The International Journal of Engineering and Science (IJES)
|| Volume || 12 || Issue || 6 || June || Pages || PP 09-14 || 2023 ||
ISSN (e): 2319-1813 ISSN (p): 20-24-1805

Hydrothermal Carbonization of Sugar Solution into Carbon Nano-Particle

Rakhman Sarwono[1]
[1] *Research Centre for chemistry – National Research and Inovation Agency, Serpong, Tang-sel, Banten (15314), Indonesia.*

---***ABSTRACT***---
Hydrothermal carbonization (HTC) process can convert sugar solution into residual solid, soluble liquid and gaseous products. Liquid product is called bio-crude or bio-oil as a fuel raw materials. The residual solid has high carbon content. Increase in temperature increase the gaseous products from 41.68 to 65.83, and also residual solid increase from 9.25 to 14.34, but the liquid product was decreased from 49.07 to 19.83. Increase the residence time resulted increase the residual solid from 1.74 to 18.63, and gaseous products increase from 25.05% to 54.4%, but the liquid products were decreased from 73.21% to 26.97%. The liquid content of levulinic acid of 46.78%, mannonic acid of 9.1%, alpha.-D-Glucopyranuronic acid, TMS derivative of 16.23%, and Galactopyranose, 5TMS derivative of 6.98%.Hydrothermal carbonization (HTC) process resulted the residual solid in the form of carbon spherical in the size of 5 to 10 micron. The spherical carbon product can be applied in many purposes.

Key word: *HTC, solid, liquid. gaseous, spherical carbon*

Date of Submission: 01-06-2023 Date of Acceptance: 10-06-2023

I. INTRODUCTION

Hydrothermal conversion is a thermo-chemical conversion technique which uses liquid sub- critical water as a reaction medium for conversion of wet biomass and waste stream. For wet biomass conversion, processes which do not require water evaporation are desired. Hydrothermal carbonization (HTC) is a thermo-chemical pretreatment process is treated under hot compressed water to produce hydrochar. Hydrochar is a stable, hydrophobic, friable solid product.[1]The complex reaction chemistry of HTC offers a huge potential for producing a variety of products, from fuel to supercapacitors, from carbon nanosphere to low cost adsorbents, from fertilizers to soil amenders.

Hydrothermal carbonization (HTC) is a promising technique among all conversion technologies. Hydrothermal carbonization is a thermochemical process for the pretreatment of high moisture content biomass under hot compressed water, making it applicable for diversified purposes. It is performed in a closed reactor at a temperature range of 180 – 280 °C under pressure of 2-6 MPa for 5 to 240 mins. [2]The primary product of hydrothermal carbonization is a coal-like product called hydrochar and also produces aqueous, and gas phases.[3] The mechanism for this process mainly entails decarboxylation, dehydration and polymerization.[4] The water content in the wet biomass is an excellent solvent and reaction medium. Water can act as a base as well as an acid at temperature between 200 °C and 280 °C because its ionic product is maximized. At this temperatures the dielectric constant of water is reduced so it acts more like a nonpolar solvent.[5]

The advantage of hydrothermal carbonization is that, without an energy-intensive drying method, the biomass can be transformed to carbonaceous solids. During the HTC phase, toxic organic molecules and residual micro-pollutants are also degraded.[6]Reaction temperature, pressure, and time are the important factors that influences the process of hydrothermal carbonization, whereas the type of biomass used affects the products of HTC.

Hydrothermal carbonization is understood to be coalification of organic material in aqueous phase under applied high temperature and pressure. Hydrothermal carbonization is based on a single chemical process, namely the splitting of water from carbohydrate (dehydration).

$$\underset{\text{Carbohydrate}}{C_6H_{12}O_6} \xrightarrow{\text{HTC}} \underset{\text{HTC-Biochar}}{C_6H_2O} + \underset{\text{water}}{5\,H_2O} + \underset{\text{Heat}}{-950\ \text{kj/mol}}$$

A simple energy balance of the process already indicates that it is exothermic, during the reaction, energy is released.[7]A further advantage of HTC is that the liquid phase can be separated considerably more efficiently from HTC-biochar than from original biomass. HTC is a mimicry of the natural coal formation. [8]HTC products depend on the type of biomass, temperature, pressure, catalysts used, residents time of reaction and biomass water ratio. The size and the size distribution of colloidal carbon spheres prepared by HTC were influenced by processing temperature, [9] reaction time, and concentration of starting material. [10]

II. EXPERIMENT

2.1. Materials and methods

All solvents are analytical reagent grade provided by Merck. Experimental Procedures were carried out in a reactor of 60 ml stainless steel cylindrical. Sugar from market was dissolved into filtered water (25gr/l, 50 gr/l).Sugar solution of 60 ml was contained into the reactor, and then the reactor was sealed properly and make sure that there is no leakage. The reactor was mounted into the furnace that the temperature can be set in certain point as the reacting temperature desired. The reactor leave there for several hours as the reacting time. After reacting time was reached the reactor was pull out and poured with tap water to chill and stop the reaction. In ambient temperature the reactor valve was open to leave the gas out, the reactor was opened properly to pull out the reaction products. The solid and liquid products are separated by filtering. The solid was rinsed with same solvent and dried at 105 ^{o} C until the weight is remained unchanged as solid product.. The liquid was evaporated in vacuum evaporator in the 50 ^{o}C until the weight is remained unchanged. The liquid was analyzed by GC-MS to know the components of the products. The solid was characterized by Scanning Electron Microscope (SEM).

Yield of bio-oil = Mass of bio-oil / mass of sugar x 100% (1)
Yield of carbon = Mass of carbon / mass of sugar x 100% (2)
Conversion rate = 100 wt% - yield of carbon (3)

2.2 Analytical

2.2.1 GS-MS

The soluble liquid products were analyzed using GCMS, Agilent technologies 7890B, with DB5 Column (30 m x 0.32 mm x 0.25 μm, detector MSD 5977A, Helium (He) was used for mobile phase or carrier gas with flow rate 1 ml/min. Injector temperature was 250 ^{o}C. The temperature of ion source and MS Quadruple were 230 ^{o}C and 150 ^{o}C, respectively.

2.2.2 Scanning Electron Microscope (SEM)

The residual solid was examination by SEM merck JEOL, to know the shape and size of particle.

III. RESULTS AND DISCUSSION

Results of the experiment were shown in Figures 1 - 4. The effects of temperatures and reaction times were examined in water media. Temperature is important parameter that has high influent to the reaction rate. Increase the temperature of 200 to 240 ^{o}C might cause increase the conversion rate, the gaseous products and also solid products were increased, but the liquid product was decreased (Figure 1).Degradation rate of sugar solution increases with increasing temperature, indicated that the solid residues were decreased temperature at 240 ^{o}C, substrate of sugar solution of 50 gr/l. The solid product was increased from 9.25 to 14.34%.The temperatureof 220 ^{o}C, and reaction time is 7 hrs, resulted the residual solid of 18.63%, that was higher value than another temperature.

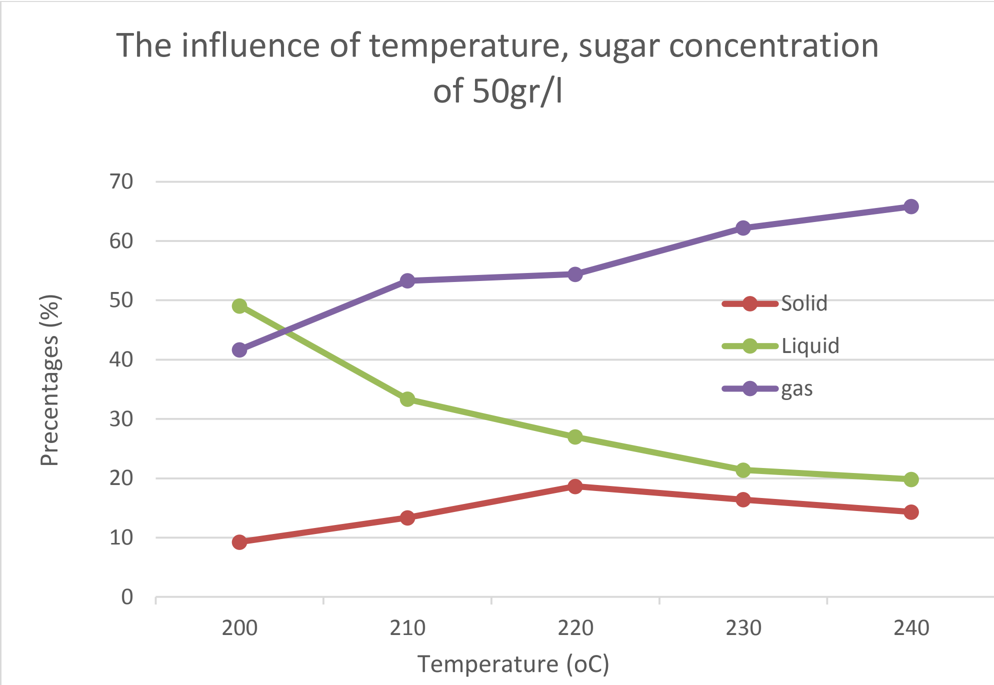

Fig. 1 The influence of temperature reaction on the sugar degradation

The liquid product was decreased from 49.07 to 19.83%. The gaseous product was increased from 41.68 to 65.83%.

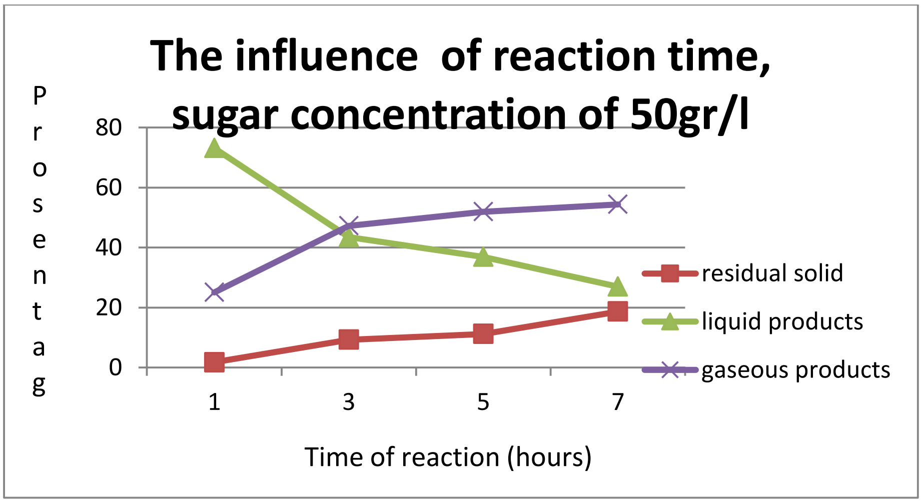

Fig.2 The influence of reaction time on the sugar degradation

Increase the reaction time (1, 3, 5, and 7 hrs). The conversion of sugar solution of 50 gr/l, resulted solid and gaseous products were increased, but the liquid products were decreased. It's meant that increase the reaction time more liquid products were converted into gaseous products. Other words gasification rate increase by increasing reaction time. Increase the reaction time, the degradation of sugar solution was increased, it can be seen that the residual solid was decreased.

The Liquid product was decreased from 73.21 to 26.97%, and gaseous product increased from 25.05 to 54.4%. It,s can be shown that residual solid increased from 1.74 to 18.63%, figure 2.

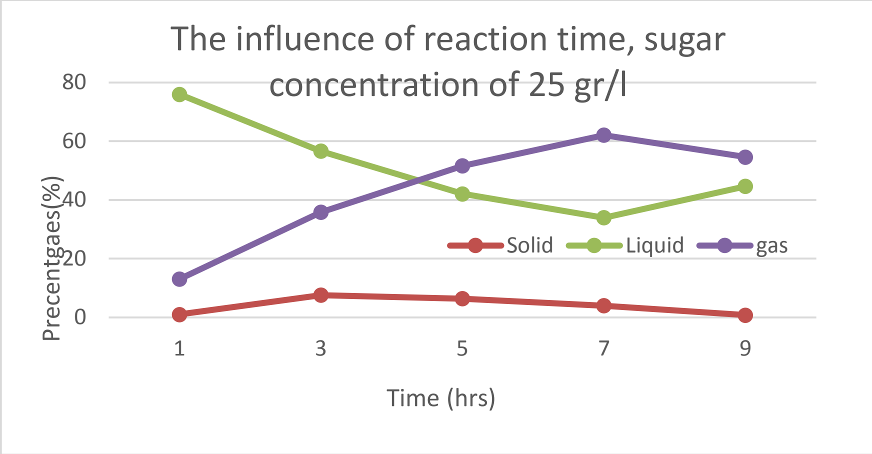

Fig. 3 The influence of reaction time on the sugar degradation

Increase the reaction time (1, 3, 5, 7, and 9 hrs). The conversion of sugar solution of 25 gr/l, resulted that the gaseous products were increased, but the solid and liquid products were decreased. It's meant that increase the reaction time more liquid products were converted into gaseous products. Other words gasification rate increase by increasing reaction time. Increase the reaction time, the degradation of sugar solution was increased, it can be seen that the residual solid was decreased.

The Liquid product was decreased from 75.96 to 44.65%, and gaseous product increased from 13.04 to 54.58%. It,s can be shown that residual solid increased maximum conversion at 3 hrs residence time and than decreased from 1 to 0.77% (Figure 3).

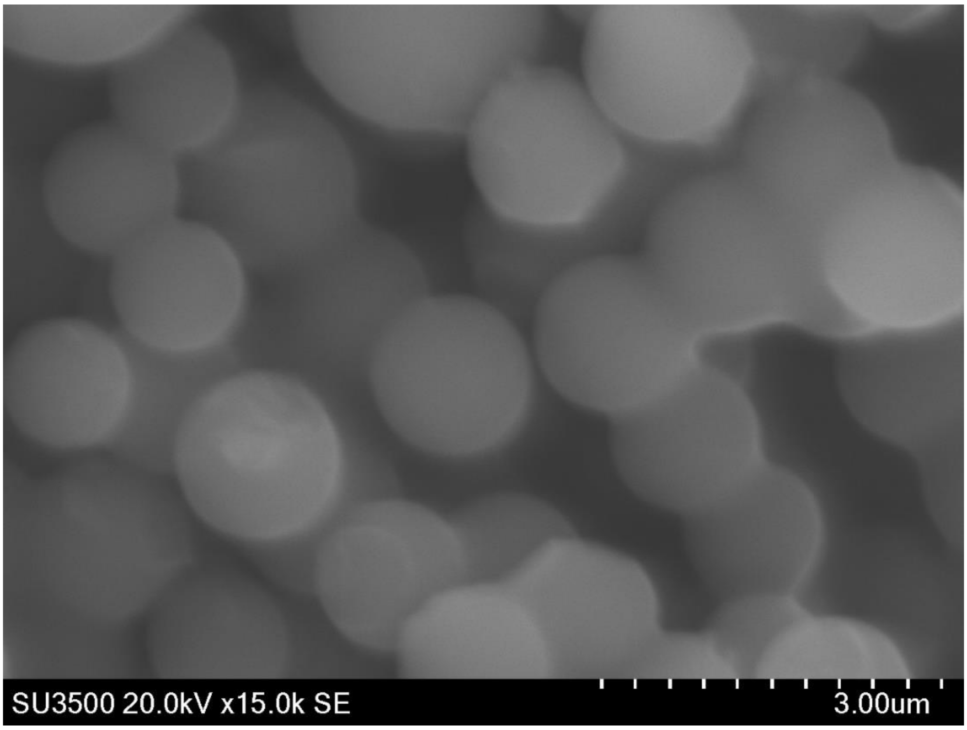

Fig.4 Typical carbon particle size and shape (sugar of 50 gr/l, T= 220 ºC, t= 7 hours)

The carbon particleas shown in Figure 4. The shape is spherical and the size between 5 to 10 micron, the particles were steak together. The particle size can be classified into fine to coarse particle.
HTC was said that is a new methodology to produce activated carbon from biomass. [11] Concerning with cost and energy, there have increased interested in biomass materials for production of activated carbons. The properties of the hydrochars could be significantly influenced by feedstock source and temperature during carbonization process. [12] Carbon nano-particle uses in wide range of application such as adsorbents, capacitors and catalyst support, [13] for drug delivery. [14,15]

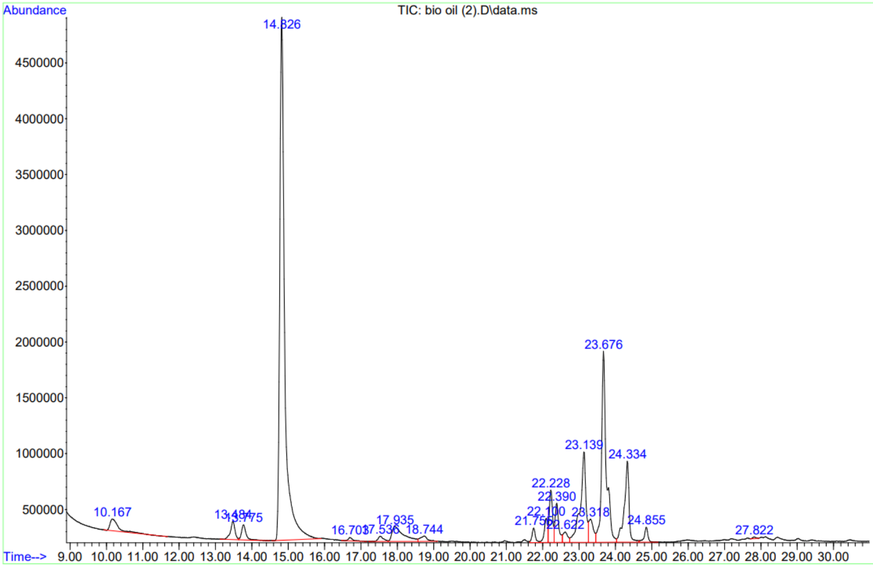

Fig.5 GCMS patterns of liquid phase of sugar degradation

Table 1. Chemical components of bio-oil from sugar degradation

Pk	RT	Area%	Library	Quality
1	10.173	1 1.76	2-Pentanone, 4-hydroxy-4-methyl-	40
2	13.487	1.48	Lactic Acid	81
3	13.777	1.25	Glycolic acid	60
4	14.823	46.78	Levulinic acid	97
5	16.701	0.26	2-Butanol, 2-nitroso-, acetate	10
6	17.533	0.53	3-Hydroxyisovaleric acid	22
7	17.936	3.06	2-Dibenzofuranamine	38
8	18.743	0.69	Carbamic acid	9
9	21.755	0.86	4,4-Dimethyl-2-pentanol	47
10	22.095	1.36	1-Propanol, TMS derivative	22
11	22.234	3.09	2-Bromosebacic acid, 2TMS derivati	47
12	22.385	2.58	Ethylmalonate, ethyltrimethylsilyl ester	43
13	22.625	0.92	L-(+)-Lactic acid, trimethylsilyl ester	47
14	23.141	9.10	Mannonic acid	38
15	23.318	1.98	acetic acid	59
16	23.671	16.23	alpha.-D-Glucopyranuronic acid, TMS derivative	43
17	24.339	6.98	Galactopyranose, 5TMS derivative	72
18	24.855	0.99	beta.-D-Allopyranose, 5TMS derivative	93
19	27.817	0.09	4-Phenyl-2-butanol, TBDMS derivative	27

The GCMS examination of liquid product results are shown in the distribution of major compounds from the degradation of sugar (Fig.5 and Table 1). The chemical distribution are varies it's depend on the operating process condition and the raw materials used. Liquid products was analysis in GC-MS to know the component of the liquid. The peak area (%) for each component identified was defined by peak quality. GC-MS analysis results of the bio-oil obtained from liquefaction of sugar solution based on peak areas are listed in Table 1. The major components of bio-oil resulted from sugar degradation consist of levulinic acid of 46.78, mannonic acid of 9.1%, alpha.-D-Glucopyranuronic acid, TMS derivative of 16.23%, and Galactopyranose, 5TMS derivative of 6.98. There are also minor component that occur in bio-oil with mostly less then 1%.

V. CONCLUSION

Hydrothermal carbonization (HTC) process can convert the sugar solution into residual solid, liquid and gaseous products. Liquid product is called bio-crude or bio-oil as a fuel raw materials.The residual solid is in the form of spherical particle. Increase in temperature increase the gaseous products and also residual solid products were increased, but the liquid product was decreased. Increase the residence time resulted residual solid and gaseous products were increased, but the liquid products were decreased. The liquid content was majority of levulinic acid of 46.78, mannonic acid of 9.1%, alpha.-D-Glucopyranuronic acid, TMS derivative of 16.23%, and Galactopyranose, 5TMS derivative of 6.98. Hydrothermal carbonization (HTC) process was resulted carbon sphere in the size of 5 to 10 micron.

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Rakhman Sarwono. "Hydrothermal Carbonization of Sugar Solution into Carbon Nano-Particle." *The International Journal of Engineering and Science (IJES)*, 12(6), (2023): pp. 09-14.