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Glycerol Etherification by *tert*-Butanol Catalyzed by Sulfonated Carbon Catalyst

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Abstract: The recent discovery of sulfonated carbon catalyst made from sugar attracts attention owing to its renewable source. The sulfonated carbon catalyst shows higher reactivity on esterification and transesterification reactions over the conventional solid acid catalysts such as nobic acid and amberlyst. These findings are remarkable because the sulfonated carbon catalyst has a surface area much smaller than any other solid acid catalysts tested for esterification and transesterification reactions. This study reports the characteristics of the sulfonated carbon catalyst and its reactivity on glycerol etherification by *tert*-butanol. Sulfonated carbon catalyst was prepared by sulphonation of the sugar char, prepared by pyrolyzing sugar (D-glucose) at 400°C for 15 h under nitrogen flow in a tube furnace. The catalyst was characterized by specific surface area, thermo-gravimetric analysis, FT-IR and total acidity, which showed that the sulfonated carbon catalyst has a surface area of less than 1 m² g⁻¹ and decomposed under inert gas at around 236°C. The catalyst has a total acidity of 4 mmol g⁻¹, mainly contributed by -SO₃ moiety as indicated by the FT-IR analysis. Etherification sample analyzed on GC-MS showed the presence of mono-glyceryl ethers isomers and di-glyceryl ether isomers; however, tri-glyceryl ether was not detected. The capability of the catalyst to promote the production of glyceryl ethers is a new application of the newly discovered sulfonated carbon catalyst; however, more experiments are required to elucidated catalyst reactivity, stability and selectivity under different reaction conditions. Di-glyceryl ethers are useful products in many applications such as biodiesel fuel additives.

Key words: Etherification, fuel additives, glyceryl ethers, sulfonated carbon catalyst, sugar catalyst

INTRODUCTION

Biodiesel (fatty acid alkyl esters) has already been commercialized and is well known as an alternative fuel with greener emissions properties compared with petroleum based diesel fuel (Demirbas, 2007). It is expected that the demand for biodiesel will continue to grow owing to its renewability and the increase in petroleum based fuel prices. However, the current world capacity to produce biodiesel is less than 1% of the fossil fuels usage (Dumelin, 2005). While, the market for biodiesel has leaped in recent years, the drawbacks of biodiesel must be addressed. The increased demand of neat vegetable oil from biodiesel industries has escalated the edible oil and grain prices affecting the economy of food supply.

Another area that needs attention in improving the overall biodiesel production process is the utilization of glycerol, the byproduct. Increased biodiesel production will inevitably increase glycerol production. Glycerol is

currently used to produce many downstream products; however, the projected surplus production will decrease the glycerol market price. One of the efforts to utilize glycerol is by converting into di- and tri-ethers via etherification reaction (Kesling *et al.*, 1994; Bradin, 1996; Nouredini, 2000; Behr and Obendorf, 2001; Klepacova *et al.*, 2003, 2005, 2006, 2007). Di- and tri-ethers are fuel oxygenates and readily used as blends to petroleum diesel. Addition of oxygenates to gasoline has a two-fold objective: to enhance the octane rating of internal combustion engines; and to reduce air pollution (summertime smog, wintertime carbon monoxide and year-round air toxins) from more complete fuel combustion in engines. Furthermore, blending of di- and tri-glyceryl ethers into biodiesel has positive results as cloud and pour point properties are improved (Nouredini, 2000). This finding paves the way for a possible integrated biodiesel production, converting oil into biodiesel and glycerol into ethers which will make the overall process more economically favourable.

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Glycerol, a by product of triglyceride transesterification reaction, can be etherified with *tert*-butanol (also known as *tert*-butyl alcohol) or isobutene in the presence of acid catalyst into mono-, di- and tri-glyceryl ethers (Behr and Obendorf, 2001; Klepacova *et al.*, 2005, 2006, 2007). Glycerol etherification with *tert*-butanol produces water as a by-product, while isobutene does not (Klepacova *et al.*, 2006, 2007). A recent patent application by Bhat and Bhat reports on the etherification of glycerol by methanol and ethanol to produce tri-glyceryl ether (Bhat and Bhat, 2007).

Klepacova *et al.* (2003, 2005, 2006, 2007) tried several commercial solid acid catalysts such as Amberlysts (15, 31, 35 and 119), ion-exchange resins (A-31 and A-119) and large-pore zeolites (H-Y and H-Beta) to catalyze glycerol etherification with isobutene or *tert*-butanol. They found that etherification with *tert*-butanol leads to lower conversion and selectivity owing to the presence of water formed by dehydration of *tert*-butanol deactivates the catalysts. Glycerol can be converted to ethers (for example by ion-exchange resin A 35) when using isobutene. However, isobutene is very expensive compared with *tert*-butanol and it requires high pressure (2 MPa) to keep isobutene in liquid form Behr and Obendorf (2001).

Recent discovery of sugar catalyst for esterification (Toda *et al.*, 2005) and transesterification (Zong *et al.*, 2007) reactions offers potential for further improvement in biodiesel processing. Sugar catalyst, or generally known as sulfonated carbon catalyst was reported to have higher biodiesel conversion over conventional solid acid catalysts such as niobic acid, nafion, sulfated zirconia and Amberlyst-15. Further elucidation of the characteristics of sulfonated carbon catalyst and its reactivity on other reactions such as etherification warrants serious attention.

This study reports on the characteristics of sulfonated carbon catalyst such as surface area, acidity, thermo-gravimetric analysis and FT-IR analysis; and sulfonated carbon catalyst reactivity on etherification reaction between glycerol and *tert*-butanol.

MATERIALS AND METHODS

Catalyst preparation: Sulfonated carbon catalyst was prepared according to the method by Toda *et al.* (2005). D-glucose (99.5%, Sigma) was pyrolyzed in a tube furnace (Thermolyne model F21135) at 400°C for 15 h under nitrogen. The resultant solid was grounded to size <180 µm, then, sulfonated using fuming sulfuric acid (20 wt.% free SO₃, ACROS Organics) (0.06 g of solid/1 mL of H₂SO₄ fuming) in a stirred round bottom flask at 150 + 3°C under the flow of nitrogen for 15 h. The mixture was

cooled to room temperature before adding 1000 mL of distilled water. The precipitate was washed with hot distilled water (>80°C) until no trace of sulfate ion in the wash water.

Catalyst characterization: BET surface area of the sample was measured using two different instruments: Micromeritic FlowSorb II 2300 and Micromeritics ASAP 2020. In the Micromeritic FlowSorb II 2300, a dynamic BET measurement, a mixture of 30% N₂ and 70% He was used as purge gas. Sample was degassed at 150°C for 2 h prior to testing. Whereas, in the Micromeritics ASAP 2020, a static BET measurement, sample was degassed at 120°C for 3 h prior to analysis, while N₂ adsorption isotherm was measured at -196°C.

The decomposition of the D-glucose char and sulfonated carbon catalyst were analyzed using a Thermogravimetric Analyzer (TGA, Varian SDT Q600). A flow of helium at 100 mL min⁻¹ was employed and the temperature was ramped from room temperature to 1000°C for data collection. In order to identify the compounds decomposed from the sulfonated carbon, the outlet gas of the TGA is connected to GC-MS (Varian CP-3800 GC, MS 4000). The TGA heating ramp was 50°C min⁻¹ from room temperature to 900°C and GC-MS sampling was programmed to inject the sample from the TGA once the temperature has reached 460°C.

The samples were further analyzed using a single-element FT-IR microscope system with a Germanium ATR crystal (610-IR microscope + Excalibur 3100 spectrometer). Collection parameters: 8 cm⁻¹ spectral resolution, 32 co-added scans, spectral range: 4000-500 cm⁻¹, with the analysis time: ~20 sec.

Determination of the total acidity of sulfonated carbon catalyst was carried out by back-titration. In a typical back-titration experiment, 0.1 g dry sulfonated carbon catalyst was placed in a 150 mL beaker with 60 mL of 0.008 M NaOH. The mixture was stirred for 30 min, then titrated with 0.02 M HCl to neutralize the excess NaOH using the automatic titrator (794 Basic Titrino, Metrohm).

Catalyst reactivity: The etherification reaction was performed between glycerol and *tert*-butanol catalyzed by the sulfonated carbon catalyst under batch conditions in a OMNI-Reactor Model 6100 at 80°C, stirred at 800 rpm. A catalyst loading of 7 wt.% based on glycerol with glycerol to *tert*-butanol molar ratio of 9 was used for the reaction. A 50 µL of sample was taken after 8 h for GC-MS analysis. The sample analyses were carried out by using a mass spectrophotometer (Varian MS4000) equipped with EI source, coupled P-3800 with column CP Wax 52CB (60 m×0.25 mm×0.25 µm). Analysis was carried as follows: The initial column temperature was 40°C (for 10 min), the

temperature was then increased at $4^{\circ}\text{C min}^{-1}$ to 115°C and then at $15^{\circ}\text{C min}^{-1}$ to 240°C . Total run time was ca. 50 min. Injection and detection chamber temperatures were set at 250°C and helium flow was set at 1.4 mL min^{-1} .

RESULTS AND DISCUSSION

Catalyst characterization: The BET surface area of the sulfonated carbon catalyst measured by Micromeritics FlowSorb II 2300 and Micromeritics ASAP2020 indicated less than $1\text{ m}^2\text{ g}^{-1}$. This data is consistent with the findings by Mo *et al.* (2008) and Toda *et al.* (2005). Low surface area suggests that the pyrolysis of char at low temperature produces a non-porous amorphous carbon. Acid functionalization of the glucose char can only occur at the surface of the glucose char particles. The total acidity of the sulfonated carbon catalyst was measured as 4 mmol g^{-1} , slightly higher than that of Mo *et al.* (2008) (3.7 mmol g^{-1}) and that of Toda *et al.* (2005) (2.5 mmol g^{-1}). Possible reason for the difference is the different type of sulfuric acid used for sulfonation: Mo *et al.* (2008) used concentrated sulfuric acid; while, Toda *et al.* (2005) used sulfuric acid fuming -15% free SO_3 .

A typical TGA of D-glucose char and sulfonated carbon catalyst are shown in Fig. 1. The decomposition of a compound is indicated by the occurrence of peak in the derivative weight profile. The first weight loss for the D-glucose and sulfonated carbon catalyst can be attributed to the loss of water at around 100°C . The carbon profile shows that two compounds decomposed at 313 and 574°C , respectively. The D-glucose char decomposition reached a plateau at around 800°C . Meanwhile, the sulfonated carbon catalyst exhibited compound decompositions at 236 , 271 , 284 , 376 and 522°C .

The multi peaks indicate that various compounds decomposed from the carbon support at different temperatures. The analysis of the compound decomposed from the sulfonated carbon catalyst showed CO_2 , COS and SO_2 . These compounds were most likely decomposed from the $-\text{SO}_3\text{H}$, $-\text{OH}$ and $-\text{COOH}$ functionalities and the polycyclic aromatic compound. The carbon and sulfonated carbon decomposition profiles show significant difference from the decomposition of the same compounds under air, where the sulfonated carbon catalyst fully decomposed at 460°C . This result shows that the sulfonated carbon heated under air undergoes reaction (oxidation) that accelerated the weight loss.

The FT-IR spectra of D-glucose char and sulfonated carbon catalyst are shown in Fig. 2. The strong peak at around 1712 cm^{-1} and the weak peak at around 1207 cm^{-1} are assigned to the stretching modes of SO_3H groups which are the active sites of the sulfonated carbon catalyst (Zong *et al.*, 2007). This strongly indicates that the method of catalyst preparation is effective in sulfonating the char.

Catalyst reactivity: Figure 3 shows the chromatogram and EI mass spectrum of the sample taken at 8 h. The standard EI mass spectra could not separate the glycerol ethers (Jamroz *et al.*, 2007). Almost all EI spectra were very similar to each other, the base peak at $m/z = 45$ corresponding to fragment ion $[\text{C}_3\text{H}_5]^+$, was detected in all spectra. Peak at $m/z = 57$ corresponds to fragment ion $[\text{C}_4\text{H}_7]^+$. Comparison with standard solution is not possible as only 3-*tert*-butoxy-1,2-propanediol available in the market. These spectra are slightly different from the one report by Jamroz *et al.* (2007) where peak at $m/z = 57$ was dominant. $[\text{C}_3\text{H}_5]$ is coming from $-(\text{CH}_2)_3$, forming *tert*-butoxy group in the glyceryl ethers.

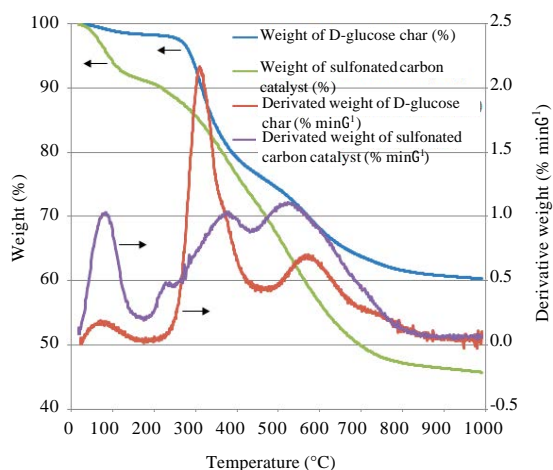


Fig. 1: Effect of temperature on weight loss of D-glucose char and sulfonated carbon catalyst

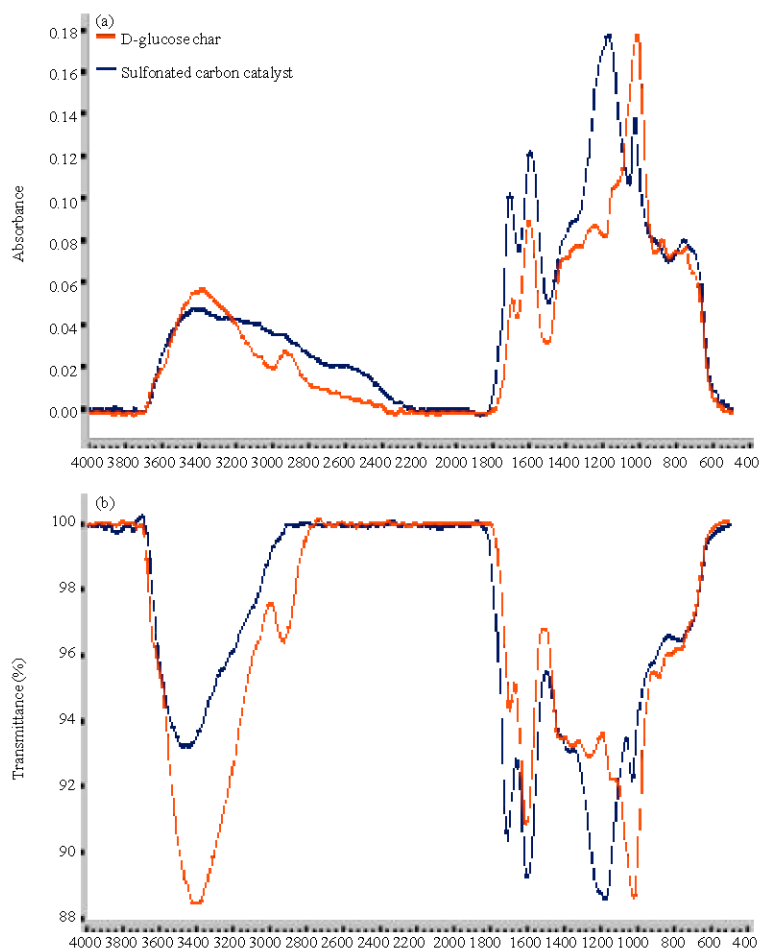
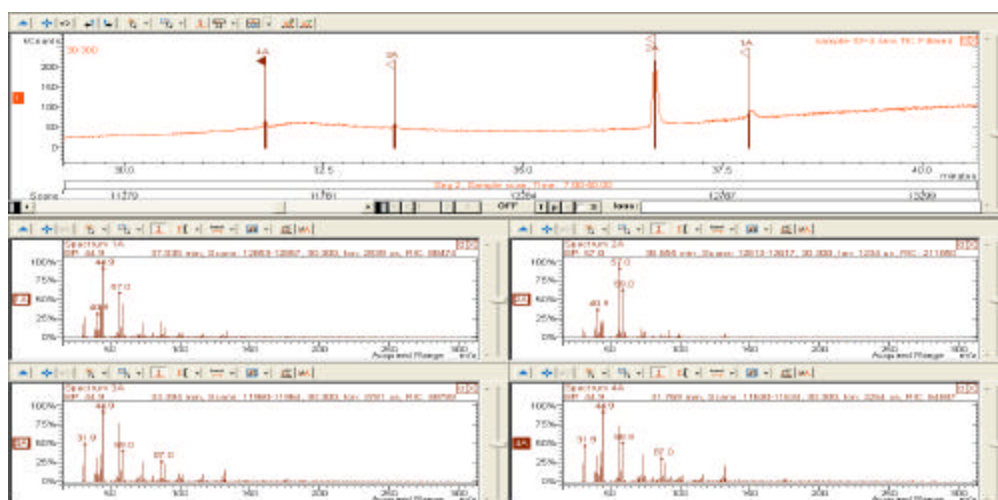


Fig. 2: FT-IR spectra showing (a) absorbance and (b) transmittance of D-glucose char and sulfonated carbon catalyst



From the preliminary catalyst reactivity study, the sulfonated carbon catalyst was capable of catalyzing the glycerol etherification by *tert*-butanol.

CONCLUSION

Sulfonated carbon catalyst is a renewable catalyst prepared from sugar. Sulfonated carbon catalyst has a low surface area, suggesting that it is a non-porous material. Functionalization by sulfonic acid moiety occurs at the bulk surface of the particle. Sulfonated carbon catalyst decomposes at higher temperature (236°C) offers its application in high temperature reaction. In this work, sulfonated carbon catalyst has been shown to produce mono- and di-glyceryl ethers from the reaction between glycerol and *tert*-butanol. Further works are underway to elucidate the glycerol conversion and the product selectivity.

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