



Research Article

Preparation and Characterization of Sugar Based Catalyst on Various Supports

Jidon Adrian Janaun, Tan Jaik Mey, Awang Bono, Duduku Krishnaiah*

Catalysis, Reaction Engineering & Drying Technology Research (CREDYT), Faculty of Engineering, Universiti Malaysia Sabah, 88400 Kota Kinabalu, Sabah, Malaysia

Received: 20th April 2016; Revised: 14th October 2016; Accepted: 17th October 2016

Abstract

A novel structured carbon-based acid catalyst was prepared by depositing the carbon precursor onto glass, ceramic and aluminum supports via dip-coating method, followed by carbonization process for converting the *d*-glucose layer into black carbon char in an inert nitrogen environment at 400 °C. Then, the $-SO_3H$ group was introduced into the framework of the carbon char by multiple vapor phase sulfonation. Four different carbonization methods were carried out (dry pyrolysis and hydrothermal carbonization with or without pressurized) in the catalyst preparation while among the carbonization methods, the samples which prepared from dry pyrolysis without pressurized process showed the strong acidity due to highest adsorption of acid group in the catalyst surface although the catalyst attached onto the support was the least compared to other preparation methods. Among the catalysts, the sulfonated carbon-base catalyst that is attached on the ceramic support exhibited the highest acidity (1.327 mmol/g) followed by the catalyst deposited on the glass (0.917 mmol/g) and aluminum (0.321 mmol/g) supports. The porous structure of ceramic surface, allowed a better interaction between reactants and $-SO_3H$ site in the carbon. Through the FT-IR analysis, it was observed that the functional groups $-COOH$, $-OH$, and $-SO_3H$ were present in the active sites of the catalysts. The surface areas of glass (Si-SC), ceramic (Ce-SC) and aluminum (Al-SC) catalysts were larger than 1 m²/g, whereas the pore size belongs to macroporous as the average pore size is more than 50 nm. It is also stable within the temperature of 400 °C as there was less than 10% weight loss revealed from the TGA analysis. Copyright © 2017 BCREC GROUP. All rights reserved

Keywords: structured sulfonated carbon-base acid catalyst; sugar catalyst; catalyst support; carbonization; multiple phase vapor sulfonation

How to Cite: Janaun, J.A., Mey, T.J., Bono, A., Krishnaiah, D. (2017). Preparation and Characterization of Sugar Based Catalyst on Various Supports. *Bulletin of Chemical Reaction Engineering & Catalysis*, 12 (1): 41-48 (doi:10.9767/bcrec.12.1.478.41-48)

Permalink/DOI: <http://dx.doi.org/10.9767/bcrec.12.1.478.41-48>

1. Introduction

Fossil fuels are currently crucial sources of primary energy supplied throughout the world and play an essential role in economic growth of the developing countries. However, due to increasing energy demand, it was estimated that the global reserves of fossil fuels will last for

another 40 to 60 years [1]. Moreover, the widespread use of fossil fuels cause escalating price of crude oil in the world market. Several adverse environmental impacts such as greenhouse effect, global warming, as well as climate change due to large emission of greenhouse gases (GHSs) and others hazardous pollutants are raising the public concern towards the alternative sources for petroleum based fuels [2]. Fatty acid methyl ester (FAME) is an alterna-

* Corresponding Author.
E-mail: krishna@ums.edu.my
Telp.: +60-88-320000 Fax.: +60-88-320348

tive promising biodiesel fuel that is derived from the renewable biomass such as vegetable oils, animal fats, waste oils and waste greases [3]. Generally, biodiesel can be produced from esterification of fatty acids (FAA) or through the transesterification reaction of triglycerides with a short-chain alcohol in the presence of homogeneous or heterogeneous alkali-, acid- or enzyme catalyst [4].

Among the catalytic processes, heterogeneous acid catalyzed process has been more widely favored compared to other catalytic processes as it can be easily separated from reaction mixture through decantation or filtration, and making the purification step much simpler with minimum energy consumption and easy to recover without waste. Thus it is more environmental friendly and more economically competitive due to the lowest total capital investment and manufacturing cost among the catalytic processes. Although the reaction of alkali catalyzed process is faster than acid catalyzed process, the alkali catalyzed process is not suitable for low-quality feedstock which contains high level of free fatty acid (FFA) and water content as soap is formed during the transesterification process. Whereas, the solid acid catalyst is ideal for the low-quality feedstock because the catalytic reaction is less affected by the presence of water and free fatty acid (FFA) [3]. Among the solid acid catalysts such as tungstated zirconia-alumina (WZA), sulfated zirconia-alumina (SZA), sulfated tin oxide (STO), and amberlyst-15 (sulfonated polystyrene-based resin), the carbon-based solid acid catalyst bearing with $-\text{SO}_3\text{H}$, $-\text{COOH}$ and phenolic $-\text{OH}$ groups exhibit remarkable catalytic performance in both esterification and transesterification processes as it is highly active and requires relatively low temperature than other typical solid acid catalyst [4]. Besides, this carbon-based catalyst is inexpensive, stable and renewable catalyst as an environmentally benign replacement for H_2SO_4 [3,4].

Sugar catalyst is also known as carbon-based solid acid catalyst, derived from the incomplete carbonization of simple sugar followed by sulfonating the pyrolyzed sugar with concentrated H_2SO_4 . These types of catalysts were reported to show excellent catalytic performance in biodiesel synthesis especially for low quality feedstock due to the presence of polycyclic aromatic hydrocarbon containing $-\text{SO}_3\text{H}$ groups and phenolic $-\text{OH}$ and $-\text{COOH}$ groups [5]. The high density of functional group of $-\text{SO}_3\text{H}$ and bending mode of $-\text{OH}\cdots\cdots\text{O}=\text{C}$ linked by a strong hydrogen bond, this catalyst is comparable to

the strong liquid Brønsted acid catalyst despite low surface area (2.5 mmol g^{-1} total and 1.2 mmol g^{-1} $-\text{SO}_3\text{H}$ density). Due to the $-\text{SO}_3\text{H}$ groups in the catalyst linked by strong hydrogen bonds, strong acidity can result by mutual electron-withdrawal. Besides, the bending mode of $-\text{OH}\cdots\cdots\text{O}=\text{C}$ linked by a strong hydrogen bond, enables the catalyst to incorporate a large amount of hydrophilic molecules, including water into the vacancies among the domains of catalyst. It enhances their accessibility to Brønsted acid sites in the carbon material, resulting higher catalytic activity than other solid acid catalysts [4,6]. However, due to the fine powder form of sugar catalyst, which is non-porous and has low specific surface area ($<1 \text{ m}^2\text{g}^{-1}$) causes agglomeration and difficulty of filtration for slurry phase operation. While, if sugar catalyst is used in packed bed reactor, it causes the large pressure drop in gas phase reaction due to low void fraction, resulting in both high energy costs and negative consequences on heat and mass transfer. Yet, these limitations can be solved by increasing the surface area per unit volume and particle size of sugar structure through the deposit of powder form of catalyst onto supports which provides an interesting alternative for conventional catalyst in packed beds or slurry reactors [7].

Herein, the coating of a carbon precursor on a structured catalyst supports such as glass, ceramic and aluminium using dip-coating method were studied. Several synthesis conditions have been employed such as hydrothermal carbonization and dry pyrolysis processes with or without pressurized.

2. Experimental Methods

2.1. Materials

All the materials, D-glucose, glass powder (Si-SC), pocelin (Ceramic, Ce-SC), and Aluminium (Al-SC) powders (0.1 mm diameter) were purchased from SIGMA-ALDRICH, USA and other reagents were: Concentrated sulfuric acid (Fisher Scientific B); Nitrogen gas (N_2) and Hydrochloric acid (EMSURE Brand, Malaysia); Sodium hydroxide, NaOH (Nack KGaA, Germany); Barium Chloride, BaCl_2 (J.T Baker@ Brand); and phenolphthalein indicator (SIGMA-ALDRICH Brand).

2.2. Apparatus

The apparatus used are: Ultrasonic Devices (SONICS Vibracell VCX750); Mass balance (Sartorius-TE2145 and OXFORD PRECISION (OXD-844-2206K); Oven (Mettler); Tube furnace (Enrotherm 2116); Heating mantle (MS-

E); Magnetic stirrer; Mass Balance; Metal crucible; Two-neck bottom flask; Condenser; Beaker; Thermometer; Conical flask; Filter paper (Whatman 125 mm); pH indicator (Macherey-Nagel); Filter funnel; and Petri dish.

2.3. Catalyst preparation

The first step for this stage was preparing the various types of structured surfaces which will act as the catalyst support. Initially, the structured surfaces were prepared by glass rod and ceramic and aluminum by cleaning ultrasonically for 15 minutes and dried in the oven at temperature 100 °C for 24 hours for removing the surface contaminates which may cause the poor coating result due to impaired coating adhesion.

In the preparation of structured carbon precursor, *d*-glucose was used as the carbon precursor and was converted into carbon char through the carbonization processes which can be carried out through hydrothermal carbonization and dry pyrolysis. Initially, 65 wt% of *d*-glucose solution was prepared as the dip-coating solvent by mixing 100 g of SIGMA-ALDRICH Brand *d*-glucose with 54 g of distilled water. The *d*-glucose solution, then, was sonicated by using ultrasonic devices until the *d*-glucose was fully mixed into the solution. Next, the substrates were weighed and dip-coated into the *d*-glucose solution for 1 hour without pressurized. Meanwhile, in order to increase the amount of the carbon char attached on the substrate, pressure vessel was used before carbonization process to increase the adhesive and cohesive strength of carbon precursor with the surface of substrate by pressurizing the samples at 15 atm for 15 minutes. After the dip-coating process, both pressurized and without pressurized samples were then dried in the

oven at 100 °C for solidifying the glucose layer on the surface substrates [7].

After the structured carbon precursor was prepared, the sample was put into the metal crucible for undergoing dry pyrolysis process. Since the heating only occur in the center of the tube furnace, so the metal crucible must place in the center of tube furnace, otherwise, inefficiency of pyrolysis process will occurs. Then, both end of tube furnace were assembled with the gasket and flanged. The apparatus set up for pyrolysis is shown in the Figure 1.

As shown in Figure 1, one end of the furnace was connected to nitrogen gas while the other end of tube was connected to the beaker containing tap water. Initially, the nitrogen gas, N₂ was purge into the tube furnace for 30 minutes with flow rate 100 mL/min without turning on the heat of furnace. Then, the heater was turn on and set at 400 °C for 4 hours pyrolysis (the time taken started when the temperature of furnace reaches 400 °C) with continuing purge of N₂ gas. After 4 hours pyrolysis, the sample was taking out from furnace and allows to cooling down at room temperature then weighed.

On the other hand, for the hydrothermal carbonization, the preparation for both pressurized and without pressurized samples were same as the procedure above, however, the samples did not undergo the drying process for solidifying the glucose layer on the surface substrates, they were directly undergoing the hydrothermal carbonization process for formation of structured carbon char, while the apparatus set up and operating condition of the hydrothermal carbonization was same with dry pyrolysis process as shown in the Figure 1.

2.4. Characterization

The total acidity of the synthesis catalysts



Figure 1. Apparatus set-up for carbonization

were determined by using acid-base back titration with 0.008 M of NaOH as titrator and 0.02 M of HCl as titrant. The 0.1 g of the sample is used in a conical flask containing 60 mL of 0.008 M NaOH. The mixture is stirred for 30 min at room temperature then by using phenolphthalein indicator, and the solution is titrated back with 0.02 M HCl. The final colour light pink indicated the end titration point. The volume of HCl used in the titration process is recorded. The total acidity was calculated using the following equation:

$$\text{Total acidity (mmol/g)} = (V_1M_1 - V_2M_2)1000/W$$

where $V_1 = 0.060$ (L NaOH), $V_2 =$ volume of HCl used in back titration (L), $M_1 =$ molarity of NaOH (gmole/L), $M_2 =$ molarity of HCl (gmole/L), $W =$ weight of catalyst (g).

The functional groups of synthesis catalysts were determined by using Fourier Transform Infrared Spectrometry (FTIR, Perkin Elmer, Spectrum 100 series, USA) with the scan range of 650 to 4000 cm^{-1} . The pore size and surface area of catalysts were determined by using Automated Mercury Porosimeter (Pascal 440 series, USA) via mercury intrusion at density temperature of 25 °C and pressure at 200 MPa. Thermal stability of synthesis catalysts was carried out using Thermal Gravimetric Analysis (Perkin Elmer model, TGA6, USA) in the nitrogen atmosphere at the flow rate of 20 mL/min and the temperature rate was set at 10 °C/min to 400 °C.

3. Results and Discussion

3.1. Preparation of structured catalyst

Table 1 shows that the results of catalyst before coating, after carbonization process and sulfonation process for both dry pyrolysis with and without pressurized and hydrothermal carbonization with and without pressurized. From the results obtained, it can be seen that the chars attached on the catalyst supports were found to be less than 1 g as the char formation occurs only on the catalyst supports and it is

due to less interaction between char molecules and carbon char layer.

3.2. Total acidity

Table 2 shows the total acidity of Si-SC, Ce-SC, and Al-SC from different preparation methods. The acidity of the synthesis catalysts is contributed by the $-\text{SO}_3\text{H}$ group, the phenolic $-\text{OH}$ and $-\text{COOH}$ groups that are contained in the catalyst [9]. Among the catalyst preparation methods, the samples which are prepared from dry pyrolysis without pressurized process showed the strong acidity which is due to the highest adsorption of acid group in the catalyst surface although the catalyst attached onto the support was the least compared to other preparation methods.

Due to porous structure of ceramic surface, it allowed a better interaction between reactants and $-\text{SO}_3\text{H}$ sites in the bulk carbon. The ceramic support has highest acidity among the three catalysts samples. However, the acidity of the synthesis catalysts which deposited on glass, ceramic and aluminum supports were lower than the powder form of sugar catalyst which has 2.5 mmol.g^{-1} total acidity and 1.2 mmol.g^{-1} $-\text{SO}_3\text{H}$ density [4,6]. The low acidity of synthesis catalysts may be due to small amount of the carbon attached on the supports during the pyrolysis process as the acidity of the catalyst depends on the amount of surface functional groups ($-\text{COOH}$, $-\text{SO}_3\text{H}$ and phenolic $-\text{OH}$ group). Besides, the structure of carbon char attached on the surface may not be accessible during sulfonation due to the compact carbon structure on the support, causing low acid density in the final sulfonated catalyst [10].

3.3. Functional groups

FT-IR analysis is useful to identify the carbon skeleton structure and groups attached on it. Figure 2 shows the IR spectrum of Si-SC, Ce-SSC, and Al-SC. Based the results from the Figure 2, several important peaks were

Table 1. Pyrolysis of catalysts

Support	Dry pyrolysis, Mass of catalyst attached [g]		Hydrothermal carbonization, Mass of catalyst attached [g]	
	Without pressurized, 1 atm	With pressurized, 15 atm	Without pressur- ized, 1atm	With pressurized, 15 atm
Glass	0.0092	0.0675	0.0155	0.0036
Ceramic	0.0018	0.0064	0.0275	0.0059
Aluminum	0.0081	0.0407	0.0108	0.1734

identified. The FT-IR spectrum of Si-SC, Ce-SC, and Al-SC showed a strong band at $\sim 1600\text{ cm}^{-1}$ which may be attributed to the polycyclic aromatic framework structure due to C=C stretching [3]. The bands at 1040 cm^{-1} and 1401 cm^{-1} corresponds to SO_3 -stretching and O=S=O stretching in $-\text{SO}_3\text{H}$, respectively [11]. Furthermore, a broad band was observed at 3400 cm^{-1} which is assigned to $-\text{OH}$ groups stretching.

The peaks attributable to O-H bond in a carboxylic acid group and O-H bond in a phenol group can be seen at 3600 cm^{-1} and 2400 cm^{-1} [12]. This result provided that the presence of OH group in the catalyst. In addition, the FT-IR band at 1680 cm^{-1} shows that the carboxyl acid group presence at the structured sugar catalysts and this band is assigned to C=O stretching of COOH groups [13]. Moreover, peaks attribute to C-H and C-O-H asymmetric stretching for all sulfonated char catalysts are observed in the region of $1130\text{-}1150\text{ cm}^{-1}$ [14]. The three structured sugar catalysts in FT-IR spectrums also show that the structured sugar catalyst acid contains resident functionalities including C-H at 960 cm^{-1} and 700 cm^{-1} which are attributed to trans-C-H and cis-C-H out-of-plane bond, respectively [15].

Besides, an aromatic acidic group (Ar-OH stretch) is shown in the IR spectrum at the peak around 1215 cm^{-1} which is due to oxidation during the carbonization. The presence of a peak at 845 cm^{-1} is due to noncovalent interaction occurred between the sulfonated pyrene group ($-\text{SO}_3\text{H}$) and the Al-SC at peak 845 cm^{-1} and is slightly more intense than Si-SC and Ce-SC [14].

3.4. Surface area and porosity

The characteristics of catalyst were investigated by using mercury intrusion at $25\text{ }^\circ\text{C}$ and 200 MPa (Pascal 440 series, USA). The data of pore diameter, porosity and specific area of the catalyst samples is shown in the Table 3.

The surface area of sulfonated carbon catalyst in powder form was less than $1\text{ m}^2\text{g}^{-1}$ [5,16]. As shown in Table 3, in this investigation, the surface area of the sulfonated carbon catalysts increased in the range of $1\text{-}5\text{ m}^2\text{g}^{-1}$. The average pore size of the structured sulfonated carbon catalysts were ranging from $116\text{-}5768\text{ nm}$ which shows the macroporosity characteristics as the pore diameter is more than 50 nm [17]. The difference in surface area, pore diameter and porosity of sulfonated

Table 2. Total acidity [mmol/g] of catalysts

Process	Glass, Si-SC	Ceramic, Ce-SC	Aluminum, Al-SC
Dry pyrolysis without pressurized, 1 atm	0.917	1.327	0.321
Dry pyrolysis with pressurized, 15 atm	0.683	0.978	0.486
Hydrothermal Carbonization without Pressurized, 1 atm	0.641	0.684	0.401
Hydrothermal Carbonization with Pressurized, 15 atm	0.886	1.134	0.545

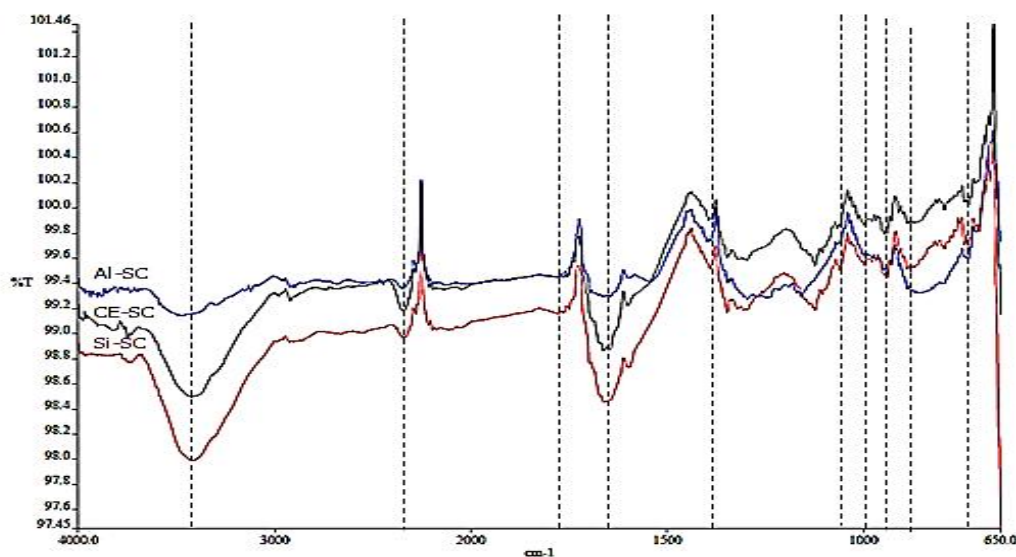


Figure 2. FT-IR spectra of Si-SC, Ce-SC and Al-SC

carbon catalysts is due to the different surface texture of the catalyst support. Among the synthesis catalysts, the catalyst deposited on the ceramic support Ce-SC had the highest surface area because of the three-dimensional cellular structure and porous structure of ceramic material [18]. As shown in Table 3, the glass support had the lowest porosity due to low surface area of catalyst Si-SC on non-porous structure of glass surface [19].

3.5. Composition of elements

The composition of the carbon-based catalyst on glass, ceramic, and aluminum support was determined by the EDX analysis. From this analysis, the content of C, O, and S of Si-SC, Ce-SC, and Al-SC was investigated. The surface elemental analysis by EDX technique of Si-SC, Ce-SC, and Al-SC is shown in Table 4.

As shown in Table 4, the sulfur element did not present in all synthesis catalysts. However, from the FT-IR analysis as shown in Figure 2, there were presence of the $-SO_3H$ groups in the Si-SC, Ce-SC, and Al-SC catalysts due to presence of peaks at 1040 cm^{-1} and 845 cm^{-1} which represent SO_3 -stretching and noncovalent interaction between the sulfonated pyrene group ($-SO_3H$). The absence of sulfur element of catalysts in EDX analysis may due to the penetration of sulfonic group into the catalyst support during the sulfonation process. Besides, the composition of the element contained in the catalyst was detected only on the surface of the catalyst by EDX analysis [20].

3.6. Thermal stability

The mass change of the catalyst samples as a function of temperature and time in a nitrogen atmosphere is shown in Figure 3. While Figure 4 shows the derivative thermal analysis

(DTA). The temperature was set from 30 to 400 °C. Figure 2 and Figure 3 show that there are two distinctive weight losses of the catalyst deposited on the aluminum support Al-SC. The first significant weight loss can be observed at 70 °C. This weight loss of moisture content in the catalyst is due to the temperature which is increased from 25 to 100 °C [5,9,17]. While, the another significant weight loss peak appears at 250 °C and it is due to the gradual desorption and thermal decomposition process of $Al-SO_3H$ group [21,22]. On the other hand, the weight loss of catalyst in glass and ceramic surface is not significant due to high melting point of catalyst supports. Besides, from the TGA analysis as shown in the Figure 3, there are significant temperatures at 100-200 °C for Si-SC, 50-200 °C for Ce-SC, and 30-40 °C for Al-SC. The weight gain at the respective temperature range is due to the absorption of nitrogen gas or reaction with gaseous substances in the purged gas. From the TGA analysis, the final weight % for Si-SC, Ce-SC, and Al-SC were 99.8%, 99.9%, and 98.8% respectively. Thus, the catalysts which deposited on the support are stable as there is only slight decrease in weight loss % compared to powder form of sugar catalyst which was 84.0 % within the 400 °C [16].

4. Conclusions

In this research, three catalyst Si-SC, Ce-SC, and Al-SC supports were used to prepare amorphous sulfonated carbon-base catalysts. Among the catalysts, the sulfonated carbon-base catalyst that is attached on the ceramic support had the highest acidity (1.327 mmol/g), followed by the catalyst deposited on the glass (0.917 mmol/g) and aluminum (0.321 mmol/g) supports. The porous structure of ce-

Table 3. Surface area, pore diameter and porosity of synthesis catalysts

Catalyst	Surface Area [m ² /g]	Pore Diameter [nm]	Porosity [%]
Glass, Si-SC	1.02	116.79	0.33
Ceramic, Ce-SC	4.56	112.50	1.94
Aluminum, Al-SC	3.56	5768.46	1.97

Table 4. Surface elemental analysis by EDX technique of the Si-SC, Ce-SC, and Al-SC catalysts

Catalyst	Elements [wt.%]			Elemental analysis by EDX [mol]			Mole Ratio to Carbon	
	C	O	S	C	O	S	O:C	S:C
Si-SC	83.35	12.53	-	6.95	0.78	-	0.11	-
Ce-SC	60.73	34.26	-	5.06	2.14	-	0.42	-
Al-SC	81.56	17.54	-	6.80	1.10	-	0.16	-

ramic surface allowed a better interaction between reactants and $-\text{SO}_3\text{H}$ site in the carbon. From the FT-IR analysis, it was observed that the functional groups $-\text{COOH}$, $-\text{OH}$, and $-\text{SO}_3\text{H}$ were present in the active sites of the catalysts. The surface areas of the catalysts Si-SC, Ce-SC and Al-SC were larger than $1\text{ m}^2/\text{g}$, whereas the pore size belongs to macroporous as the average pore size is more than 50 nm. It is stable within the temperature of 400 °C as there was less than 10% weight loss through the TGA analysis.

References

- [1] Chen, W.H., Chen, C.J., Hung, C.I., Shen, C.H., Hsu, H.W. (2013). A Comparison of Gasification Phenomena among Raw Biomass, Torrefied Biomass and Coal in an Entrained-flow Reactor. *Applied Energy*, 112: 421-430.
- [2] West, A.H., Posarac, D., Ellis, N. (2008). Assessment of Four Biodiesel Production Processes using HYSYS Plant. *Bioresource Technology*, 99: 6587-6601.
- [3] Janaun, J., Ellis, N. (2010). Perspectives on Biodiesel as a Sustainable Fuel. *Renewable Sustainable Energy Reviews*, 14: 1312-1320.
- [4] Cho, H.J., Kim, S.H., Hong, S.W., Yeo, Y.K. (2012). A Single Step Non-catalytic Esterification of Palm Fatty Acid Distillate (PFAD) for Biodiesel Production. *Fuel*, 93: 373-380.
- [5] Mo, X., Lotero, E., Lu, C., Liu, Y., James, G.G.J. (2008). A Novel Sulfonated Carbon Composite Solid Acid Catalyst for Biodiesel Synthesis. *Catalysis Letters*, 123: 1-6.
- [6] Suganuma, S., Nakajima, K., Kitano, M., Kato, H., Tamura, A., Kondo, H., Yanagawa, S., Hayashi, S., Hara, M. (2011). SO_3H -bearing Mesoporous Carbon with Highly Selective Catalysis. *Microporous and Mesoporous Materials*, 143: 443-450.
- [7] Hosseini, S., Janaun, J., Choong, T.S.Y. (2015). Sulfuric Acid Functionalized Carbon Coated Honeycomb Monolith as Solid Acid Catalyst for Synthesis of Methyl Esters from Palm Fatty Acid Distillate (PFAD). *Process Safety and Environmental Protection*, 98: 285-295.
- [8] Janaun, J., Ellis, N. (2010). Role of Silica Template in the Preparation of Sulfonated Mesoporous Carbon Catalysts. *Applied Catalysis A: General*, 394: 25-31.
- [9] Liu, X.Y., Huang, M., Ma, H.L., Zhan, Z.Q., Gao, J.M., Zhu, Y.L., Guo, X.F. (2010). Preparation of a Carbon-based Solid Acid Catalyst by Sulfonating Activated Carbon in a Chemical Reduction. *Process Molecules*, 15: 7188-7196.
- [10] Konwar, L.J., Boro, J., Deka, D. (2014). Review on Latest Developments in Biodiesel Production using Carbon-based Catalysts. *Renewable Sustainable Energy Reviews*, 29: 546-564.
- [11] Lu, Y., Liang, X., Qi, C. (2012). Synthesis of Novel Carbon/Silica Composites based Strong Acid Catalyst and its Catalytic Activities for Acetalization. *Bulletin of Materials Science*, 35: 419-424.
- [12] Fu, Z., Wan, H., Hu, X., Cui, Q., Guan, G. (2012). Preparation and Catalytic Performance of a Carbon-based Solid Acid Catalyst with High Specific Surface Area. *Reaction Kinetics Mechanism and Catalysis*, 107: 203-213.
- [13] Liang, F., Song, Y., Huang, C., Zhang, J., Chen, B. (2013). Preparation and Performance Evaluation of a Lignin-based Solid Acid from Acid Hydrolysis Lignin. *Catalysis Communications*, 40: 93-97.
- [14] Liu, X.Y., Huang, M., Ma, H.L., Zhang, Z.Q., Gao, J.M., Zhu, Y.L., Han, X.J., Guo, X.Y. (2010). Preparation of a Carbon-Based Solid Acid Catalyst by Sulfonating Activated Carbon in a Chemical Reduction Process. *Molecules*, 15: 7188-7196.

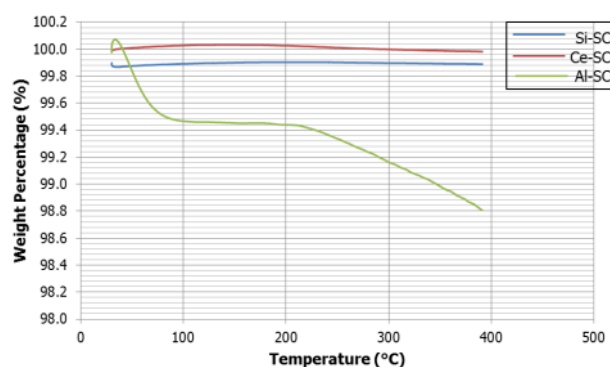


Figure 3. Thermo-gravimetric analyses of Si-SC, Ce-SC, and Al-SC under nitrogen.

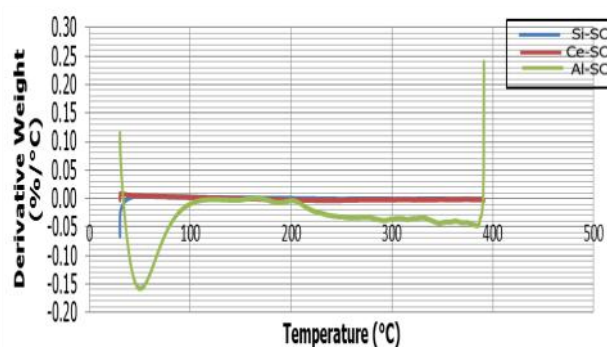


Figure 4. Derivative thermal analyses of Si-SC, Ce-SC, and Al-SC under nitrogen.

- [15] Meyers, R.A. ed. (2000). *Interpretation of Infrared Spectra, A Practical Approach*. Encyclopedia of Analytical Chemistry. John Wiley & Sons Ltd, Chichester.
- [16] Janaun, J. (2012). Development of Sulfonated Carbon Catalysts for Integrated Biodiesel Production. *Ph.D Dissertation*, University of British Columbia, Canada.
- [17] Hayes, R., Kolaczowski, S.T. (1998). *Introduction to Catalytic Combustion*. CRC Press, UK.
- [18] Carty, W.M., Lednor, P.W. (1996). Monolithic Ceramics and Heterogeneous Catalysts: Honeycombs and Foams, *Current Opinion in Solid State & Material Science*, 1: 88-95.
- [19] Janaun, J., Ellis, N. (2010). Glycerol Etherification by tert-Butanol Catalyzed by Sulfonated Carbon Catalyst. *Journal of Applied Sciences*, 10: 2633-2637.
- [20] Pua, F., Fang, Z., Zakaria, S., Guo, F., Chia, C. (2011). Direct Production of Biodiesel from High-acid Value Jatropha Oil with Solid Acid Catalyst Derived from Lignin. *Biotechnology Biofuels*, 4: 56 (doi: 10.1186/1754-6834-4-56)
- [21] Lee, D., (2013). Preparation of a Sulfonated Carbonaceous Material from Lignosulfonate and Its Usefulness as an Esterification, *Catalysis Molecules*, 10: 8168-8180.
- [22] Thermogravimetric Analysis (TGA) / Differential Thermal Analysis (DTA) Testing & Analytical Services. (2015) <http://www.eag.com/mc/thermogravimetric-differential-thermal-analysis.html>