



# HYDROTHERMAL CARBONIZATION KINETICS OF SUGARCANE BAGASSE TREATED BY HOT COMPRESSED WATER UNDER VARIABEL TEMPERATURE CONDITIONS

Dewi Agustina Iryani, Satoshi Kumagai, Moriyasu Nonaka, Keiko Sasaki and Tsuyoshi Hirajima

Department of Chemical Engineering, University of Lampung, Bandar Lampung, Indonesia

Department of Earth and Resources Engineering, Research & Education Center of Carbon Resources, Kyushu University, Fukuoka, Japan

E-Mail: [dewi.agustina@eng.unila.ac.id](mailto:dewi.agustina@eng.unila.ac.id)

## ABSTRACT

This study investigated kinetics of hydrothermal carbonization (HTC) decomposition reaction of sugarcane bagasse treated with hot compressed water under varied temperature in range 200-300 °C. Experiments were carried out using a batch type reactor with a temperature controller. Characterization results showed that the decomposition reaction was influenced by temperature and reaction time. Degradation of hemicellulose began at 200°C (3 min) and was completed at 240°C (5 min) to form arabinose and xylose. Cellulose started to decompose at 240°C (5 min) and was completely degraded at 270°C (20 min). Lignin decomposed at temperature range 200-300°C, and produced aromatic and phenolic compounds.

The kinetics calculation for decomposition reactions such as hydrolysis and dehydration reactions are adopted as the heterogeneous reaction model. The model assumes that solid particle is cylindrical shape and this size is shrinking with reaction (cylindrical shrinking core model). Results of calculation indicated that the reaction is controlled with the diffusion through product layer. From these calculation and the results of decomposition mechanism can be explained as follows: (i) hydrothermal carbonization cellulose and hemicellulose are decomposed preferentially and un-reacted lignin part to be diffusion layer. (ii) the hydrolysis and dehydration reaction started at 200°C and 240°C respectively and reaction rate increased with increasing temperature.

**Keywords:** kinetic, shrinking core, hydrothermal, biomass.

## 1. INTRODUCTION

Recently, hydrothermal carbonization has attracted some interest as a possible application for biomass conversion due to it uses water which is non-toxic, environmental friendly and inexpensive medium. Hydrothermal carbonization can be regarded as a biomass treatment technology similar to wet torrefaction [1-3]. This process is an artificial coalification process which converts raw biomass into three phase products: gas, liquid and solid product that has a resemblance to coal-product such as lignite or also called bio-coal [1-3].

In the hydrothermal carbonization, biomass is covered with water and heated in a pressure vessel within some minutes or hours at elevated temperature and pressure. The process is particularly suitable for wet biomass. The process has high efficiency compared with others thermal conversion such as pyrolysis and gasification, because it does not require energy for drying [4-6]. In this process, sub-critical water or (hot compressed water) is not only act as a solvent, but because its dielectric constant is lowered at higher temperatures, thus driving the solvation characteristics of water towards that of polar organic [7]. The higher compressibility of hot-compressed water compared to ambient water lead to a strong influence of solutes on the microscopic structure, which in turn it has an impact on chemical reactions.

The chemical or decomposition reactions of biomass under the hydrothermal carbonization cannot be

described easily and detailedly as a single reaction step. The reason is that biomass consists of three major components such as cellulose, hemicellulose and lignin. Under the treatment, the components interact with each other in a complex chemistry mainly heterogeneous process proceeding inside and, in particular, on the surface of biomass particles [13].

The presence of water in hydrothermal treatment initiates the hydrolysis reactions which decomposes lignocellulosic structure of biomass and yielding saccharides such as pentoses and hexose, and fragments of lignin [3,7,8-10]. Alongside of hydrolysis reaction, the other a reaction that might appear during hydrothermal carbonization are dehydration, decarboxylation, condensation polymerization and aromatization [1, 5, 12, 13, 15]. All of the reactions do not represent by consecutive reaction steps but rather form a parallel network of different reaction paths [1]. More after, the reaction produces many intermediate compounds such as 5-HMF and furfural, organic acids, aldehydes [14] and phenolic compounds [9]. In addition, during the process is also ongoing the polymerization reaction and form insoluble solid or char and partly precipitate to form coal like product [1, 12].

An understanding of kinetics is necessary for reactor design and optimization. To the date, the detail about reaction pathway and kinetic of hydrothermal carbonization process of lignocellulosic biomass has not



been well-studied due to the complex nature of biomass material. Although, there are many studies in the literature reported about reaction pathway and kinetic reaction of lignocellulosic biomass by the hydrothermal conversion [16-19], there is limited data about degradation and formation pathways and decomposition mechanisms of real biomass. The majorities of the previous studies were focused on model compounds, particularly cellulose, glucose, and xylose.

Therefore, to provide a comprehensive insight about kinetic hydrothermal carbonization of real biomass, in this study by using sugarcane bagasse as a raw material, the determinations of the kinetic reactions are conducted.

## 2. METHOD AND EXPERIMENTAL

### a) Material preparation

Sugarcane bagasse provided by the sugar industry was ground using a cutting mill to form powder with a maximum particle size of 1.0 mm, and dried in an oven at 60°C for 24h before commencing treatment. The properties and composition analysis was previously described in our previous study [14].

### b) Hydrothermal carbonization treatment experiment

The hydrothermal carbonization experiments were conducted in a batch-type reactor (SUS 316, 14ml) and equipped with K-thermocouple to measure temperature of reaction. Slurry consisting of 10 ml water and 1.2 g sugarcane bagasse were placed in the reactor. A stream of N<sub>2</sub> gas was used to replace air in the reactor and to regulate initial internal pressure of 0.5 MPa. The reactor was immersed into a preheated salt bath at the desired temperature and a given reaction time. The reactor was then removed from the salt bath and further it was quickly quenched by immersion of the reactor into a water bath to room temperature. The temperature range was from 200 to 300°C and reaction time (including heating period i.e. 3 min) from 3 to 30 min.

### c) Analysis methods

The compositions of solid product were determined using same procedure with previously described [14]. The total organic carbon (TOC) for liquid product was measured by using Shimadzu TOC-5000 A. Total carbon in liquid phase is calculated according to equation (1) and (2).

$$C_m = \frac{\text{TOC}}{1 \times 10^6} \times V_{\text{sol}} \quad (1)$$

$$Y_{C,l} = \frac{C_m}{C_{R,\text{biomass}}} \times 100 \% \quad (2)$$

Where

C<sub>m</sub> is carbon amount in the liquid phase, Y<sub>c,l</sub> is the carbon yield in the liquid phase, to convert ppm (mg/L) to g/mL,

TOC (in ppm) values should be divided by 1×10<sup>6</sup>, C<sub>R,biomass</sub> is carbon amount in raw material (g dry base). V<sub>sol</sub> is volume of solution (in ml). Further, the carbon yield in solid phase is calculated with equation (3).

$$Y_{C,s} = \frac{Y_{Wl} \times C_{C,s}}{C_{R,\text{biomass}}} \times 100 \% \quad (3)$$

Where:

Y<sub>wl</sub> is yield of solid product, C<sub>C,s</sub> is carbon content in solid product and Y<sub>C,s</sub> is yield of carbon in solid product. Determination of distributions carbon in each phases conducted by using carbon balance. Further, the organic carbon content in gas fraction and the weight loss during filtration were calculated based on carbon balance:

$$\text{Yield of carbon in gas+loss} = 100 - Y_{C,l} - Y_{C,s} \quad (4)$$

Furthermore, the solid products were characterized using several methods: the Yanaco CHN Corder MT-5 elemental analyzer conducted to determined carbon content in raw and treated material. Scanning electron microscopy (SEM KEYENCE/VE-9800) was performed to evaluate the effect of hydrothermal carbonization on the sugarcane bagasse morphology.

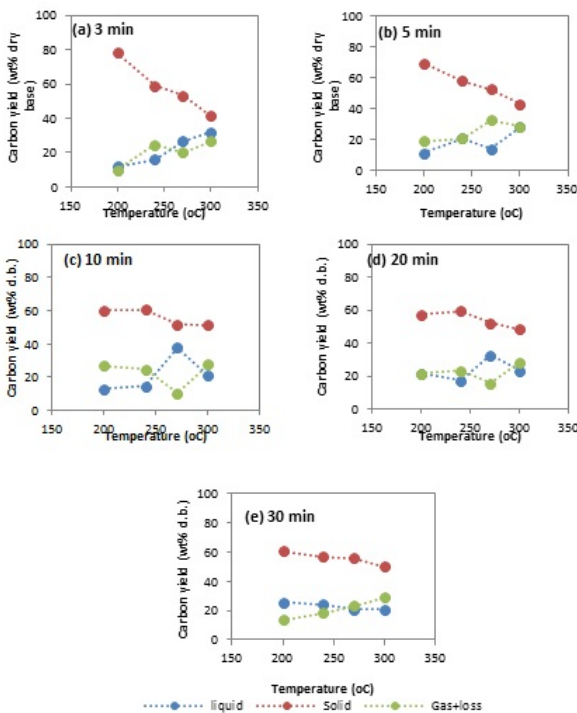
## 3. RESULTS AND DISCUSSION

### a) Effect of reaction conditions on carbon distribution product

The physical and chemical bond in feed material were change under the treatment. The long chain compounds such as hemicellulose, cellulose and lignin which contains in feed material gradually decomposed into smaller and simple organic molecules. It molecules further then distributed into three phases such as liquid, solid and gases and represented by percentage carbon.

The carbon yields of three phases of product from hydrothermal treatment of sugarcane bagasse at various conditions are shown in Figure-1. The carbon yield in solid phase denoted that most of the carbon remained in the solid phase gradually decreased as the temperature increased due to feedstock solubilization. The solubilization reflected that continuous decomposition of carbohydrate from hemicellulose and cellulose due to hydrolysis reaction.

Figure-1 obviously indicated that at the time of 3 and 5 min, the yield of carbon in solid residue decrease from 78.4 into 41.6 wt% and 69.4 into 43.2 wt%. In the longer reaction time (10-30 min), less significant changes in carbon distribution observed. The less changes of carbon yield in solid product at high temperature and long reaction time could be attributed to the condensation of lighter compounds derived from cellulose and lignin [20-21]. Further, decomposition of the compound produces the formation of coke/char which precipitate in solid residue.



**Figure-1.** Percentage yield distribution of carbon of organic compounds in the gas, liquid, and solid phases.

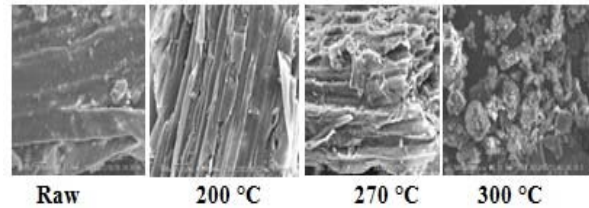
In case of liquid phase, consistent with observation in previous studies [9] about 11% to 33% carbon in feed transferred into the liquid phase. Moreover, it indicated that the carbon yield slightly increases in temperature range 200-240°C with increase of reaction time. At 270°C in range reaction time 10-20 min, a unique characteristic was observed. The relative amount of carbon yield increased to a maximum in this temperature. The possible reasons to account for the leveling off of the carbon yield in liquid phase at higher temperatures and longer reaction time might be occur due to: (1) cracking of the solid and liquid products to gas or volatile fractions and (2) formation of solid residue by condensation, cyclization, and re-polymerization [21].

Conversely, the proportion of carbon in the gas phase steadily increased with temperature. The carbon yield in gas fraction increased continuously with increasing temperature over the whole temperature. Approximately, 10-20% carbon was transferred to the gas phase. Yuliansyah et al. [9] reported that the predominant gas produced under the hydrothermal treatment is CO<sub>2</sub> (about was the predominant gas observed ( $\geq 80$  vol.%), followed by CO and H<sub>2</sub>.

#### b) SEM (scanning electron microscopy) images

SEM analysis was conducted to determine the effect of hydrothermal treatment on the material structure. The SEM images in the Figure-2 presented the surface of raw and treated sugarcane bagasse in various conditions. The surface of sugarcane bagasse before the treatment shows basic and compact of fiber surface structure. At

200°C, the deformation of fibers and some of cracks were apparent on the surface of solid product. At 240°C, the treated material surface is covered with 'debris' and a thin layer of deposits seemed to cover the whole surface. Under stronger conditions, structural rupture was observed and the surface was more cracked and covered with more small debris. This debris could be made up of the acid insoluble residue or char deposit, as reported by literature [12, 20, 21].

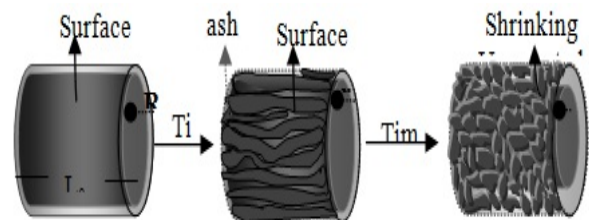


**Figure-2.** SEM images of raw and treated sugarcane bagasse at 5 min in various treatment temperature.

#### c) Decomposition reactions under hydrothermal carbonization reaction

In this study based on the characterization results, mechanism reaction under hydrothermal carbonization treatment could be stated into two simple model reactions i.e. hydrolysis (or liquefaction) and dehydration reactions. Both of the reactions assumed to be simultaneously occurs within biomass particle and all the chemicals reactions assumed to be first order with respect to the fraction weight of reactant and rate of constant are expressed in Arrhenius form.

The kinetic models calculations for all of the reactions are adopted that heterogeneous reaction model. The model which elucidates the mechanism of reaction on the surface of a solid particle is described as a shrinking core or grain model. The shrinking core model seems applicable to describe decomposition reaction under hydrothermal carbonization. Figure-3 described the progress of the non-catalytic reaction of biomass particle under the treatment.



**Figure-3.** Scheme for representation shrinking core model of solid particle under hydrothermal carbonization.

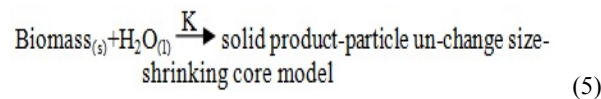
In the hydrothermal carbonization, the solid particle was surrounding by water. Water as reactant is formed in both as the aqueous bulk and the aqueous film near to the solid particle. By referring to Figure-3, it was assumed that the reaction first begins at the outer surface



of solid particle and deeper layers do not take in the reaction until all the outer layer has transformed into liquid, gas or solid product. Furthermore, the reaction zone gradually moves toward the inside of solid, constantly reducing un-reacted solid core size and remaining converted solid product and inert material. The following steps occur during reaction can be explained as follow:

- Water molecules diffuse into the external surface of solid particle from the bulk aqueous phase through the aqueous film. Further, diffusion of water molecules through the aqueous film surrounding the particle to the surface of solid particle (external diffusion).
- Penetration of water by diffusion through the pores and cracks in the blanket (layer) of ash to surface of the un-reacted core pore (internal diffusion).
- Reaction of water with solid at the surface of un-reacted core. And, Diffusion of liquid product was back to the exterior surface of solid product through the ash layer (reverse internal diffusion).

The SEM analysis results considered that the kinetic models of hydrothermal carbonization are calculated with a cylindrical-shaped grain. Further, based on the shape of raw particle, the conversion equation is developed by considering each of the following steps separately to be rate controlling reaction [22]. The equation kinetic reaction by using shrinking core model for solid product particle un-changing size shrinking core model explained as follows:



In all of solid-liquid reactions, all of steps below may exist. Therefore, the mathematical derivation of the kinetic models were explained as follow with assumed that a biomass particle is a cylinder shape with initial particle diameter is  $R$  and core diameter is  $r_c$  ( $\mu\text{m}$ ).

### i. Diffusion through aqueous film controls (controlling resistance- aqueous film diffusion)

For the first mass-transfer step of water molecules, it was assumed that a linear approximation for transportation of a water molecule from the bulk aqueous phase into the surface of a particle. The mass transfer of the water molecule through aqueous film is explained as equation (6).

$$-\frac{1}{S(X)} \frac{dW_A}{dt} = \frac{1}{S(X)} \frac{dW_B}{dt} = K_w(C_w - C_s) \quad (6)$$

Where:  $W_A$  is mass of water,  $W_B$  is mass of solid particle,  $K_w$  is the mass transfer coefficient of water,  $S(X)$  is surface area of particle,  $C_w$  and  $C_s$  concentration of water in aqueous bulk and surface of particle, respectively.

### ii. Chemical reaction controlling

Based on surface of un-reacted core, the mass transfer occurs on the surface can be explained as following:

$$-\frac{1}{S(X),c} \frac{dW_B}{dt} = -\frac{1}{S(X),c} \frac{dW_A}{dt} = k_s C_w \quad (7)$$

### iii. Diffusion through product layer control

$$-\frac{dW_A}{dt} = 2\pi r L Q_A \quad (8)$$

$$Q_A = D_e \cdot \frac{dC_A}{dr} \quad (9)$$

Where:  $Q_A$  is flux layer of surface and  $D_e$  is external diffusion through of surface.

From all of steps which are above mentioned offer resistance to overall reaction. Further, the step with the higher resistance is considering as the rate controlling or rate determining for the overall reaction process [22].

### d) Determination conversion rate of sugarcane bagasse under HTC

After determination of the highest resistance as reaction controller, the calculation for conversion rate was conducted. The conversion rate of all of reactions under HTC treatment based on shrinking model can be explained as following:

$$\frac{dV(X)}{dt} = \frac{dW_B(X)}{dt} = -k_s \cdot S(X) \quad (10)$$

Where:  $k_s$  ( $\text{cm s}^{-1}$ ) is the surface reaction-rate constant, and  $S$  ( $\text{cm}^2$ ) and  $V$  ( $\text{cm}^3$ ) are the surface area and the volume of the particle, respectively. Further, the calculation for overall conversion rate constant for each reaction can be explained as follow:

$$K = \frac{k_s}{r_{c,0}} = \frac{X_B + (1 - X_B) \ln(1 - X_B)}{\tau} \quad (11)$$

Where:  $K$  ( $\text{min}^{-1}$ ) is the overall conversion rate constant of biomass. The  $K$  value was determined from the slope of the straight line. And, the rate constant for each reaction is a function of temperature, by using the Arrhenius' law.

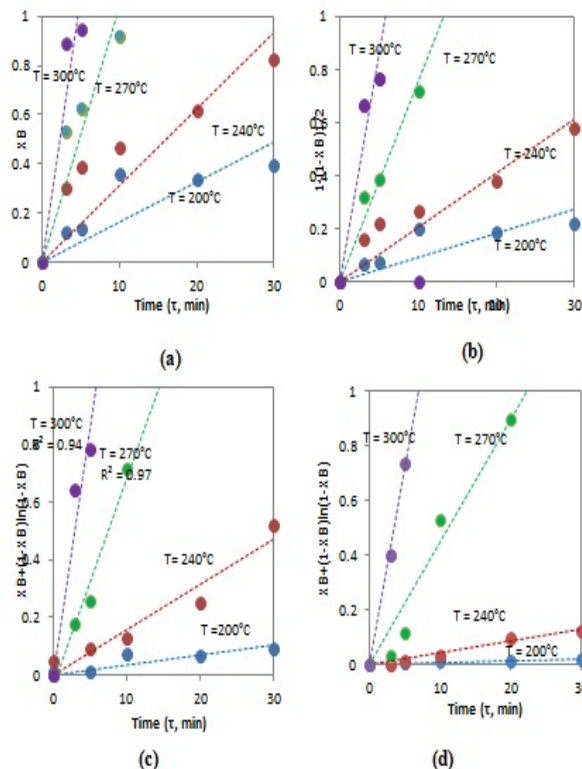
$$K = A_0 \cdot \exp(-E_a/RT) \quad (12)$$

Where,  $A_0$  and  $E_a$  are the general expression for the frequency factor and the activation energy of the reaction. The  $X_B + (1 - X_B) \ln(1 - X_B)$  values at all the reaction conditions were plotted against the reaction time (min). Further, the Arrhenius' plots for each overall conversion values.



### e) Determination of kinetic conversion parameter of hydrolysis and dehydration reaction of sugarcane bagasse under HTC

Figure-4.a – 4.b showed the result of determination kinetic conversion parameter which controlled the hydrolysis reaction of sugarcane bagasse under the treatment. The results suggested that the hydrolysis reaction of sugarcane bagasse particles mainly took place at their internal or inner pores surface in hot-compressed water. The hydrolysis reaction occurs in the temperature range reaction 200-270°C with the conversion maximum achieved at 270°C 5 min. Based on conversion rate calculation, it found that the reaction rate controlled by diffusion through solid product layer.



**Figure-4.** Determination of conversion parameter controlling resistance of hydrolysis reaction at various conditions; (a) diffusion through aqueous film, (b) chemical reaction, (c) diffusion through solid product, (d) diffusion through solid product).

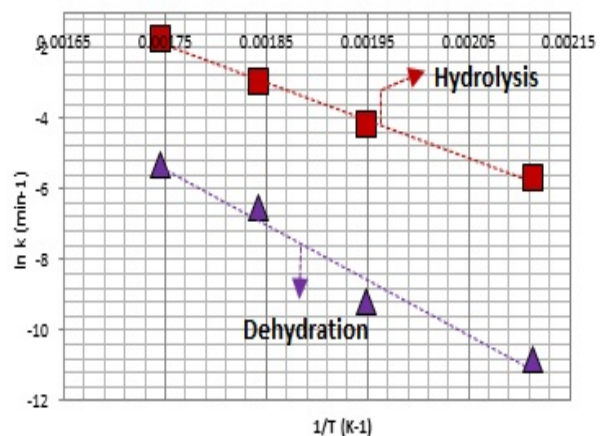
Under hydrolysis reaction hemicellulose and cellulose decompose in a first-order reaction in various condition treatments and produces a solid product, aqueous chemicals and gases [14, 17, 18, 23]. In the hydrolysis reaction, we calculate the transformation weight for hemicelluloses and cellulose, while lignin is inert. Conversion was subsequently evaluated based on the amount of cellulose and hemicellulose reacted with respect to the initial quantity of cellulose and hemicelluloses in feed. The values obtained for the conversion at the different temperatures plotted against with reaction times.

In the Figure-4 the conversion values at 270°C ( $\geq 10$  min) and 300°C ( $\geq 5$ min) were not plotted due to complete conversion.

Figure-4(a) – (d), shown the result of determination kinetic conversion parameter which controlled the hydrolysis reaction of sugarcane bagasse under the treatment. The results suggested that the hydrolysis reaction of sugarcane bagasse particles mainly took place at their internal or inner pores surface in hot-compressed water. The hydrolysis reaction occurs in the temperature range reaction 200-270°C with the conversion maximum achieved at 270°C 5 min. Based on conversion rate calculation, it found that the reaction rate controlled by diffusion through solid product layer.

Figure-4(d) shows the result of determination kinetic conversion parameter which controlled the dehydration reaction of sugarcane bagasse under the treatment. The results suggested that similar with the hydrolysis reaction, the dehydration reaction was also mainly took place at their internal or inner pores surface particle. The dehydration reaction occurs in the temperature range reaction 200-300°C with the conversion maximum achieved at 270°C (20 min) and 300°C (5 min). The reaction rate of dehydration is controlled by diffusion through solid product layer.

Figure-4(c) and 4(d) showed the values were proportional to  $\tau$  in all temperatures, indicated that biomass conversion under hydrolysis and dehydration can be described by this reaction-rate model. Further, the Arrhenius' plots for overall conversion values of three reactions are shown in Figure-5, Activation energies and pre-exponential frequency factors are obtained from the slopes of each curve in Figure-5.



**Figure-5.** Overall Arrhenius plots of the rate constant of conversion on hydrothermal carbonization of sugarcane bagasse ( $k$ ) in hot-compressed water based on the shrinking-core (or grain) model.

Based on Figure-5., the activation energies for hydrolysis and dehydration reactions are 88.1 and 129. 4, respectively. While, the pre-exponential frequency factors are  $1.6 \times 10^7$  and  $2.9 \times 10^9$ , respectively. The results



suggested that the energy activation for dehydration is the highest than other reactions. Further, the validation of the activation energy and frequency factor was conducted, which were listed in Table-1. This result suggested that the validity of proposed model for calculation rate of conversion of sugarcane bagasse under hydrothermal carbonization.

**Table-1.** The data of activation energies and frequency factors as obtained from literature study.

Reaction decomposition	Temperature (°C)	EA KJ/MOL Frequency factor ( $A_0$ )	Reference
Microcrystalline cellulose	290-400 $\leq 370$ $\geq 370$	145.9 kJ/mol 547.9 kJ/mol	Sasaki et al. (2004) [17]
Hemicellulose and cellulose from wood	225-300	76 152 and kJ/mol $2.48 \times 10^4$ and $1.1 \times 10^{10}$ kJ/mol	Prins et al. (2006) [23]
Hemicelluloses and cellulose from loblolly pine	200-260	30 and 73 kJ/mol	Reza et al. (2013) [24]

#### 4. CONCLUSIONS

The results of study showed that, the carbon yield of solid material denoted that most of carbon remained in the solid phase gradually decreased due to feedstock solubilization. The solubilization reflected that continuous decomposition of carbohydrate from hemicelluloses and cellulose due to hydrolysis reaction.

In this study the rate reaction based on mass loss of reactant which involves under hydrothermal carbonization has been measured. The examination based on kinetic conversion parameter explained that all of reactions involved on the hydrothermal carbonization of sugarcane bagasse particles mainly took place at their internal or inner pores particle surface. The calculation of kinetic reaction by using shrinking core model showed the reasonable validity of activation energies. The activation energy for both of reactions namely hydrolysis and dehydration are 88.1, and 129.4, And the pre-exponential frequency factors are  $1.6 \times 10^7$ , and  $2.9 \times 10^9$ , respectively.

The hydrolysis of sugarcane bagasse occurs at the temperature range 200-240°C and reaches its equilibrium at 270°C. Meanwhile, the dehydration reaction occurs in two stage reaction at temperature range 240-270°C and 270-300°C. In the first step the dehydration occurs in the temperature range 240-270°C due to dehydration of sugars from hemicelluloses and cellulose to furans and aldehyde compounds. While, at temperature range 270-300°C the dehydration reaction occurs due to decomposition of furans compound and lignin. The parameter kinetic showed at lower temperature conversion reaction rate of dehydration slower than hydrolysis reaction.

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