Effect of activated carbon catalyst on the cracking of biomass molecules into light hydrocarbons in biomass pyrolysis

Teguh Suprianto¹²*, Winarto¹, Widya Wijayanti¹, ING Wardana¹
1 Mechanical Engineering Department, Brawijaya University
MT Haryono 167, Lowokwaru, Malang 65145, Indonesia
2 Mechanical Engineering Department, Politeknik Negeri Banjarmasin
Brigjen Hasan Basri Komplek Unlamp, Banjarmasin, Indonesia
*Email: teguh.suprianto@poliban.ac.id

Abstract. Syngas which is rich in methane and hydrogen gas can be produced through the biomass pyrolysis process. This study uses an activated carbon (AC) catalyst in the pyrolysis process using a fixed bed reactor. The result showed that using AC reduces the temperature of methane production from 395 °C to 380 °C and increases CH₄ production from 202.800 ppm to 223.500 ppm. The increase in the production and decrease in temperature of light hydrocarbon formation occurs due to the influence of properties of the aromatic ring on the activated carbon surface. The presence of aromatic rings causes electrostatic forces so that influences atomic bond in structure biomass molecule. From simulations that have been carried out using Avogadro Software, it shows that the length of C-C bonds increases and this means the bonds become weaker. This condition triggers the accelerating process of cracking hydrocarbon molecules and produces lighter hydrocarbon gas.

Keywords: pyrolysis, activated carbon, biomass, methane.

1. Introduction

Oil reserves are decreasing rapidly due to the increased need for oil for transportation and industry [1]. One of the potential energy alternatives is biomass. Biomass is a sustainable, renewable energy source, and carbon-neutral fuel [2]. Through the pyrolysis process, biomass can be converted into syngas rich in H₂, CO, CH₄, and CO₂ gas. Pyrolysis is the process of thermal degradation of biomass without oxygen to produce solids, liquids, and gas fuels. The results of pyrolysis depend on the operating conditions and reactor configuration. Syngas produced from the pyrolysis process can be used as an alternative fuel for internal combustion engines.

Biomass has the main content in the form of cellulose, hemicellulose, and lignin. The actual reaction scheme of the pyrolysis of wood is very complex because of the formation of more than one hundred types of intermediate products [3]. During the pyrolysis process, biomass decomposes into gas in the form of oxygenated hydrocarbons, nonoxygenated hydrocarbons, and char (eq. 1) [4]
The pyrolysis gases continue to react until a new equilibrium occurs. As long as the molecule still receives enough energy to react, the hydrocarbon molecule from biomass decomposition will be degraded again into a lighter molecule. Oxygenated hydrocarbons and non-oxygenated hydrocarbons crack into permanent gases and lighter molecules (eq. 2).

Using the right catalyst can increase gas yield, reduce tar content, and increase energy efficiency. Many types of catalysts have been tested in recent experiments, especially for biomass pyrolysis and gasification, such as HZSM-5, dolomite, zeolite, alkali metal salts, Ni-based catalysts, and their derivatives [5]. Catalysts from metal can increase hydrogen production [6], but metal catalysts rapidly increase deactivation due to the buildup of carbon layers during the hydrocarbon decomposition process [7]. In addition, this catalyst is relatively more expensive and can cause pollution after use.

One of the potential non-metal catalysts is activated carbon. Activated carbon as a nonmetallic catalyst has been shown to increase reaction and is environmentally friendly. Activated carbon consists of graphite and graphene composition. The carbon structure in graphite and graphene has an activity that can function as a catalyst [8]. The use of activated carbon as a catalyst has been widely used. Activated carbon can increase the process of decomposition of tar into a gas [9] and decomposition of plastic into jet fuel [10]. Activated carbon shows a higher activity in methane decomposition compared to active alumina. Besides being used directly, activated carbon is also used as a supported catalyst for other catalysts, especially metal catalysts [11].

Activated carbon has a large surface area. This surface area affects reactivity as a catalyst. Several studies have shown that reactivity of activated carbon is determined by the area [12]. Not only the area, functional group, composition, and chemical structure of activated carbon greatly affect the nature and reactivity of activated carbon. Graphene, as part of activated carbon, is sp² hybridized carbon-based material in the form of a hexagonal network (benzene ring). The surface of activated carbon has an aromatic structure. The aromatic structure of graphite has strong diamagnetic susceptibility [13]. The magnetic properties of aromatic compounds originate from the cyclically conjugated π system [14].

Many studies have discussed the use of activated carbon as a catalyst in the decomposition process, but as far as we know there has been no discussion about how bonds of atoms in a hydrocarbon molecule when it passes through the surface of activated carbon. Therefore, this paper will discuss how the effect of activated carbon on the cracking of hydrocarbons (biomass) into lighter molecules and their effects on the bonding of atoms making up hydrocarbon molecules in the pyrolysis process.

2. Material and method
The material used in this study was biomass from coconut wood sawdust (Cocos nucifera L) and its composition is presented in Table 1. Sawdust was dried until the moisture content is 5%. Sawdust is then filtered with a mesh size of 40. Activated carbon is used as a catalyst. Pyrolysis reactor made of stainless steel with a diameter of 10 cm and height of 15 cm. 10 grams of biomass is placed in the middle of the reactor in an aluminium container. The activated carbon catalyst is placed on the biomass such that volatile gases from pyrolysis vapor pass through activated carbon. The heat is supplied to the reactor using LPG gas with heating rate 50 °C min⁻¹. The gas produced from the pyrolysis reactor is flowed through a 5 mm copper pipe into the ice bath for cooling and condensation of water vapor. A K-type thermocouple installed just above the surface of the
biomass to measure the temperature of the decomposition process. The MQ-6 methane gas sensor is mounted on the gas outlet to measure the concentration of methane production. Arduino Uno set is used as an interface to input temperature and methane concentration data into the computer. The experiment scheme is presented in Figure 1.

Table 1. Chemical content of coconut wood [15]

| Components     | content (%) |
|----------------|-------------|
| Lignin         | 30.99       |
| Cellulose      | 31.95       |
| Hemicellulose  | 35.09       |
| Ash content    | 1.97        |

Figure 1. Experiment setup pyrolysis of biomass

Simulations using Avogadro Version 1.2.0 have been carried out to demonstrate the effect of activated carbon on the biomass atomic bond structure. Avogadro is an open-source molecular builder and visualization tool. In the simulation, a hydrocarbon molecule was placed between aromatic molecules as a representation of the surface of activated carbon. The bond length of atoms in hydrocarbon molecule is measured before and after exposure to the surface of activated carbon. Changes in the bond length are then analyzed to identify their effects on the decomposition process.

3. Results analysis and discussion

3.1 Experiment results analysis

From the experiments conducted obtained results as in Figures 2, 3 and 4. Figure 2 shows that by using an activated carbon catalyst there is a decrease in the temperature of methane formation. Methane gas has begun to form at a temperature of 380 °C whereas without a catalyst of 395 °C. This shows that the use of activated carbon catalysts reduces the energy needed to decompose biomass molecules into light hydrocarbons. Figure 3 shows that the level of CH₄ production is
higher when using activated carbon. CH$_4$ concentration without activated carbon was 202,800 ppm and increased to 223,500 ppm. This shows that the biomass molecule is split into lighter hydrocarbons in greater numbers. Figure 4 shows that the peak of methane production using AC occurs at a temperature of 385 °C whereas without AC occurs at 410 °C. This shows that there has been an acceleration in production of methane in lower temperature by using an AC catalyst.

**Figure 2.** Effect of use of activated carbon (AC) on the formation temperature of methane gas

**Figure 3.** The use of Activated Carbon increases methane gas production
3.2 Simulation results analysis

In this simulation the C₆H₁₂O₆ hydrocarbon molecule is placed between two aromatic surfaces (Figure 5). This condition illustrates when hydrocarbon molecules pass through pores in activated carbon. Table 2 shows the change in the bond length of the cellulose atoms when placed between the aromatic molecules. C-C bonds have increased length while C-H, CO and OH bonds have decreased. In chemical bonds the closer the distance between atoms, the stronger the bond and the farther the distance between atoms, the weaker the atomic bond. This proves that when the cellulose molecule is close to the surface of activated carbon there is a weakening of the C-C bond. The distance of the C-C bond is in line with the results of graph 1 which shows that cracking occurs faster when there is the use of activated carbon as a catalyst. The faster cracking process shows that breaking the C-C bond is easier when using activated carbon as a catalyst. The average bond lengths of C-C, O-H and C-O atoms are presented in Table 3.

Figure 4. Effect of AC catalysts on the rate of CH₄ production

Figure 5. Cellulose molecules closer to aromatic molecules
Table 2. Properties of atomic bonds in cellulose molecules when exposed to aromatic molecules

| Bond Type | Bond length without aromatic (Å) | Bond length with aromatic (Å) | Difference (Å) |
|-----------|----------------------------------|------------------------------|----------------|
| Bond 1    | C-C                              | 1.53584                      | 1.53539        | -0.00045 |
| Bond 2    | C-C                              | 1.54688                      | 1.54531        | -0.00157 |
| Bond 3    | C-C                              | 1.55272                      | 1.55345        | 0.00073  |
| Bond 4    | C-C                              | 1.54847                      | 1.55429        | 0.00582  |
| Bond 5    | C-C                              | 1.50585                      | 1.51295        | 0.0071   |
| Bond 6    | C-O                              | 1.40076                      | 1.40061        | -0.00015 |
| Bond 7    | C-O                              | 1.40608                      | 1.40502        | -0.00106 |
| Bond 8    | C-O                              | 1.40755                      | 1.40806        | 0.00051  |
| Bond 9    | C-O                              | 1.4077                       | 1.40643        | -0.00127 |
| Bond 10   | C-O                              | 1.22134                      | 1.22115        | -0.00019 |
| Bond 11   | C-O                              | 1.40825                      | 1.4073         | -0.00095 |
| Bond 12   | C-H                              | 1.11352                      | 1.11409        | 0.00057  |
| Bond 13   | C-H                              | 1.11265                      | 1.11259        | -6E-05   |
| Bond 14   | C-H                              | 1.11649                      | 1.11578        | -0.00071 |
| Bond 15   | C-H                              | 1.11785                      | 1.11741        | -0.00044 |
| Bond 16   | C-H                              | 1.11643                      | 1.11048        | -0.00595 |
| Bond 17   | C-H                              | 1.08541                      | 1.08514        | -0.00027 |
| Bond 18   | C-H                              | 1.11253                      | 1.11166        | -0.00087 |
| Bond 19   | O-H                              | 0.992447                     | 0.992448       | 1E-06    |
| Bond 20   | O-H                              | 0.992867                     | 0.992756       | -0.00011 |
| Bond 21   | O-H                              | 0.992871                     | 0.992769       | -0.0001  |
| Bond 22   | O-H                              | 0.992857                     | 0.992815       | -4.2E-05 |
| Bond 23   | O-H                              | 0.992797                     | 0.99294        | 0.000143 |
| Bond 24   | O-H                              | 0.992167                     | 0.990149       | -0.00202 |

Table 3. Changes in bond length before and after exposure to aromatic structures

| Type of Bonding | Bond length without aromatic (Å) | Bond length with aromatic (Å) | Change (Å) |
|----------------|----------------------------------|------------------------------|------------|
| C-C            | 1.53795                          | 1.540278                     | 0.01163    |
| C-O            | 1.37528                          | 1.374762                     | -0.00311   |
| C-H            | 1.11069                          | 1.109593                     | -0.00110   |
| O-H            | 0.99266                          | 0.992313                     | -0.00213   |

4. Discussion
The pyrolysis process cracking biomass molecules into gas and volatiles. Hemicellulose decomposition occurs at 220-315 °C. Cellulose decomposition is focused at a higher temperature range of 315-400 °C while lignin is the most difficult to decompose of 300 - 900 °C. Activated carbon has a graphene layer consisting of a combined C sp³ bond. This bond forms an aromatic ring that has a magnetic field and cause the electrostatic force on the graphene surface. When the electrostatic force meets another molecule that has a positive dipole moment, this affects the dipole moment. The hydrocarbon molecule from pyrolysis process, CᵡHᵢₒᵢ, which is volatile is close
to the graphen surface with a strong electrostatic force, atoms which have a positive dipole induced. This induction causes changes in the distance between atoms. The longer distance between C-C atoms causes the bonds to weaken thus accelerating the cracking of heavy hydrocarbons to light hydrocarbon gas. Other studies have also shown changes in polarity on the surface of cellulose which cause changes hydrogen atoms in the hydrocarbon structure and cause it to become more reactive [16].

5. Conclusion
Pyrolysis of biomass with activated carbon catalyst to produce syngas gas was carried out in this study. Activated carbon as catalyst increase the concentration of methane gas produced. Concentration of methane gas without catalyst was 202.80 ppm and increased to 223.50 ppm with AC. In addition, increases in methane concentration occur at lower temperatures. With AC catalyst, the methane concentration rises when it reaches 380 °C while it is without AC at 395 °C. This proved that activated carbon decreases the hydrocarbon cracking energy. The presence of aromatic rings on the graphene sheets cause electrostatic forces on the surface of the graphene so that it accelerates cracking hydrocarbon molecules and produce lighter hydrocarbon.

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