Lignin itself has a link with monomers in their structures and the linkage with furfural produced more complex polymeric structures. Both lignin and furfural are biomass-based side products of many biofuel processes. The use of lignin and furfural in the synthesis of the carbon gel as catalyst is expected to benefit the biofuel industry for improving the sustainability.

Carbon cryogel could be produced in monolith or particles form depending on the gel synthesis and preparation method. Usually water would affect the gel formation. It is imperative that water is removed after the polycondensation reaction or water would develop into ice crystals inside the pore due to pore shrinkage during freeze drying. Solvent exchange with *t*-butanol was used to prevent the pore shrinkage on carbon cryogel by maintaining the gel structure (small pore volume change) and shortening the drying time (Kraiwattanawong et al., 2007). It was reported the usage of *t*-butanol led to formation of ice crystals, which strongly modified the texture of the materials when the amount of solvent was too high (Job et al., 2005). The pore volume during the synthesis and drying process should be controlled to produce carbon cryogel of different shapes and sizes for various applications.

Vegetable or waste oil is the usual feedstock for synthesizing biodiesel, but it contains high compositions of free fatty acid (FFA). Oleic acid has been investigated as a model compound for FFA content in oil (Deshmane et al., 2013; Liu et al., 2013; Shao et al., 2013; Yin et al., 2012). Other FFAs have also been used in esterification process such as lauric (Zhai et al., 2011), caproic (Alsalmeh et al., 2008), palmitic (Kastner et al., 2012), and stearic (Ghiaci et al., 2011) acids. The FFAs must be treated with alcohol using acid catalyst to reduce its acid value to produce fatty acid esters or biodiesel. Thus, the acid catalysts such as carbon cryogel have potential to catalyze reactions with high FFA feedstocks to reduce the high FFA content and produce large fatty acid ester yield in a single-step process.

In this paper, carbon cryogel was synthesized from commercial lignin–furfural mixtures via sol–gel poly-condensation reaction followed by drying and carbonization. For preparation of the carbon cryogel, the conditions for gel synthesis were initially investigated at various lignin to furfural ratios, lignin to water ratios and acid concentrations. The carbon cryogel was further characterized using surface area analyzer (BET), temperature programme desorption (TPD), thermogravimetric analyzer (TGA), Fourier transform infrared spectroscopy (FTIR), Energy dispersive X-ray (EDX), X-ray diffraction (XRD) and scanning electron microscope (SEM). Subsequently, the performances of the carbon cryogels were tested for the esterification of oleic acid into fatty acid methyl ester or biodiesel.

2. Experimental

2.1. Materials and chemicals

Ethanol, C₂H₆O (95%), sulfuric acid, H₂SO₄ (95–97%), oleic acid, C₁₈H₃₄O₂ and methanol, CH₄O were purchased from QRec, New Zealand. Meanwhile, lignin and furfural were purchased from Sigma–Aldrich, USA and Merck, Germany, respectively. Ethanol, sulfuric acid, lignin and furfural were utilized for gel synthesis

while methanol and oleic acid were used as feeds in the esterification process over the prepared carbon cryogel.

2.2. Preparation of carbon cryogel

Commercial lignin (7 g) and furfural was mixed in a Schott bottle at different ratios. Distilled water and ethanol were used to dilute and homogenize the mixture using H₂SO₄ as the acid catalyst. The lignin–furfural mixture was heated in silicon oil bath at 90 °C for 0.5 h. Lignin to furfural (L/F) ratios of 0.77–1.43, lignin to water (L/W) ratios of 0.5–1.5 and acid concentrations of 2–8 M were varied to study the effect of the variables on gel synthesis.

After the reaction was completed, the gel produced was let to cool to room temperature. The dark colored resin gel was immersed with twice the volume of *t*-butanol for solvent exchange and then rinsed with *t*-butanol to displace excess liquid. The product was pre-frozen for 24 h in the refrigerator and freeze dried at –60 °C (condenser temperature) for 8 h in the freeze dryer to form cryogel. Finally, the cryogel was carbonized under inert flow at 500 °C for 5 h to produce carbon cryogel.

2.3. Characterization of carbon cryogel

The Brunauer Emmett Teller (BET) surface area of the carbon cryogel was evaluated using Micromeritics 3Flex 3.01 instrument based on nitrogen adsorption and desorption at –196 °C. Meanwhile, the acidity of the carbon cryogel was analyzed via NH₃-TPD using thermal conductivity detector (TCD) by passing 10% NH₃/He gas up to 900 °C. The stability and main composition of sample products were determined using TGA (Perkin Elmer TGA 7) from 30 to 900 °C under nitrogen flow at 10 °C/min. The chemical bonding of the product was studied using FTIR (Perkin-Elmer Spectrum) using KBr pellet for IR range of 650–4000 cm^{–1} and the spectra obtained were further analyzed. EDX (Hitachi SU8020) was used to measure the weight composition of C, O and S. XRD was used to study the structure of the product and the analysis was evaluated using a Bruker D8 Advance diffractometer system (Cu K α radiation, 40 kV, 30 mA) for angle 2 θ between 10° and 80°. The morphology of the sample product was observed using SEM (model: JSM-6390LA, brand: JEOL). Further characterizations with TGA, FTIR, XRD, and SEM were conducted on selected carbon cryogel. Lignin and cryogel characteristics were also compared with the carbon cryogel.

2.4. Esterification of oleic acid

The performance of the carbon cryogels as a catalyst was tested in the esterification of oleic acid with methanol. The yield of methyl ester fatty acid (FAME) was also used as a criterion in the screening of parametric study for the synthesis of carbon cryogel. The reaction was conducted in a three-neck flask equipped with a reflux condenser. The condenser was cooled (20 °C) through a circulating water bath. Esterification of oleic acid was performed at 65 °C and 5 h with 20:1 molar ratio of methanol to oleic acid and 5 wt.% catalyst loading. After reaction, the product mixture was cooled to room temperature before it was evaporated in the oven at 105 °C to remove water and excess methanol. Selected experimental runs were randomly repeated to test the reproducibility of the data.

Fatty acid methyl ester (FAME) was characterized using a GC–MS 6890 N network gas chromatograph system and a 5975 inert mass selective detector under the following condition: column, HP-5MS (length, 30.0 m; diameter, 250.0 μ m); injector temperature, 250 °C; column temperature, 140 °C (4 min) \rightarrow 250 °C (5 °C/min); carrier gas, helium (1.2 mL/min). Identification of product was made by comparing the peak at the same retention time

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