Design, Performance Evaluation and Synthesis of Sulfonated Carbon Based Catalyst for Hydrolysis of Microcrystalline Cellulose

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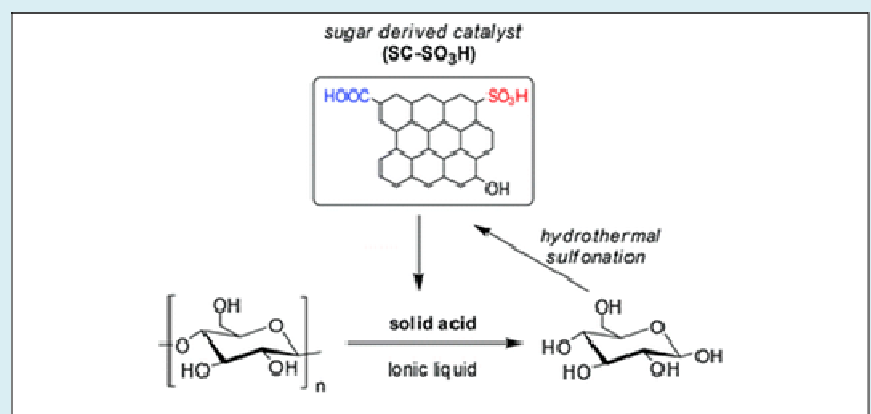
ABSTRACT

Microcrystalline cellulose can be converted into valuable products such as glucose via hydrolysis reaction at mild condition using sulfonated carbon catalyst. A sulfonated carbon material was prepared by carbonization of bamboo sawdust followed by sulfonation. Prepared catalyst was studied for its ability to catalyze microcrystalline cellulose yield via hydrolysis reaction. Three carbon-based catalysts at three different temperatures (400, 450 and 500℃) were prepared. The sulfonated catalysts were characterized using the following analyses: elemental analysis, total acid density, FT-IR, SEM and XRD. Based on the above characterization results, sulfonated carbon prepared at 500℃ and sulfonated via ultra-sonication was found to have a higher acid density that is suitable to catalyze the hydrolysis reaction. The first step in the catalyst development approach was to increase the hydrolysis reaction by employing a stronger sulfonation procedure during catalyst preparation. The total acid density obtained for sulfonated carbon catalyst at 500℃ was 4.16 mmol/g which significantly increases glucose yield. According to the FTIR analysis the sulfonated bio char contained sulfonic, carboxylic, and phenolic groups, which are responsible for the exhibited high catalytic performance during hydrolysis of cellulose. The yield of glucose obtained was 60.5% at 149.0℃ in 8hour reaction time.

KEYWORD: *Bamboo, bio char catalyst, sulfonation, hydrolysis reaction*

INTRODUCTION
1. Background

Cellulose is a linear β-glucose homo-polymer and constitutes with hemicellulose the carbohydrate part of the biomass(Rinaldi and Schuth, 2009). It may be obtained from wood or derived in very high purity from cotton fibers, which are about 92% pure cellulose. Glucose of a monomer is expected as a renewable feedstock molecule, which can be efficiently converted into various chemicals, fuels, foods, and medicines(Huber et al. 2006).For example, glucose, a monomer of cellulose, is a key intermediate of various useful chemicals such as polymers, medicines, surfactants, gasoline, and diesel fuels (corma et al. 2007; Kobayashi et al. 2010). Thus, selective hydrolysis of cellulose into glucose is a key process for the beneficial use of biomass.

The hydrolysis of cellulose to obtain reducing sugars such as glucose is essential for using biomass in chemical processes, since the reducing sugars can be transformed into a wide range of important chemicals such as ethanol, 5-hydroxymethylfurfural and hexitols (Rinaldi and Schuth 2009; Vyver et al. 2011). However, conversion of cellulose offers great challenges due to its recalcitrant nature. Thus far, many efforts have been devoted to the depolymerization of cellulose with mineral acids, bases, enzymes(Ramakrishnan et al. 2010), and supercritical water(Sasaki et al. 2000). Liquid acid catalyzed hydrolysis of cellulose is efficient; however, corrosion, waste disposal and solvent recycle make this method unattractive. The hydrolysis of cellulose with enzyme is efficient, but it is slow and sensitive

to inhibitors such as furfural and 5- hydroxymethylfurfural. De-polymerization of cellulose in sub- or supercritical water is highly efficient and only requires reaction times on the order of several seconds, but the process gives a complex product distribution and generally has low glucose selectivity due to the high reaction temperature(Peterson et al. 2008).

Solid acid catalytic systems for cellulose hydrolysis have advantages of simplicity, and efficiency since they are easily separated from reaction products and they show good catalytic activity for many substrates. Various solid acids have been examined for cellulose hydrolysis, including ion-exchange resin(Qi et al. 2011), heteropolyacids (Belderok, 2007), sulfonated activated carbon (Onda et al. 2008; Y. Wu et al. 2012), and layered transition- metal oxides(Lai et al. 2011; Tagusagawa et al. 2010). In these research works, the hydrolysis of cellulose is generally carried out in water.

Bio char, a by-product from biomass pyrolysis process, is another potential carbon source to be used as a support for solid acid catalyst (Lai et al. 2011; Tagusagawa et al. 2010). Pyrolysis of agricultural waste (biomass) is one of the promising thermo-chemical methods to produce bio-oil, bio char and combustible gases. The fast pyrolysis process typically yields up to 75 wt% bio-oil as its main product, and the non-condensable gases (10-20 wt%) and the bio char (15-25 wt%) as by-products (Mohan et al. 2006). Numerous recent studies (Demirbas, A. 2002; Gaskin et al. 2008; Mohan et al. 2006; Yaman 2004) have focused on the utilization of these products, but bio char has received very little attention. As the main scope of this study, the upgrading of bio char as a value added catalyst is investigated in order to increase both the environmental and economic viability of the biomass pyrolysis process. Utilization of bio char support as a catalyst would not only help the commercialization of glucose production, but also increase the environmental viability of the pyrolysis process.

The conventional processes for the hydrolysis of cellulose involve the use of sulfonated carbon catalyst (Fan et al. 2009). The corrosion and waste disposal problems, however, significantly lower the attraction of liquid acid-catalyzed hydrolysis. In order to minimize the environmental impact, new green approaches have been developed, such as the use of cellulose enzymes, hydrolysis in sub- or super-critical water, ionic liquid promoted dissolution and hydrolysis of cellulose, hydrogenolysis into polyols as well as hydrolysis into glucose by solid catalysts(Onda et al. 2009).

Response surface methodology (RSM) is a collection of statistical and mathematical techniques useful for developing, improving and optimizing processes in which a response of interest is influenced by several variables, and the objective is to optimize this response (Bas, D. and H. 2007). Analyzing the effects of the independent variables, this experimental methodology generates a mathematical model which describes the chemical processes within the experimental range (Myers et al. 2009).

Therefore, the aims of this work was to hydrolysis microcrystalline cellulose into glucose using sulphonated carbon catalyst and optimize the process conditions using RSM.

2. Methods
2.1. Proximate Analysis of Bamboo
As defined by ASTM; D1762-84 (Reapproved 2001), proximate analysis separates the products into four groups: moisture, volatile matter, consisting of gases and vapors driven off during pyrolysis, fixed carbon, the nonvolatile fraction of biomass, and ash, the inorganic residue remaining after combustion.

A. Volatile Matter
The sample was measured and placed in a closed crucible. It was then heated up to 900°C for exactly 7 min in a furnace. The crucible was then cooled in a desiccator and weighed. The weight of the sample before heating and after heating was used to determine the amount of volatile matter present in the sample.

$$\text{Volatile matter},\% = \frac{W_1 - W_2}{W_1} \times 100 \quad (3.1)$$

Where: W_1 = weight of dry sample and closed crucible before heating (g), W_2 = weight of dry sample and closed crucible after heating (g).

B. Ash Content:
Sample was measured and taken in a crucible. It was then heated to 650 °C for 3hr. During this test the crucible was left open. The heating was done in a muffle furnace. After the required heating, the crucible was cooled in a desiccator and then weighed. In this test, the amount of residual substance is equal to the ash present in the sample.

$$\text{Ash content},\% = \frac{W_2}{W_1} \times 100 \quad (3.2)$$

Where: W_1 = weight of dry sample before heating (g), W_2 = weight of ash (g).

C. Moisture Content:
Sample was measured and taken in a petri dish. It was dispersed nicely on the petri dish. It was then heated at 105°C for 12hr. The petri-dish was left open during the heating process. After heating, the petri-dish was cooled in desiccator and then weighed. This specifies the amount of moisture content present in the sample.

$$\text{Moisture},\% = \frac{W_1 - W_2}{W_1} \times 100 \quad (3.3)$$

Where: W_1 = weight of sample and petri dish before drying (gram), W_2 = weight of sample and petri dish after drying (gram).

D. Fixed Carbon Content
The fixed carbon content is determined by subtracting the sum of percentage compositions of moisture content, volatile matter content, and ash content form 100. The value obtained is the amount of fixed carbon present in the sample expressed in percentage.

Fixed carbon (%) = 100 – (moisture, % + ash, % + volatile matter, %) (Wet basis)

Fixed carbon (%) = 100 – (ash, % + volatile matter, %) (Dry basis)

2.2. Ultimate (CHNS) analysis of bio char

The Ultimate Analysis of a sample determines the elemental composition of the sample. It is based on the principle of Dumas method which involves the complete and instantaneous oxidation of the sample by flash combustion. The results are in percentage composition of Carbon, Hydrogen, Nitrogen and Sulphur. From these results the oxygen composition is determined by subtracting the sum of Carbon, Hydrogen, Nitrogen, and Sulphur compositions from 100. The Ultimate Analysis was carried out in EA 1112 Flash CHNS/O- analyzer under the condition of carrier gas (He-gas) flow rate of 120 ml/min, reference flow rate of 100 ml/min, and oxygen flow rate of 250 ml/min with furnace temperature of 900° C and oven temperature of 75 °C.
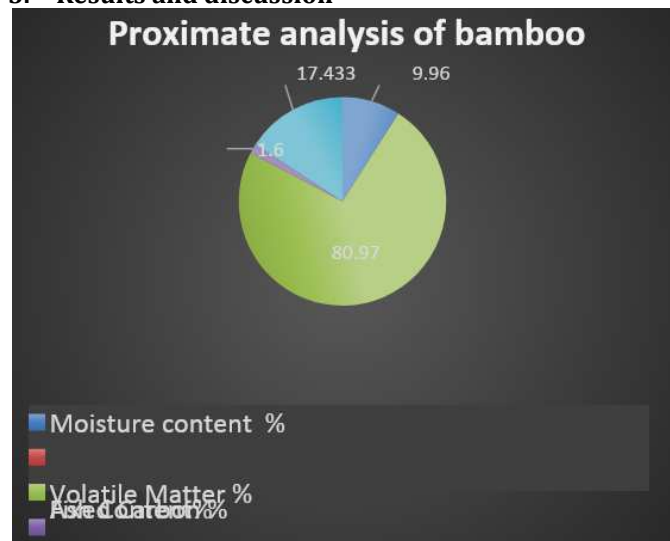
3. Results and discussion

Figure 4.1: Proximate analysis of bamboo

The fixed carbon content of bamboo is 17.433%. The bamboo sample was rich in volatiles (80.97%) but low in ash content (1.6%) (Figure, 4.1). The low ash content would result in minimal effects of inorganic impurities on pore development during pyrolysis process. Previous studies suggested that suitable bio char should be low in ash but rich in carbon and volatiles. This gives an overview about the properties and components of bamboo.

3.1. Proximate composition of bio char

For total content of elements in bio char samples, C, H, N and S were measured by using EA 1112 Flash CHNS/O- analyzer. The percentage of oxygen content was estimated by difference as follows: O (%) = 100 - (C + H + N + S) (Calvelo Pereira et al, 2011).
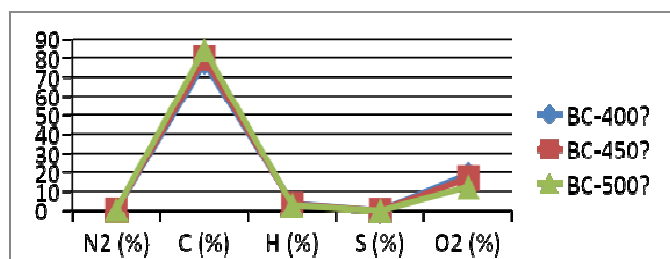

Figure 4.2: Elemental analysis of the bio char

The elemental content of bio chars is showed that carbon content was increased with temperature, but the loss of O, and H was recorded (figure, 4.2). The increase in carbon content with temperature is due to increasing degree of carbonization. However, these decline in O and H elements may be attributed to breaking of weaker bonds in bio char structure and highly carbonaceous materials yielded with increased temperature (Demirbas.A, 2002). The decrease in S with temperature could be explained by the volatilization of sulfur during pyrolysis process. But, the result shows no sulfur content in the carbonization temperature of 450 and 500℃. It indicates that the volatilization of sulfur above 400℃ is very high. Our results suggest that temperature could conserve N in wood chars. This can be explained by incorporation of N into complex structures that are resistant to heating and not easily volatilized (Gaskin et al. 2008). In consistent with our results, (Calvelo Pereira et al. 2011) also found that N enrichment relative to the original feedstock was recorded upon charring of woody material.

3.2. Bulk density of bio char and its catalyst

Bulk density is used to characterize the particles of char and its catalyst and also useful for the estimation of tank or packing volume. For determination of bulk density method described by ASTM Test Methods (D 2854 – 96 (Reapproved 2000) was used with a slight modification.
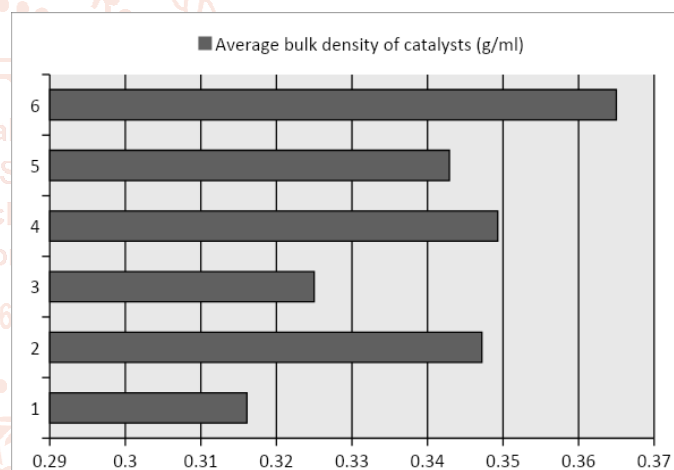

Figure 4.3: Bulk density of bio char and its catalyst

The bulk density of sulfonated bio chars is higher than its bio chars due to sulfonation of bio char (figure, 4.3). This indicates the sulfonated catalyst (BC-SO$_3$H) is -SO$_3$H functional group on the surface of bio char. Thus, the bulk density of sulfonated bio char can be related to its functional groups. The density of bio chars was increased with carbonization temperatures (from 0.2698 to 0.2839 g/ml). Because, the particle size of bio chars were decreased with the pyrolysis temperature but the pore sizes were increased and also more volatile matter was vaporized with temperature increment.

3.3. Acidity characteristics of sulfonated bio char catalyst

Total acidity was observed in the bio char than the density of SO$_3$H group (figure, 4.4) which can be interpreted as due to the presence of many acidic groups like phenolic OH or CO$_2$H groups in addition to SO$_3$H groups in the materials.
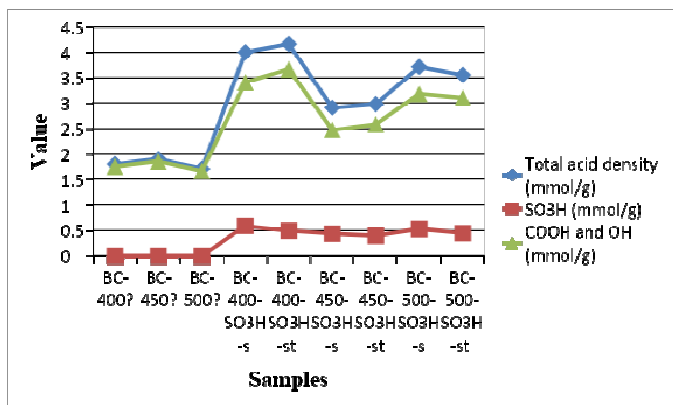
Figure 4.4: The acid density of the bio char and sulfonated bio char catalyst

The contents of $-SO_3H$, -OH, -COOH groups on $BC-SO_3H$ are usually among 0.1-4.9, 0-0.9, 0-7.8 mmol/g, respectively (Benak et al. 2002; Nakajima and Hara 2012; Onda et al. 2008, 2009; Suganuma et al. 2012; Toda et al. 2005; Youyu Wu et al. 2012; Yamaguchi et al. 2009). Though $-SO_3H$ groups are considered as the key active acidic site, the existence of -OH and -COOH groups would provide hydrophilic reactants accessing to the$-SO_3H$ groups, which would be in favor of effective catalytic performance. According to literature(Nakajima and Hara 2012; Onda et al. 2009), it is assumed that all sulfur content of each sample is in the form of $-SO_3H$.

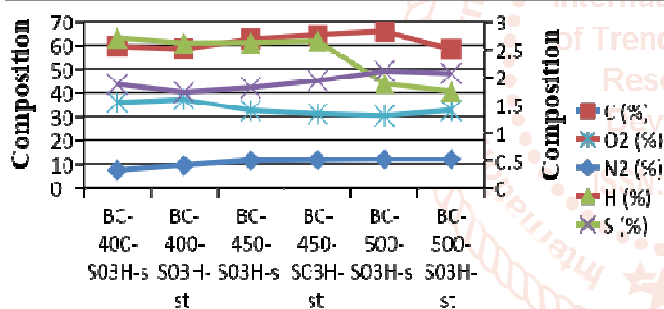## 3.4. Elemental Analysis (CHNS analysis) of sulfonated carbon catalyst

Figure 4.5: Elemental analysis of the sulfonated catalyst.

The sulfur content was increased from $BC-400-SO_3H$ to $BC-500-SO_3H$, but the loss of C, N and H was recorded (figure, 4.5). The increase in sulfur content with temperature is due to increasing degree of carbonization. Though it has been reported by many authors that sulfonation lead to reduce C, H and N content of sulfonated bio chars (Song, W., Guo 2012), and relative increases in oxygen content were observed in samples of catalyst in this study.

3.5. Characteristic of the morphology (SEM)

Scanning Electron Microscopy (SEM) was extensively used to characterize the microstructure of bio char and sulfonated bio char catalyst. The surface morphology, such as the surface shape, pattern, and feature of the selected bio char and bio char sulfonated catalyst was observed using JEOL JSM-IT300 SEM attached with Energy Dispersive X-ray (EDX).
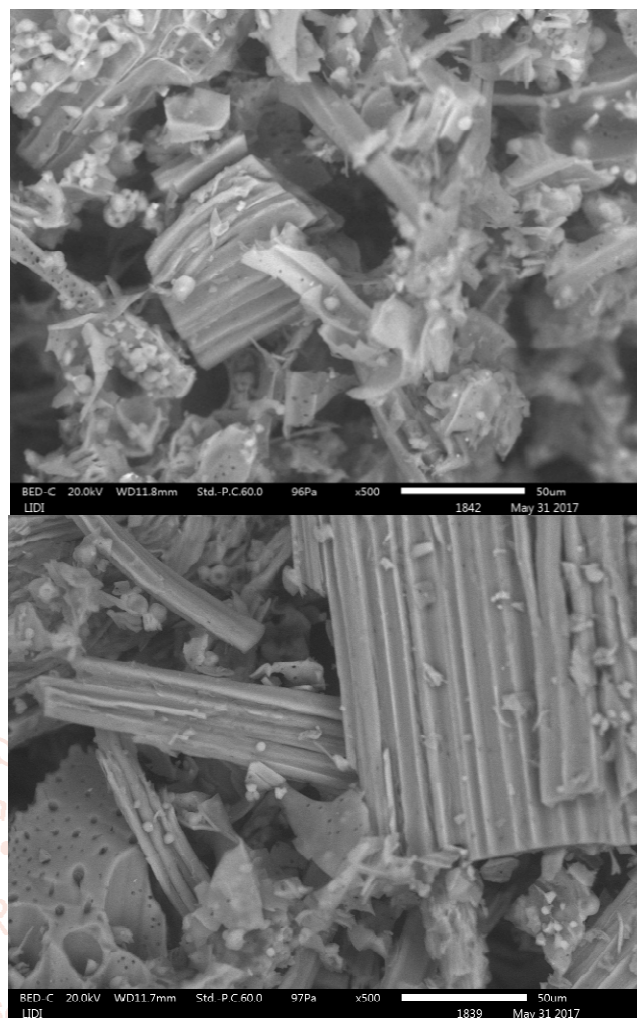

Figure 4.6: SEM images of: A) BC-500 at 50µm; and B) BC-500-SO₃H-s at 50µm indicating morphologies and pore sizes.

The SEM was used to get proper images of samples at the microscopic level (figure, 4.6). These images are primarily used to determine the structure and distribution of the pores that are present on the surface of the bio char and sulfonated bio char. It also determines the nature of the size of the pore, depending on the magnification of the image taken. The SEM images of the bio char and sulfonated bio char are depicted in figure 4.6. From these images (figure 4.6), it can be seen that the bio char (BC-500) and sulfonated bio char (BC-500-SO_3H-s) consisted mainly of aggregates of carbonaceous microspheres that had diameters of several mm. When bio char was sulfonated with H_2SO_4 and bio char, a morphological change occurred and the obtained bio char had a sponge like structure with large conchoidal cavities due to sulfonation agglomerations occur.
mx

3.6. X-ray Diffraction (XRD) Spectroscopy

X-ray diffraction (XRD) is one of the most important non-destructive tools to analyze all kinds of matter - ranging from fluids, to powders and crystals and also to identify crystalline phases and orientation. XRD patterns for BC-400-SO_3H-s (figure, 4.7) exhibited one strong diffraction peak at 2=19–30° and one broad, and for BC-400-SO_3H-st exhibited one strong diffraction peak at 2=18–29° and one broad. These XRD patterns are typical of amorphous carbonaceous materials that consist of aromatic carbon sheets oriented in a random fashion.
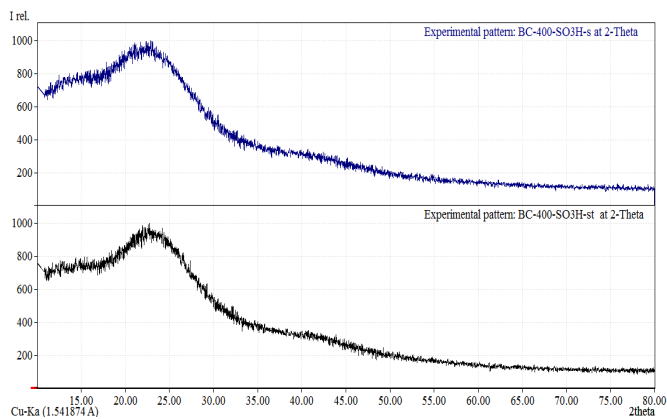
Figure 4.7: XRD patterns of BC-400-SO$_3$H-s and BC-400-SO$_3$H-st

Typical crystal diffraction peaks were not seen, and the width and weak diffraction peak at 2=17° - 29° for BC-450-SO$_3$H-s and 2=17° - 29° for BC-450-SO$_3$H-st, both patterns implied that the structures of both samples were amorphous (Figure, 4.8). The diffraction peaks were 2=22, and 23 in the pattern of BC-450-SO$_3$H-s and BC-450-SO$_3$H-st respectively. These diffraction peaks of crystalline carbon were still visible, which implied an incomplete carbonization.
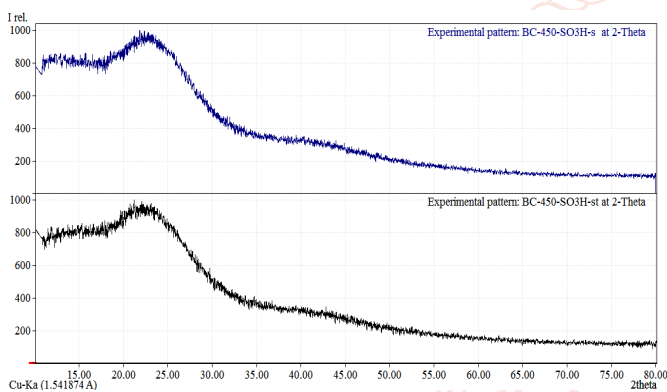

Figure 4.8: XRD patterns of BC-450-SO$_3$H-s and BC-450-SO$_3$H-st

Similarly, typical crystal diffraction peaks were not seen, and the width and weak diffraction peak at 2=18° - 27° for BC-500-SO$_3$H-s and 2=18° - 27° for BC-500-SO$_3$H-st, which implied the structures of both samples were amorphous (figure, 4.9).
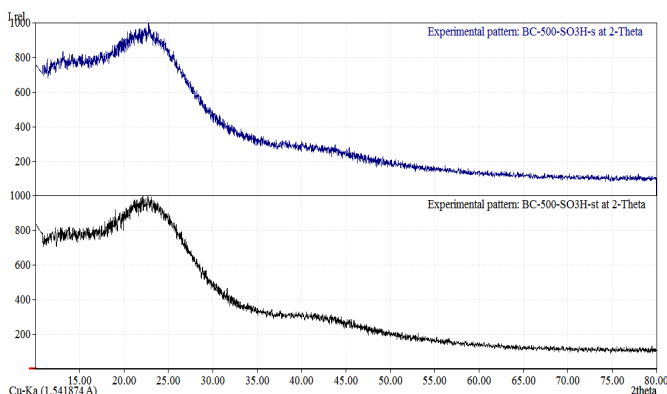

Figure 4.9: XRD patterns of BC-500-SO$_3$H-s and BC-500-SO$_3$H-st

3.7. Fourier Transform Infrared (FT-IR) Spectroscopy

Samples were measured on Spectrum 65 FT-IR (PerkinElmer) in the range 4000-400cm^{-1} using KBr pellets. Fourier Transform Infrared Spectroscopy (FTIR) is a non-destructive analytical technique used to identify organic and inorganic materials.

FTIR analysis results in absorption spectra which provide information about the chemical bonds and molecular structure of a material and also helps to identify the carbon skeleton structure and groups attached on it.
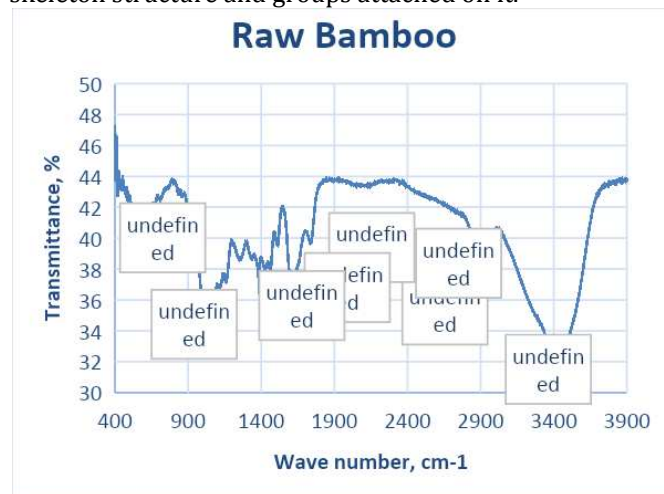

Figure 4.10: FT-IR spectra for raw bamboo sawdust.

All of the bands in the bamboo spectrum appeared broader and sharper than the bamboo char, especially those in the absorption bands at 3434cm^{-1} and 2926 cm^{-1}, which are attributed to the stretching vibrational bands of the O–H group and C–H group in–CH$_2$ and –CH$_3$, respectively (Liao et al, 2015). In addition, the absorption bands at 1161, 1221, 1030 and 1058 cm^{-1} corresponding to the C–O–C stretching vibrations, considered to be important characteristics of cellulose (Fan et al. 2009; M. Liu et al. 2013), were also more intense in the bamboo spectrum. The hydrogen bonds of bamboo were broken down when the catalysts were in contact with cellulose, which led to more C–H, C–C, C–OH and C–O–C exposed on the surface; as a result the intensity of these peaks increased (Tong et al. 2013).
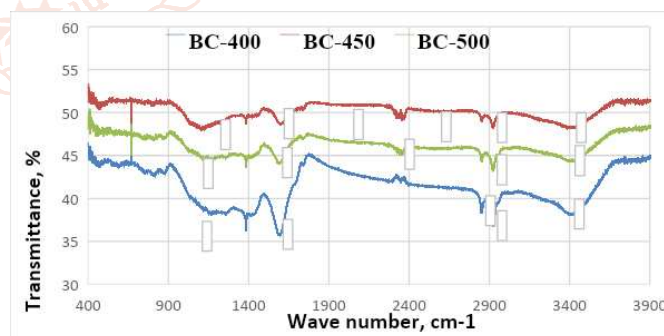

Figure 4.11: FT-IR spectra for bio char carbonized at 400, 450 and 500℃

The band 1750 cm^{-1} were C=O stretching vibration peak and 3430 - 2364cm^{-1} belonged to O-H stretching vibration peak. In addition to, phenolic C-OH, C=C, C=O,OH stretching vibration, and carboxylic C-OH bending vibration bands appear at 1191cm^{-1}, 1608cm-1, 1750-1788cm^{-1}, 2928cm^{-1}, and 1425cm^{-1}, respectively, demonstrating the presence of COOH and phenolic OH groups on the surface of the catalyst (Qi et al. 2012). These peaks were seen in spectra showed that there were plentiful of oxygen-containing groups such as phenolic hydroxyl, ester, ether, and carboxylic groups in polycyclic aromatic skeleton. And a band at 2924.33 – 2921.51 cm^{-1} is attributable to saturated C-H stretching

vibration, showed that the carbonization incomplete (Qi et al. 2012; Tong et al. 2013).
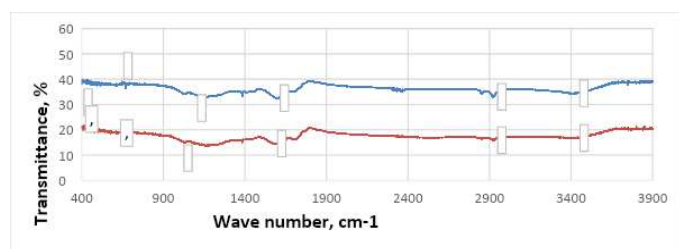

Figure 4.12: FT-IR spectra for BC-400-SO$_3$H-s and BC-400-SO$_3$H-st

The band at 3404-3693 cm^{-1} is attributed to -OH stretching vibrations, which indicates that large numbers of hydroxyl groups are present on the as-prepared bio char materials (Qi et al. 2012).The absorption bands at 1711-1795cm^{-1} and 1604 cm^{-1}are attributed to COO and C=C stretching vibrations, respectively (Qi et al. 2012).The vibration bands at 1050 (SO$_3$-stretching) and 1495 cm^{-1} (O=S=O stretching in SO$_3$H) indicate that the as-prepared bio char materials have surface-SO$_3$H groups (Suganuma et al. 2008)and are likely to promote solid-acid catalyzed reactions. Therefore, the prepared sulfonated char materials had an amorphous carbon structure that probably consisted of polycyclic aromatic carbon sheets with randomly attached SO$_3$H, COOH, and phenolic OH groups.
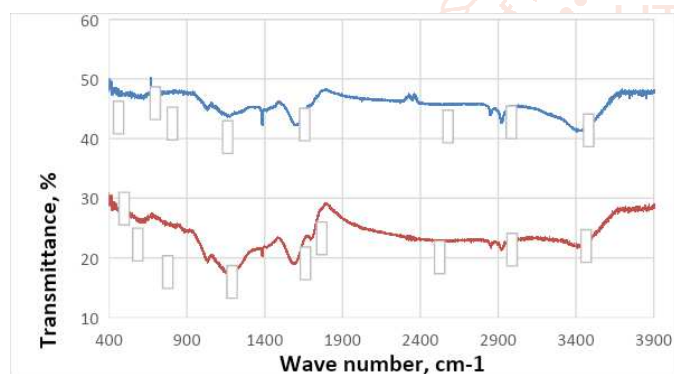

Figure 4.13: FT-IR spectra for BC-450-SO$_3$H-s and BC-450-SO$_3$H-st

The absorption bands at 1716 and 1617 cm^{-1}, correspond to COO- and C=C stretching vibrations, respectively (Titirici, 2012) and also the peaks at 1696-1800 cm^{-1} and at 1171-1176 cm^{-1} are due to the presence of COOH and C-O functional groups, respectively (Figure, 4.13). The band at 3397 cm^{-1} can be assigned to C–OH stretching vibration and – OH bending, and these imply that large numbers of hydroxyl groups exist on the as-prepared bio char material (X. Liu et al. 2010). The vibration bands at 1385cm^{-1} (O=S=O stretching in SO$_3$H) and 1034 cm^{-1} (SO$_3$- stretching) are evidence that the resulting material has surface –SO$_3$H groups (Suganuma et al. 2008) which may have catalytic activity.
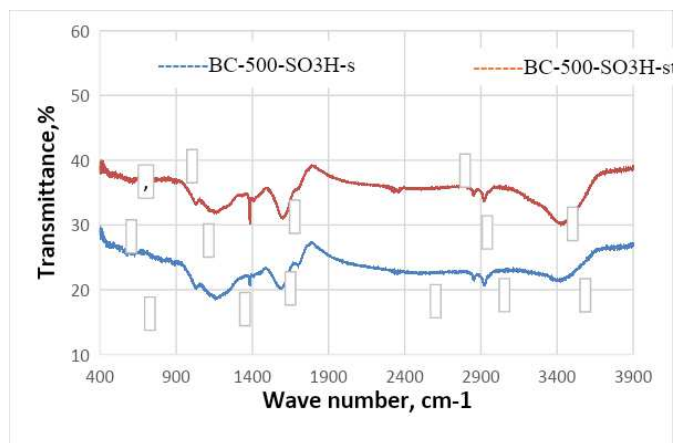

Figure 4.14: FT-IR spectra for BC-500-SO$_3$Hs- and BC-500-SO3H-st

In spectrum of BC-500-SO$_3$Hs- and BC-500-SO3H-st, the peaks attributable to aliphatic C-H bond, aromatic C-H bond, O-H bond in a carboxylic acid group, and O-H bond in a phenol group are seen as a broad peak between 3750 cm-1and 2359 cm^{-1}and also peaks appeared at 1177-1179 cm^{-1} and 1037 cm^{-1} assigned to S=O double bond stretching vibration, and the characteristic band about 628-668 cm^{-1} was the C-S stretching vibration peak. The vibration bands at 1037 (SO$_3$- stretching) and 1384 cm^{-1}(O=S=O stretching in SO$_3$H) in the FTIR spectrum indicate that the resulting material possesses SO$_3$H groups (Suganuma et al. 2008). The FT-IR spectrum of BC-500-SO$_3$H (figure, 4.14) compares with other works, demonstrates bands at 1089cm^{-1}, 1037cm^{-1}, and 1179cm^{-1}, which are consistent with S0$_3$H groups (X. Zhang et al. 2013). It is shown that the carbon-based solid acid have the group of –SO$_3$H.

3.8. Performance analysis for hydrolysis reaction of microcrystalline cellulose

The microcrystalline cellulose of vivapur® 102 was white and insoluble in water and not treated by the ball-milling method. The XRD pattern of cellulose before the hydrolyzed reaction is shown in figure 4.15. The XRD pattern of the raw cellulose showed diffraction peaks of cellulose crystalline around 14.87°, 22.28°, and 34.77°. From the XRD pattern, the crystalline size of cellulose was calculated to be about 62Å.
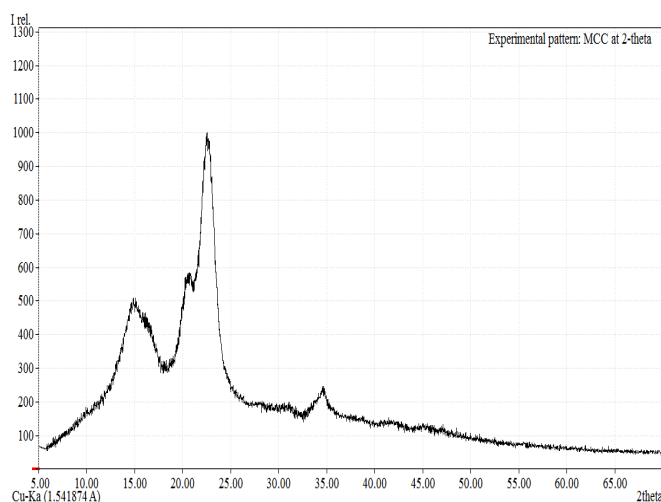

Figure 4.15: XRD patterns of microcrystalline cellulose before hydrolysis
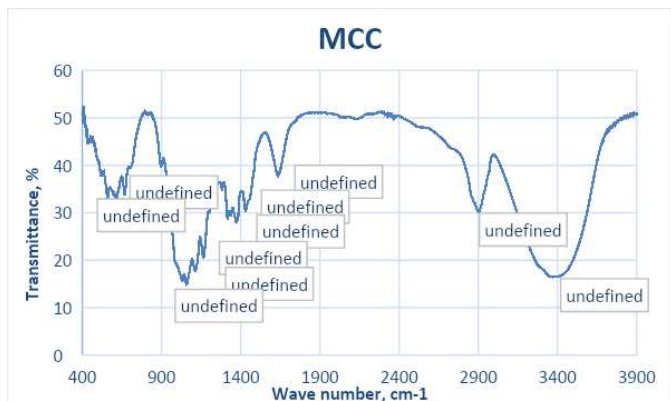
Figure 4.16: FT-IR spectra for microcrystalline cellulose (MCC)

All of the bands in the MCC spectrum appeared broader and sharper, especially those in the absorption bands at 3386 cm^{-1} and 2905 cm^{-1}, which are attributed to the stretching vibrational bands of the O–H group and C–H group in–CH$_2$ and –CH$_3$, respectively (Liao et al, 2015) Figure 4.16. In addition, the absorption bands at 1166, 1114, 1059 and 1058 cm^{-1} corresponding to the C–O–C stretching vibrations, considered to be important characteristics of cellulose (Liu et al. 2014; Fan et al. 2013), were also more intense in the MCC spectrum. The hydrogen bonds of cellulose were broken down when the catalysts were in contact with cellulose, which led to more C–H, C–C, C–OH and C–O–C exposed on the surface; as a result the intensity of these peaks increased (Tong et al. 2013). Also the intensity of the "crystallinity band" ascribed to the saturated –CH bending vibration at 1433 cm^{-1} increased in MCC, demonstrating a higher degree of crystallinity (Kalita et al. 2013).

3.9. The Interaction Effect of Process Variables for hydrolysis reaction

The process variables were found to have significant interaction effects but less interaction effect of reaction temperature with catalyst to cellulose ratio. Figure 4.17 showed the interaction effect of reaction temperatures with reaction time, the interaction effect of reaction time with catalyst to cellulose ratio on yield of glucose, respectively.

As shown on the figure 4.17A, both temperature and time have increased up to optimum to increase the yield of glucose. Lower reaction temperatures could not depolymerize cellulose efficiently and thereby reduces the yield of glucose. And on the other hand higher reaction temperatures increases the depolymerize cellulose that can be hydrolyzed and increases the yield of glucose, but if reaction temperatures increases beyond optimum value it will degrade the glucose into other chemicals.

Figure 4.17 (B) showed, the interaction effect of reaction time with catalyst to cellulose ratio on yield of glucose. Similarly, as lower reaction time could not depolymerize cellulose efficiently because the catalyst need enough time to involve on the hydrolysis reaction and thereby reduces the yield of glucose. But, higher reaction time increases the

activity of catalyst to depolymerize cellulose that can be hydrolyzed.

A

B

C
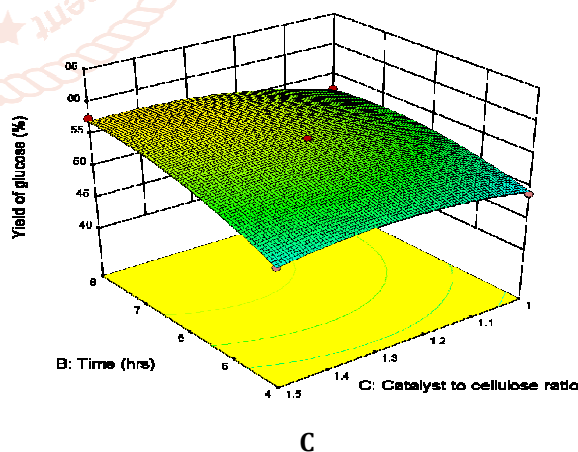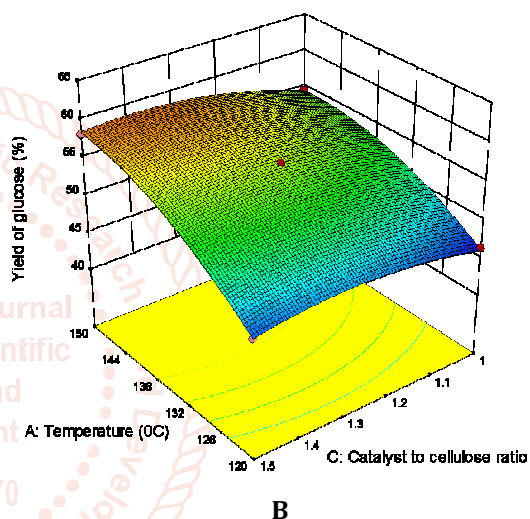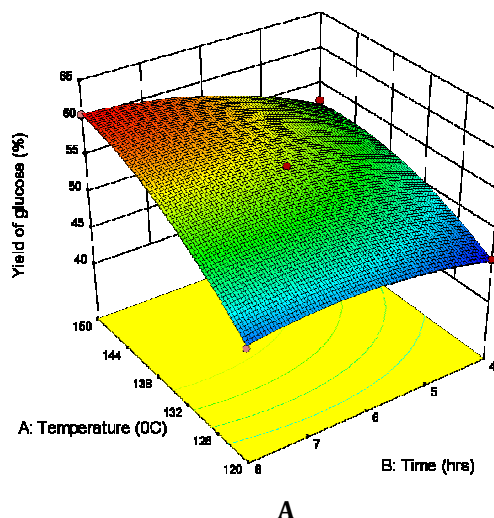
Figure 4.17: Three dimensional response surface plots representing interaction effects: (A) temperature with time (B) temperature with catalyst to cellulose ratio, and (C) time with catalyst to cellulose ratio.

3.10. Optimal process condition for the hydrolysis reaction

Process parameter optimization (interaction between reaction temperature and reaction time, interaction between reaction time and catalyst to cellulose ratio) is necessary in order to obtain the highest yield of glucose. This function searches for combination of independent parameter levels that simultaneously satisfy the requirement for response in the design (Yamaguchi et al. 2009). So in order to obtain the maximum yield of glucose, the predicted combination of parameters was as follows: temperature of 149.787°C, reaction time of 8hr and catalyst to cellulose ratio of 1.469:1. Under these conditions, the model predicted of 61.898% with a desirability value of 0.999(figure, 4.18).
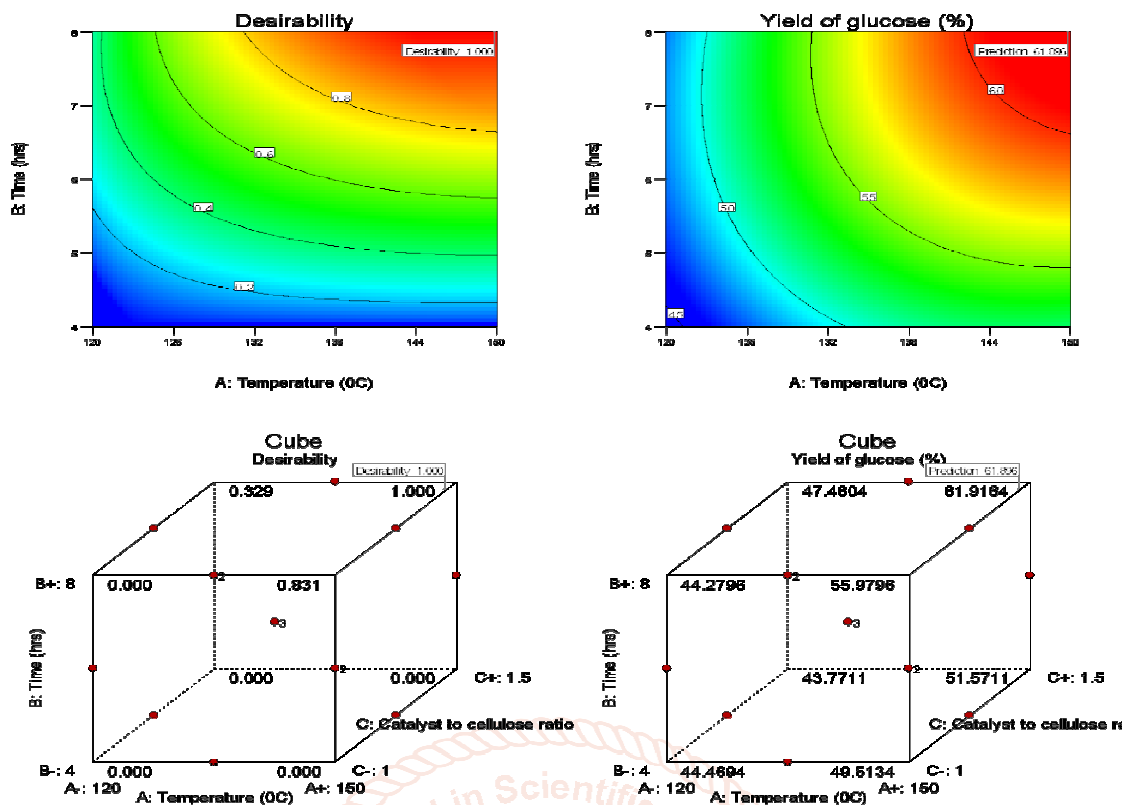
Figure 4.18: The desirability and the optimum yield of glucose at optimum process conditions of cubic and contour plots.

4. Conclusions

A promising heterogeneous catalyst for depolmerization of cellulose has been prepared through sulfonation of bio char, i.e., a by-product of pyrolysis of woody biomass, with 96% sulphuric acid. Applying a stronger sulfonation procedure by using stronger sulfonation reagent (concentrated sulphuric acid) and higher mass ratio of sulphuric acid (10:1) to bio char resulted in higher hydrolysis activity. The high catalytic activity for the reaction can be attributed to the ability to adsorb -1, 4 glucan, the large effective surface area in water, and SO_3H groups tolerable to hydration in the carbon material.

The main objective of this research was to synthesize high surface area, porous, and high acidity carbon-based catalysts that have high activities on hydrolysis reactions. All synthesized catalysts were physically and chemically characterized using bulk density, acid density, elemental analysis, FT-IR, XRD, and SEM. Structural study through Elemental Analysis and FT-IR spectroscopy suggests that bio char-based catalyst consists of polycyclic aromatic carbon sheets bearing three different acidic groups of phenolic, carboxylic, and sulfonic, and the catalyst is stable up to temperature of 250°C.

The first major contribution was the synthesis of porous and high acid density carbon based catalyst using a pyrolysis method. Bamboo was used as a carbon precursor to produce the catalyst support, while pyrolysis at different temperatures 400, 450 and 500°C. In general, as pyrolysis temperature increases the total acid density of the catalyst also increases because total pore volume increased with increasing activation temperature, it was expected that the total acid density of the catalyst samples would increase, as the increase in the pore size would allow the sulfonic groups

to be more easily incorporated onto the carbon matrix. Sulfonation with sonication produces a catalyst with a high acid density and sulfur content than the catalyst with stirring or without sonication. The outputs of the experiment conducted have been analyzed by employing Design-Expert 10.0.0, three-level with three-factor BBD, in which all samples were analyzed on absorbance value of the product using DNS method and the optimum value obtained from glucose yield of each samples.

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Statement of novelty

The paper kept its originality and no one did it before. The work produces active and simple heterogeneous catalyst for conversion of polymer compound. The produced catalyst was unique in saving time and reducing byproduct. Therefore, the work introduces new catalyst and analyzes its behavior in conversion by applying on cellulose polymer.

Acronyms

AC	Activated Carbon
ANOVA	Analysis of Variance
AGUs	β-D- anhydroglucopyranose units
ASTM	American Society for Testing and Material
BBD	Box-Behnken Design
BC	Bio char
BC-SO$_3$H-s	Sulfonated bio char with sonication
BC-SO$_3$H-st	Sulfonated bio char with stirring (without sonication)
BET	Brunauer-Emmett-Teller
CHNS	Carbon, Hydrogen, Nitrogen and Sulfur
CI	Confidence Interval
DF	Degree of freedom
DNSA	3, 5-Dinitrosalisyclic Acid
DP	Degree of Polymerization
EA	Elemental Analysis
FT-IR	Fourier Transform Infrared Spectroscopy
MCC	Microcrystalline Cellulose
HPAs	Heteropoly Acids
RSM	Response Surface Methodology
SEM	Scanning electron microscopy
TAPPI	Technical Association of the Pulp and Paper industry
TCD	Thermal Conductivity Detector
TGA	Thermo gravimetric Analysis
UV-VIS	Ultraviolet-Visible
XRD	X-ray Diffraction Spectroscopy