INTRODUCTION

Substitution of fossil fuel with renewable resources is triggered by decreasing of fossil fuel reserve [1,2]. Sugarcane, one kind of solid biomass, is potential renewable resources in Indonesia. Total production of Indonesian sugarcane was 33.7 million tons in 2014 [3]. As feed stock for sugar mill, sugarcane will produce primary product of sugar and byproducts such as sugarcane bagasse (24-30%), filter cake (3-4%), molasses (3-5%), and furnace ash (0.3%). Besides as raw material to produce white sugar, sugarcane also became a potential renewable resource of energy in the form of sugarcane-bagasse [4, 5, 6]. Conversion of biomass (i.e., sugarcane bagasse) will be a promising technology to substitute non-renewable fossil fuel with renewable biomass to produce energy and chemical platform. Sugarcane bagasse has great potential economic value when converted from direct combustion become source of bio-energy and biochemical. Increasing added-value of bagasse can be done with gasification process. Gasification has high thermal efficiency as compared to direct combustion [7]. Application of gasification of biomass is widely used as promising technology to convert biomass into syngas such as production of syngas from oil palm empty fruit bunches [8].

The main obstacle often encountered in gasification of biomass from agricultural products was bed agglomeration, and then caused defluidization of biomass, unplanned stop time and additional costs. Another factors which must be considered in the gasification of sugarcane bagasse are high moisture content, fiber content and its low density [6, 9].

Defluidization of agricultural biomass can be reduced by increasing quality of biomass, using treatment of torrefaction. This torrefaction process is a promising thermal pretreatment to increase quality of solid biomass into more homogeneous biomass products [10]. Torrefaction will improve the usability of biomass such as thermal gravimetric value, grindability and hydrophobic properties [11]. Thermal characteristics of biomass in torrefaction have important role in pretreatment of biomass before used as feedstock in gasification. Torrefaction defined by heating of biomass in wet or dry conditions at a certain temperature and time under atmospheric condition. Torrefaction at temperature of 200-300°C was conducted to reduce the moisture content and convert the characteristic of biomass from hygroscopic into hydrophobic biomass which will reduce its ability to bind water. Benefit of torrefaction is improvement of biomass quality, then it can be stored in the long term, increase efficiency, reduce transportation and storage costs, easy handling and improve the energy density [12].

Study about torrefaction have been made both in wet or dry condition. Effects of dry torrefaction on the...
gasification performance of switch grass have studied to increase yield and quality of syngas [13]. The result showed better yield of syngas and its quality as compared to without torrefaction. Dry torrefaction also showed a significant effect on Miscanthus x giganteus (MG) where the properties of MG increases. Dry torrefaction performed at a temperature of 230 to 290 °C for 10 to 30 minutes [14].

Biomass quality showed increasing after treated with dry torrefaction at temperature of 150-160 °C and time variation of 0 to 50 minutes. The result showed increasing heating value of biomass corresponds to increasing temperature of torrefaction [15]. Dry torrefaction also conducted in sugarcane bagasse under temperature of 150-300 °C for 1 hour. Torrefaction temperatures of 150 °C provide increasing sugarcane bagasse quality, fixed temperature of gasifier and better yield of syngas [16].

Improvement of agricultural biomass quality will improve process of biomass gasification. The gasification process is an integration of thermal and chemical energy into chemical energy of syngas. The syngas resulted from biomass gasification is prospective source of renewable energy and chemical platform. State of the art gasification technology still continues for improvement, especially based on partial combustion at temperatures above 1000 °C [17]. A study of biomass gasification conducted for methanol synthesis and the influence of biomass drying to energy balance. The efficiency of the system can be enhanced with an integrated drying process. The addition of H2 replace the WGS (water-gas-shift) has potential effect to increase methanol yield of 35% [18]. Gasification was approached using concept of four zones i.e., drying and pyrolysis, char gasification, volatile reforming, and hot catalytic-gas cleaning zones. In this study, clean and high quality syngas can be obtained at atmospheric pressure and temperatures below 1000°C. Tar can be minimized below 100 mg/Nm³ in the gasification process using hot cleaning gas catalyst-based char [19]. Effect of gasifier diameter on gasification also studied to obtain influence of ratio of fuel/air, increase the yield and quality of the syngas [20].

The mechanism of pyrolysis-gasification of biomass is conducted in four stages; drying process (50-150 °C), pyrolysis (above 160 °C), the oxidation reduction (1000-1200 °C) and reduction reaction (600-900 °C) [5]. The study of reaction mechanism and parameter of the gasification process will be continued to develop. Pyrolysis in the mechanism of pyrolysis-gasification is a thermochemical decomposition process of biomass in absence of oxygen. Biomass will have reaction of pyrolysis at temperatures above 160 °C. Volatile matters will be separated from dry biomass during the pyrolysis process. The main product of the pyrolysis process is carbon (C), hydrogen (H₂), carbon monoxide (CO), carbon dioxide (CO₂) and methane, tar and other hydrocarbons. Pyrolysis reaction is expressed in the following chemical equation:

\[
\text{C}_n\text{H}_x\text{O}_y \rightarrow n\text{C} + n_2\text{H}_2 + n_2\text{H}_2\text{O} + n\text{H}\text{CO} + n_6\text{CO}_2 + n_6\text{CH}_4 \tag{1}
\]

In this equation, Molecular formula CH₂O₃₂ is the nature of molecular formulas biomass, and n₁ to n₆ is a constant of reaction determined by state of gasification.

In the mechanism of pyrolysis-gasification sugarcane bagasse, model which used to determine reaction kinetic of pyrolysis have developed from lumped models. There are three models of pyrolysis reaction kinetic of cellulose that usually use in study of reaction kinetic of pyrolysis in the mechanism of pyrolysis-gasification of sugarcane bagasse[21].

The aim of this paper is to study experimental work of pyrolysis-gasification of sugarcane bagasse interpreted using model of one-step global single reaction to obtain reaction kinetics of pyrolysis in the mechanism of pyrolysis-gasification of sugarcane bagasse.

In this model, yield of product predicted based on reaction condition by assuming ratio of volatile matter and residue of bio-char. Decomposition of biomass based on equation of reaction below:

\[
\text{Biomass} \rightarrow \text{Char} + \text{Volatiles}
\]

\[
B \rightarrow C + VM \tag{2}
\]

Rate of pyrolysis depends on weight of unreacted biomass. Rate of biomass decomposition is approaching using equation 3 as follow:
\[
\frac{dm_B}{dt} = -k(m_B - m_C)^n
\]  
Biomass conversion defined with equation 4:
\[
X = \frac{m_B - m_C}{m_B - m_C}
\]
where:
- \( m_B \) = weight of biomass at certain time
- \( m_B_0 \) = weight of initial biomass
- \( m_C \) = weight of char until end of reaction
- \( n \) = reaction order, if \( n = 1 \), \( n = 1 \)
- \( k \) = constant of reaction \([\text{time}^{-1}]\)

Substitute equation 4 into 3 can be resulted an equation
\[
\frac{dX}{dt} = K (1-X)^n
\]

Where A is constant reaction of biomass conversion \([\text{time}^{-1}]\). While, weight of biomass and residual char can be weighed at the end of reaction and it will be able to determine equation of rate of reaction including constant of pyrolysis reaction of biomass. Thermogravimetric analysis by TG / DTA analyzer is a method that has been widely used to determine the reaction kinetics and equation of reaction in the mechanism pyrolysis-gasification of biomass.

Application of quantitative thermogravimetric analysis in pyrolysis-gasification was applied to determine reaction kinetic of steam gasification in many kind of wood charcoal [22]. Temperature of gasification set at 750-900 °C and steam pressure 0 and 0.27 bar. The ratio of potassium to silicon given positive effect on reaction kinetic. Thermogravimetric analysis used to measure the properties of BMF (biomass fuel micron) gasification in different concentration of oxygen [10]. Application of TGA analyzer was studied for non-isothermal mechanism and reaction kinetic of low sulfur coal and bagasse gasification using \( \text{CO}_2 \) gas as gasification agent [23]. Result of analysis showed gasification of bagasse will occur in two stages, the first stage released volatile matters (<500 °C). Then second stage occurs char gasification (>700 °C) while the low sulphur coal only has one stage gasification at temperature >800 °C.

Thermogravimetric analysis (TGA) conducted to determine the composition of the catalysts in hydrothermal catalytic reforming of lignin in aqueous alkaline medium. TGA was used to compare relatively weight change for fresh catalyst / spent Ru-N / AC and new AC at a heating rate of 5 °C/min in air flow at 150 mL/min [24]. TGA also used in research to determine reaction kinetic of char gasification of woody biomass from hydrothermal treatment. Reaction kinetic of char in steam gasification follow first order reaction kinetics. Steam gasification of char carried out at a temperature of 850 °C, with the ratio of steam to \( \text{N}_2 = 20/80 \) (v/v) and heat rate 30 °C/min [25].

In this study the kinetic of pyrolysis reaction in the mechanism pyrolysis-gasification of sugarcane bagasse is determined using thermogravimetric analysis (TGA) with TG / DTA analyzer. Reaction kinetic model will involve one-step single global reaction model.

**EXPERIMENTAL**

**Materials and preparation**

Sugarcane bagasse (SCB) obtained from PT Madubaru Sugar Mill, Jogjakarta, Indonesia. Before treating with dry-torrefaction, bagasse was sun dried for 8 hours until its moisture content in range 3-5%. Then SCB treated with dry torrefaction for 1 hour in temperature of 150 °C. Proximate and ultimate analysis of bagasse listed in Tables-1 and 2.

This study has two kind of samples; sun-dried SCB (SCB0) and dry-torrified SCB (SCBT). Before used in experimental, two samples grinded and pulverized and sieved with rota-sieve to make a uniform size of sample in range 0.2-0.3 mm.

**Thermogravimetric analysis procedures**

In this study the kinetic of pyrolysis reaction in mechanism pyrolysis-gasification of sugarcane bagasse determined using thermogravimetric analysis (TGA) with TG / DTA analyzer. Reaction kinetic model will use one-step single global reaction model.

Model of kinetic reaction of pyrolysis will performed for two biomass samples, SCB0 and SCBT. Both SCB0 and SCBT have pulverized and weighed accurately in 5 mg. \( \text{N}_2 \) gas was used as carrier gas in this experiment. The experimental procedures initiated with heating sample from ambient temperature to a temperature of 500 °C. In this pyrolysis, heating rate set in 10 °C/min and \( \text{N}_2 \) gas flow rate in 50 mL/min. Even temperature reaches 500 °C, temperature of analysis holded about 15 minutes to ensure pyrolysis reaction was complete.

*Table-1. Proximate analysis of fresh-SCB (SCBF), sun-dried SCB (SCB0) and torrified-SCB (SCBT).*

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fixed Carbon</td>
<td>7.0</td>
<td>13.51</td>
<td>14.27</td>
</tr>
<tr>
<td>2</td>
<td>Volatile Matters</td>
<td>42.5</td>
<td>71.25</td>
<td>71.66</td>
</tr>
<tr>
<td>3</td>
<td>Moisture</td>
<td>49</td>
<td>11.59</td>
<td>9.53</td>
</tr>
<tr>
<td>4</td>
<td>Ash</td>
<td>1.5</td>
<td>3.85</td>
<td>4.54</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

*Table-2. Ultimate analysis of fresh-SCB (SCBF), sun-dried SCB (SCB0) and torrified-SCB (SCBT).*

<table>
<thead>
<tr>
<th></th>
<th></th>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Carbon (C)</td>
<td>23.7</td>
<td>41.69</td>
<td>42.77</td>
</tr>
<tr>
<td>2</td>
<td>Hydrogen (H)</td>
<td>3.0</td>
<td>6.47</td>
<td>6.52</td>
</tr>
<tr>
<td>3</td>
<td>Oxygen (O)</td>
<td>22.3</td>
<td>47.66</td>
<td>45.9</td>
</tr>
<tr>
<td>4</td>
<td>Moisture (H2O)</td>
<td>49.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>Ash</td>
<td>1.5</td>
<td>3.85</td>
<td>45.4</td>
</tr>
<tr>
<td>6</td>
<td>Nitrogen (N)</td>
<td>0.29</td>
<td>0.28</td>
<td>0.23</td>
</tr>
<tr>
<td>7</td>
<td>Sulphur (S)</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>8</td>
<td>GCV (kcal/kg)</td>
<td>3.960</td>
<td>4.034</td>
<td></td>
</tr>
</tbody>
</table>
Syngas analysis procedures

Syngas which obtained from pyrolysis of SCBT is analyzed to determine the quality of syngas. Gas analysis carried out using GC Analysis in the Laboratory of Analysis and Instrumentation, Chemical Engineering Department, Gadjah Mada University, Yogyakarta, Indonesia.

Apparatus

Ro-tap®, Testing Sieve Shaker, Model B, Serial No. 3365. W.S.Teyler Inc. was used for screening of pulverized samples. Moisture test of samples measured using Moisture Analyzer, Phoenix Instrument BM– 65. Thermogravimetry Analysis conducted with TGA Analyzer, Diamond TG/DTA® Type, Perkin Elmer Instruments.

RESULTS AND DISCUSSIONS

Thermogravimetry analysis

DTA (Differential Thermal Analysis) and TGA (Thermogravimetric Analysis) are required to observe thermal properties and thermal decomposition of biomass, even TG / DTA can be used to obtain influence of cellulose and lignin in pyrolysis reaction. Result of TG analysis for pyrolysis both SCB0 and SCBT using N₂ gas is presented in Figure-1.

Figure-1 shows relationship between the weights of biomass (vertical axis) towards increasing temperature (horizontal axis). Figure-1 also shows weight loss of biomass during pyrolysis process both SCB0 and SCBT. From this figure, conversion of biomass or weight loss of biomass is divided into two steps. The first step is the stage of drying, it takes place at temperatures 20-260 °C. At this step, beside released H₂O, biomass also released light volatile matters. While, the second step is pyrolysis that began to occur at range of temperature 260-480 °C. At temperature above 480 °C, weight of biomass relatively constant because it has almost totally converts into char.

Figure-1 also gives information about pyrolysis step, that occurs into two zones: the first zone is called rapid pyrolysis in term of fast reducing of biomass weight occurs and the second zone is termed as slow pyrolysis, in which reducing of biomass weight find slow decline. This zone or rapid pyrolysis took place at a temperature of 260-340 °C, and the second zone or slow pyrolysis took place at 340-480 °C.

In biomass pyrolysis, rapid zone is caused by volatilization and decomposition of cellulose mass while slow zone triggered by the lignin decomposition. In zone of rapid pyrolysis, thermochemical decomposition of cellulose occured in a low and narrow temperature range. In zone of slow pyrolysis, lignin decomposition occurs at higher temperature and rate of lignin decomposition is lower than cellulose decomposition. A cellulose compound has structure of branched-chain polysaccharides and without aromatic compounds, so it easy decomposed. Lignin compounds consist of various -O- and C-C containing functional groups and aromatic structural units. This composition reflects that lignin is more stable with temperature than cellulose [26].

As shown in Figure-1, reaction of rapid pyrolysis of cellulose took place in temperature of 260-340 °C while lignin degraded completely at a temperature of 340-480 °C. At temperature above 480 °C, weight of biomass relatively constant. Final product of pyrolysis is char. Zone of pyrolysis determined by composition of biomass. Composition of sugar cane fiber consists of 40-58% cellulose, 24-32% hemicellulose, lignin 13-22% and 1- 4% of other compounds [6]. This composition was greatly affected on thermochemical reaction of pyrolsis SCB. From Figure-1 also shown thermochemical decomposition of SCBT and SCB0, thermal decomposition of SCBT is better than SCB0. This is indicated by residual char smaller than SCB0. Figure-1 also provides information related to an increase in quality after treated with dry-torrefaction. Dry-torrefaction also improves composition of lignin in SCBT, as shown by the slow zone of pyrolysis is wider than SCB0.

Above DTA curves represent correlation of heat flow to the temperature during pyrolysis of SCB0 and SCBT as shown in Figure-2. This figure shows endothermic and exothermic phases during pyrolysis. At an early stage, can be shown that pyrolysis process is an endothermic reaction that associated with thermal decomposition of cellulose depolymerisation and volatilization. Figure-2 shows the endothermic reaction of decomposition and volatilization SCB0 and SCBT more dominant than the exothermic reaction of polymerization and aromatization lignin. Large endothermic peak as SCB0, indicating depolymerization reactions and volatilization more dominant than the exothermic reaction [27].

Figure-1. TG curves of SCB0 and SCBT during pyrolysis in N₂ atmosphere at the heating rate 10°C/min.
Lowest endothermic peak occurred at a temperature of 328 °C for SCB0 while SCBT only at the beginning of the reaction. At temperature of 328 °C, SCB0 require heat for decomposition of cellulose. On the other hand at same temperature, SCBT decompose lignin. SCBT has exothermic peak in temperature of 351 °C and 450.7 °C. DTA curve of SCB0 also provides information that endothermic reaction more dominant than exothermic reaction during the process of pyrolysis of SCB0. It means decomposition of cellulose is more dominant than the decomposition of lignin.

DTA curve of SCBT shows endothermic reaction required only at beginning of pyrolysis process. Decomposition of lignin is more dominant than the decomposition of cellulose. This figure also shows an increase in the quality of SCB after dry-torrefaction.

Figure-3 shows relationship between conversion rate per unit time of biomass (dX / dt) to temperature changes. For SCBT, cellulose conversion in fast pyrolysis zone occurs at a temperature of 242 °C to 331 °C temperature. After this zone, rate of pyrolysis decreased sharply and then get into zone of slow pyrolysis of lignin which contained in SCBT. Value of dX / dt for SCB0 lower than SCBT on fast pyrolysis zone, whereas slow pyrolysis zone value dX / dt is relatively not different.

Kinetic of pyrolysis reaction

Solving equation (5) will provide information about equation rate of pyrolysis reaction stage in pyrolysis-gasification mechanism SCB both SCB0 and SCBT. Determination of reaction rate constants is proposed by modification of equation (5) becomes:

\[-\ln(dX/dt) = - \ln (k) – n\ln(1-X)\]  \hspace{1cm} (6)

Solving this equation is approached using linear equation:

\[Y=aX+b\]  \hspace{1cm} (7)

where:

- \[Y=-\ln(dX/dt)\];
- \[X=-\ln(1-X)\];
- \[a=\text{order of reaction,}\]
- \[b=-\ln(k)\].

Modification of TG / DTA data was adjusted to confirm with equations 6 and 7, it obtained Figure 4 as development of Figure-1.

Figure-4 shows relationship between conversion rate per unit time of biomass (dX / dt) to temperature changes. For SCB0, cellulose conversion in fast pyrolysis zone occurs at a temperature of 242 °C to 331 °C temperature. After this zone, rate of pyrolysis decreased sharply and then get into zone of slow pyrolysis of lignin which contained in SCB0. Value of dX / dt for SCB0 lower than SCBT on fast pyrolysis zone, whereas slow pyrolysis zone value dX / dt is relatively not different.

The vertical axis shows rate of conversion of biomass per unit time in the pyrolysis zone of temperature 260-480 °C. Figure-4 also shows two equations of reaction kinetic, i.e., reaction kinetics equation for fast and slow pyrolysis zones. Determination of reaction kinetic equations was done by smoothing curve in Figure-4, by eliminating transition curve before and after rapid pyrolysis.

From smoothing Figure-4 resulting in Figure-5 which shows curve in straight line of equation 7.
Based on an analysis, TG/DTA data can be obtained reaction kinetic equations of pyrolysis SCB0 and SCBT after confirmed with equation 5, as shown in Table-3.

Table 3. Reaction kinetic parameter.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Zone</th>
<th>K [sec^{-1}]</th>
<th>n [order]</th>
<th>Range of Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCB0</td>
<td>Rapid Pyrolysis</td>
<td>15.348</td>
<td>5.245</td>
<td>260-340°C</td>
</tr>
<tr>
<td></td>
<td>Slow Pyrolysis</td>
<td>0.065</td>
<td>0.356</td>
<td>340-480°C</td>
</tr>
<tr>
<td>SCBT</td>
<td>Rapid Pyrolysis</td>
<td>17.167</td>
<td>5.040</td>
<td>260-340°C</td>
</tr>
<tr>
<td></td>
<td>Slow Pyrolysis</td>
<td>0.145</td>
<td>0.553</td>
<td>340-480°C</td>
</tr>
</tbody>
</table>

A laboratory scale of pyrolysis is conducted to obtain syngas quality from pyrolysis of SCBT. Composition of syngas as shown in Table-4.

Table 4. Composition of resulted syngas.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CH₄, %</th>
<th>H₂, %</th>
<th>CO₂, %</th>
<th>CO₂, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCBT</td>
<td>4.95</td>
<td>4.43</td>
<td>27.0</td>
<td>19.8</td>
</tr>
<tr>
<td>SCBF (25)</td>
<td>2.2-6.7</td>
<td>1.1-2.4</td>
<td>28.6-31.8</td>
<td>48.2-56</td>
</tr>
</tbody>
</table>

Resulted syngas of SCBT is compared with syngas which produced from laboratory pyrolysis of sun-dried SCB (moisture content 6-8 wt.%) and its pressure was kept below 8 kPa [28]. From this table, torrefaction of SCB will significantly increase syngas quality.

CONCLUSIONS

Pyrolysis step is an important step in the mechanism of pyrolysis – gasification of biomass. Based on TG/DTA analysis, rate of pyrolysis reaction is influenced by the composition of biomass i.e., composition hemicellulose, cellulose and lignin in biomass.

From this study, it has found two steps of pyrolysis in sugarcane bagasse, equations of reaction pyrolysis in rapid zone of pyrolysis and slow zone of pyrolysis. While torrefaction of SCB gives better thermal decomposition than SCB0. And increasing composition of lignin in SCB, reducing endothermic phase of cellulose decomposition and increasing exothermic phase of lignin decomposition.

Torrefaction of SCB also gives better kinetic reaction of pyrolysis than SCB0 which stated in constant of reaction and order of reaction of pyrolysis.

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