The influence of composition and final pyrolysis temperature variations on global kinetics of combustion of segregated municipal solid waste

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Abstract. The combustion of segregated municipal solid waste (MSW) and the resulted char from the pyrolysis process were investigated in this research. The segregated MSW that was collected and used can be divided into organic and inorganic waste materials. The organic materials were bamboo and banana leaves and the inorganic materials were Styrofoam and snack wrappings. The composition ratio of the waste was based on the percentage of weight of each sample. The thermal behaviour of the segregated MSW was investigated by thermo gravimetric analysis. For the pyrolysis process the prepared samples of 200gram were heated from ambient temperature until a variance of final pyrolysis temperature of 550°C, 650°C and 750°C at a constant heating rate of 25°C/min. It was found that the highest activation energy of the raw materials is achieved from sample CC1 (Char with 100% inorganic materials). The activation energy of the raw materials is relatively lower than that of the char. The higher the final pyrolysis temperature, the lower the calorific value of char. The calorific value gradually increases with the amount of inorganic materials.

1. Introduction
An increasing world population with new developments in technology and economy increases the demand in resources such as food and other living essentials. These developments result in an increase in the amount of waste that is being produced. USEPA defines solid waste as any garbage, refuse, sludge from a wastewater treatment plant, water supply treatment plant, or air pollution control facility, and other discarded material, including solid, liquid, semisolid, or contained gaseous material, resulting from industrial, commercial, mining, and agricultural operations and from community activities [1,2]. In the city Surakarta, often called Solo the growing economy is also noticeable. This is a city in Central Java, Indonesia with a total population around 588.110 people (in 2011) with an average density of 13.354 people/km². According to the Department of Sanitation in Surakarta the waste generation in Surakarta has been estimated at around 250 tons/day.
In the last decade adopting new renewable energy resources have increased although it will take a lot more years to decrease the dependency of the use of fossil fuels. Turning MSW into a renewable energy source can be a beneficial solution for both decreasing the amount of waste and for creating a new energy source.

Biomass is any type of organic material that is available on a renewable or reoccurring basis, and includes such things as agricultural crops and waste, wood and wood wastes, animal wastes, aquatic plants, and organic fractions of municipal and industrial waste \[3,4\]. Depending on the operating condition, pyrolysis can be classified into three main categories: conventional, fast and flash pyrolysis.

Combustion of biomass or waste in combination with a base fuel is a simple and economically way to replace fossil fuels by biomass and to utilize waste. The burning characteristics of biomass may vary considerably depending on the composition of the raw material used \[5,6\].

The kinetics of the In this research the global kinetics of combustion of municipal solid waste (MSW) is being studied to have a better understanding of the thermal degradation of MSW. Segregated MSW that has no economic value yet on the market is used in this research and have been collected from the TPA. The original condition of the selected samples of waste is that it already has been mixed with other MSW. The composition of the segregated MSW can be divided into two main groups: organic and inorganic MSW.

Combustion characteristics are influenced by different factors. In this research the composition and the final pyrolysis temperature will be varied in order to identify the influences on the global kinetics. The problem statement in this research can be formulated into two questions: The variations of the composition of waste influence the global kinetics on combustion of segregated MSW ; The variations of the final pyrolysis temperature influence the global kinetics on combustion of segregated MSW.

2. Research Methods

The equipment used in this study consists of test pyrolysis equipment, combustion equipment, supporting equipment and measuring equipment.

2.1. Characteristics of slow pyrolysis equipment:
The slow pyrolysis equipment is a model fixed bed that is equipped with a thermo controller that goes until 1000 °C

2.2. Characteristics of combustion equipment:
The combustion equipment is in the form of a cylindrical tube with a diameter of 96 mm that is getting heat from the coil heating element with heat settings up to 1000°C using a thermo-controller.

2.3. Supporting equipment:
2.3.1. Crusher equipment
This tool is used to cut the materials into a size of 20 mesh. This smoothing tool type disk mill is powered with 1 HP that rotates the inside blade. After the material has been cut, it is sieved with an output of a size of 20 mesh.

2.3.2. Measuring equipment are a digital scale with an accuracy of 0,01gram, thermocontroller and thermocouple type-K.

2.3.3. Analyzing equipment
The Thermogravimetric Analyzer (TGA) is an essential laboratory tool used for material characterization. Thermogravimetric Analysis is a technique in which the mass of a substance is monitored as a function of temperature or time as the sample specimen is subjected to a controlled
temperature program in a controlled atmosphere. In other words, TGA is a technique in which, upon heating a material, its weight increases or decreases.

2.3.4. Software
The software that is being used to record the data is WinCT that records the mass change and Adam.NET utility records the data temperature. In the program WinCT the Rs Key is included. The Rs Key is a program that is used to record data scales during the pyrolysis and combustion process. The obtained data is stored in MS Excel format that subsequently will be process into a graph.

2.4. Sample of the research
The materials that will be used in this research are segregated municipal solid waste collected in Surakarta, Central Java, Indonesia. These waste are mainly waste that are not being collected by the waste collectors or have no value for them. The beginning weights of the samples are each 20 grams. The organic materials that are being used are banana leaves and bamboo. The inorganic materials are styrofoam and snack wrappings.

3. Result and Discussion
3.1. TGA Analysis
The combustion process of the raw MSW materials in this research is accordance to the theory of solid fuels [7,8] where there are 3 physical stages that can be identified that includes drying, devolatilization and the stage of char combustion where then ash will be left over. The drying stage can be characterized by the slow mass losses in the beginning. The burning profile of the samples can be divided into 4 different temperatures points. The first is the volatile matter initial temperature (ITVM) where the mass starts to decrease. The second is the fixed carbon initial temperature (ITFC) when the rate of the mass loss accelerates due to the onset of the char combustion. The third is the peak temperature (PT) when the rate of the mass loss has reached a maximum value. The last important point is the burn out temperature (BT) when the mass becomes constant at the completion of burning. The ITVM, ITFC, PT.

The fluctuations in the temperature in the samples can be caused by a restricted airflow into the inside of the samples; the ash covers the sample.

The combustion profiles of 0%, 10%, 20%, 70% and 100% organic materials are given below in the form of graphics. In the combustion of char, the boundary of the combustion stages where unclear so that the ITVM cannot be identified of sample CC10, CC11, CC12 and CC21 (see graphs in Appendix 1). The BT stage of sample CC13, CC14, CC15, CC21 and CC24 could also not be identified. The BT could not be identified for these samples due to incomplete combustion. Inorganic materials tend to cover the organic materials during combustion. The samples should be mixed thoroughly to get even layers for a complete combustion process.

Comparing these results to a previous research done by Himawanto et. al in 2013, the ITFC, PT and BT are relatively similar while the ITVM differs with more than 100°C. A possibility of this difference can be the moisture content of the organic material of this research is lower than that [9]. The combustibles of a solid fuel are volatile matter and fixed carbon. In the combustion of char, it was shown that the drying zones occurred in a shorter time than the combustion of raw materials and the ITVM occurred relatively above 100°C. The fluctuations in the remaining mass may be caused by the layer of ash covering the sample inhibited the diffusion of oxygen into the sample and the combustion gases out of the sample. In the raw materials the PT was higher than that of the char combustion. ITFC of all the samples are relatively the same within the temperature range 200-400°C.
Figure 1. Combustion profile of raw materials.

At the point that intersects the line drawn parallel to the gradient of the dots until you get to the point of zero mass fraction values decline. From that point again draw a straight line down to cross the x axis.

For the combustion of raw materials MSW the decomposition zone was easier to analyze than that of the char MSW. Taking the pyrolysis reactions into account, the degradation reaction was accompanied by the release of water, gaseous products and eventual formation of char. With the presence of oxygen the char residues underwent ignition during the combustion reaction resulting in an appearance of the second decomposition zone.

For 20%, 50% and 90% organic materials the Tonset gradually decreases with the final pyrolysis temperature variation. For 90% organic materials the Tonset, h combustion, the weight loss of cellulose (Tshoulder) started at higher temperature and finished at lower temperature. This behavior is attributed to the fact that the cellulose composes of only one simple repeating unit, cellubiose. Therefore, cellulose decomposes through a rapid depolymerization process by cleavage of glycosidic bonds during the combustion process. Tshoulder is relatively the same for all this composition with different final pyrolysis temperature. The Toffset is the highest for the sample with the highest final pyrolysis temperature (CC24). The fluctuations in the decomposition of char graphs can be explained by the amount of oxygen that is still available at which point the char residues underwent ignition. The decomposition of hemicellulose started at a higher temperature for the combustion of the raw materials than that of the combustion of char MSW. The breakdown of cellulose also started at a higher temperature and finished at a lower temperature for the combustion of char MSW.

It takes more energy to burn the maximum amount of MSW (Tpeak- maximum mass loss) in the samples with a higher amount of inorganic material than in the raw waste material samples. The Toffset temperatures are lower than the Tpeak of all the samples with an exception of a few. A higher peak temperature indicates that the sample reacts slower. Identifying the devolutilization zones in the combustion process were more difficult due to the influences of oxygen and the surrounding air that fluctuate the combustion process.

3.2. Activation Energy

The activation energy indicates the amount of energy where the sample can be burned or ignited at which point a chemical reaction starts. The higher the activation energy, the more difficult the char is ignited. The highest activation energy is achieved from sample CC1 (Char MSW with 100% inorganic materials). The activation energy is the lowest with 100% organic materials. The activation energy of the raw waste materials is all under 130kJ/mol. The highest activation energy of the raw materials is 130,3kJ/mol (20% organic) and the lowest is 45,59kJ/mol (10% organic).
The highest activation energy of char with a final pyrolysis temperature of 550°C is 643.36 kJ/mol (0% organic) followed by 225.35 kJ/mol (30% organic). The highest activation energy of char with a final pyrolysis temperature of 650°C is 288.81 kJ/mol (90% organic) followed by 238.44 kJ/mol (30% organic). The highest activation energy of char with a final pyrolysis temperature of 750°C is 155.56 kJ/mol (10% organic) followed by 121.8 kJ/mol (50% organic). According to these results, the higher the final pyrolysis temperature, the lower the activation energy will be.

3.3. Calorific Value Analysis
The calorific value of inorganic raw materials (snack wrappings and styrofoam) is higher than that of organic raw materials (banana leaves and bamboo). The char MSW with the composition of 100% inorganic materials has also the highest calorific value. The composition of 70% organic and 30% inorganic raw materials, which composes the rough calculation of the MSW composition in Surakarta, has a calorific value of 21.49 MJ/kg (final pyrolysis temperature of 550°C), 19.55 MJ/kg (final pyrolysis temperature of 650°C) and 18.46 MJ/kg (final pyrolysis temperature of 750°C) [11]. All mixed compositions reaches the minimum calorific value similar of conventional biomass. The samples that underwent a higher final pyrolysis temperature have lower calorific values. A higher calorific value is obtained at a final pyrolysis temperature of 550°C. The higher the final pyrolysis temperature, the lower the calorific value of char MSW. The calorific value gradually increases with the amount of inorganic materials.

4. Conclusions
The variation in composition of MSW influences the global kinetics on combustion of segregated MSW. The highest activation energy is achieved from sample CC1 (Char MSW with 100% inorganic materials) and the lowest with 100% organic materials. The activation energy of the raw materials is relatively lower than that of the char. The higher the final pyrolysis temperature, the lower the activation energy of the char is.

The combustion process of the raw MSW materials in this research is accordance to the theory of solid fuels where there are 3 physical stages that can be identified that includes drying, devolatilization and the stage of char combustion where then ash will be left over. The burning stage can be characterized by the slow mass losses in the beginning. The burning profile of the samples can be divided into 4 different temperatures points: ITVM, ITFC, PT and BT. In the combustion of char MSW the drying zones occurred in a short time. The fluctuations in the remaining mass may be caused by the layer of ash covering the sample inhibited the diffusion of oxygen into the sample and the combustion gases out of the sample. The decomposition of hemicellulose started at a higher temperature for the combustion of the raw materials than that of the combustion of char MSW. The
breakdown of cellulose also started at a higher temperature and finished at a lower temperature for the combustion of char MSW.

It takes more energy to burn the maximum amount of MSW (T peak maximum mass loss) in the samples with a higher amount of inorganic material in the raw waste material samples. The higher the final pyrolysis temperature, the lower the calorific value of char MSW. The calorific value gradually increases with the amount of inorganic materials.

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