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Characterization and Utilization of Char Derived from Fast Pyrolysis of Plastic Wastes

Jindaporn Jamradloedluk^{a,*}, Chaloenporn Lertsatitthanakorn^b

^aFactulty of Engineering, Mahasarakham University, Khamriang, Kantarawichai, Maha Sarakham, Thailand 44150 ^bSchool of Energy, Environment and Materials, 126 Pracha Uthit Rd., Bang Mod, Thung Khru, Bangkok 10140, Thailand

Abstract

HDPE plastic wastes were fast pyrolyzed at temperature of 400-450°C and char (solid residues) obtained were collected and analyzed. Proximate and ultimate analyses showed that pyrolysis char had a large amount of volatile matter (51.40%) and fixed carbon (46.03%), small amount of moisture (2.41%) and little amount of ash (0.16%). Contents of carbon, hydrogen and nitrogen were found to be 42.65, 3.06, 0.43%, and 1.80%, respectively. Calorific value and density of the char were also determined and reported as 4,500 cal/g and 1.59 g/cm³, respectively. Char derived from the fast pyrolysis of HDPE plastic wastes was crushed into powder and extruded to produce briquettes. One kilogram of the char based briquette was used as a fuel for the combustion process (boiling water). Atmospheric-pressure thermal activation at 900°C for 3 hours was performed to promote surface area and specific pore volume of the char. Undergoing such an activation process, BET surface area and pore volume of the char were increased by 55% and 44% whereas pore size was reduced by 5%, corresponding to the values of 16.77 m²/g, 0.2080 cm³/g and 496°A, respectively.

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1. Introduction

Various outstanding packages have been recently designed to meet the requirement of customers. However, these packages are finally the packaging wastes. Pollution Control Department, Ministry of Natural Resources and

^{*} Corresponding author. Tel.: +66-4375-4316; fax: +66-4375-4316. *E-mail address:* jindaporn.msu@gmail.com

Environment, Thailand reported that in 2011, 2.78 million tons (18.27%) of plastic wastes were found from the total wastes collected. Most of plastic wastes in the municipal solid wastes are high density polyethylene (HDPE), low density polyethylene (LDPE), and polypropylene (PP) corresponding to 39.54%, 29.20%, and 16.10% of the total plastic wastes, respectively. Plastic wastes are unsystematically separated and this makes the plastic wastes recycling difficult, resulting in the low percentage (26%) of plastic recycling [1]. To propose alternative methods for plastic waste disposal, management, and value adding, a large number of research works have been extensively conducted. Fast pyrolysis is one of the processes used to covert plastic waste to different types of fuels.

Fast pyrolysis is a thermo-chemical process in the absence of oxygen to decompose large molecules of biomass and polymer [2]. Products obtained from fast pyrolysis can be divided into 3 categories; oil, gas, and char. Yield and properties of the products depends upon type and size of the raw materials, type of reactor [3] and operating conditions (temperature, pressure, heating rate, time, and type and amount of catalysts). Pyrolysis temperature was found to increase oil and gas yields and decrease char yield [2-6]. Different yield was found for different type of plastic used. During the past decades, much attention has been paid on oil and gas products obtained from fast pyrolysis. Although study on chars, a byproduct, is rather limited, influence of pyrolysis temperature on properties of char was investigated. Carbon content and surface area of char tended to be increased as increasing pyrolysis temperature [3, 4, 7]. It was mentioned that char can be used as a raw material for producing activated carbon and carbon nano-tube [8] and can be used as a fuel for combustion and gasification. As aforementioned that information of char derived from fast pyrolysis of waste, especially for the plastic waste is scarce. This work is therefore aimed at studying the properties of char derived from fast pyrolysis of waste, area of HDPE plastic wastes and using it as a raw material for producing briquette and activated carbon.

2. Materials and Methods

2.1. Raw Materials Preparation

HDPE plastic wastes were pyrolyzed in a pilot-scale free falling pyrolyzer at temperature of 400-450°C. After completion of the reaction, char (solid residue) at the bottom of the pyrolyzer was naturally cooled down to the ambient temperature and was kept for further characterization and utilization.

2.2. Char Characterization

Char obtained from fast pyrolysis of HDPE plastic wastes was sieved and screen to receive a particle size smaller than 250 µm. Proximate analysis viz. contents of moisture, volatile matter, and ash of the char was conducted according to ASTM 3173, ASTM D 3175, and ASTM D 3174, respectively. Elemental composition of the char was determined using an elemental analyzer (Leco, TruSpec Micro CHNS, USA). Colorific value was determined according to ASTM D 5865, using a bomb calorimeter (Gallenamp, Adiabatic, UK).

2.3. Activated Carbon Preparation and Characterization

To prepare activated carbon from char powder, the powder was thermally activated under air atmosphere at 900°C for 3 hours, using a muffle furnace (Carbolite, CWF 1200, UK). Microstructure of the activated powder was observed by a scanning electron microscope (JEOL, JSM 6460LV, USA), at an accelerating voltage of 10 kV. Nitrogen adsorptions at 77 K of the activated and untreated powder were determined using an automatic adsorption analyzer (Quantachrome Instruments, Autosorb 1, USA). The specific surface area, specific pore volume, pore size, and sorption isotherm of the samples were analyzed and compared.

2.4. Briquetting Process and Combustion Test

Char obtained from fast pyrolysis of HDPE waste was used as a fuel for combustion process in this study. Prior to be used as a fuel for the combustion process, char powder was briquetted using a laboratory-scale extruder. The briquette prepared was 35 mm diameter and 140 mm long. It was then used for boiling water in a pot via a high

efficiency cookstove. One kg of the briquette was used to boil one kg of water at the volumetric flowrate of air of $350 \text{ m}^3/\text{h}$. Temperatures of flame and water during combustion process were measured and recorded every minute.

3. Results and Discussion

3.1. Characteristics of Chars Derived from Fast Pyrolysis of HDPE Plastic Wastes

Proximate analysis, elemental composition, particle density, and calorific value of the char obtained from pyrolysis of HDPE wastes were tabulated in Table 1. It was obvious that volatile matter and fixed carbon were the main components (>97%). This was because plastic was generally composed of 75.5-100% volatile matter, 0.1-2.75% moisture content, and 0.2-4% ash [9-11]. After being thermally decomposed via pyrolysis process, volatile matter was still in majority whereas moisture and ash were in minority. Compared to the gasification process, the pyrolysis process provided the char with higher volatile matter content and lower fixed carbon. Similar result was reported by Brewer et al. [12].

Table 1. Characteristics of chars derived from different thermochemical processes of plastic wastes.

| | | Fast pyrolysis | Gasification |
|---------------------------------------|-----------------|-----------------|---------------|
| Proximate analysis (% wt) | Moisture | 2.41±0.36 | 0.43±0.37 |
| | Volatile matter | 51.40±0.28 | 46.57±0.12 |
| | Fixed carbon* | 46.03±0.32 | 53.74±0.18 |
| | Ash | 0.16±0.23 | nd |
| Ultimate analysis (% wt) | С | 42.65±0.98 | 31.97±0.30 |
| | Н | 3.06±006 | 3.03±0.03 |
| | Ν | 0.43 ± 0.04 | 0.99±0.04 |
| | S | 1.80 ± 0.02 | 1.86 ± 0.04 |
| Particle density (g/cm ³) | | 42.65±0.98 | 31.97±0.30 |
| Calorific value (cal/g) | | 4,500 | 4,950 |

*by difference

Since plastic is the hydrocarbon compound, carbon and hydrogen are the major elements. Percentages of carbon, hydrogen, nitrogen, and sulfur in general plastic wastes (except PVC) were in the ranges of 81-91%, 8-15%, 0-0.1%, and <0.1%, respectively [9, 11, 13]. Due to having chlorine as a component, PVC plastic wastes had the lower contents of carbon and hydrogen compared to other plastic types. As shown in Table 1, carbon had the maximum content, however, its value was rather small compared to that reported by Miranda et al. [13]. It was also noticed from Table 1 that calorific values of the char obtained from both thermo-chemical processes were less than those of the general plastics.

3.2. Morphology and Pore Properties of Untreated Char and Activated Char

Attributed to having carbon as the main component, it is of interest to study the feasibility of preparing activated carbon from char obtained from fast pyrolysis of plastic wastes. Morphology of the chars obtained from fast pyrolysis and gasification of HDPE plastic wastes with and without activation was depicted in Fig. 1. It was apparent that after being thermally activated, a larger number of pores were observed.



Fig. 1. Micrograph of chars derived from fast pyrolysis of plastic wastes (a) without activation; (b) with activation under air atmosphere at 900°C for 3 hours.



Fig. 2. Micrograph of chars derived from gasification of plastic wastes (a) without activation; (b) with activation under air atmosphere at 900°C for 3 hours.

BET surface area, specific pore volume, and pore size of chars derived from fast pyrolysis of HDPE plastic wastes were presented in Table 2. The pore size of the untreated chars can be categorized as transitional pores (radius of 20-1,000 °A). BET surface area and specific pore volume were increased by 55% and 44%, whereas the pore size was decreased by 5% after being activated. During activation, a physical change occurred at the carbon surface of the sample. Carbon reacted with carbonized substance and converted to carbon dioxide. Carbon dioxide diffused through the surface of carbon resulting in the large number of pores in the char structure.

| | - | - | | |
|--------------------------------------|---|--|----------------|--|
| Samples | BET surface area (m ² /g) | Specific pore volume (cm ³ /g) | Pore size (°A) | |
| Without activation | 10.83 | 0.1441 | 521.30 | |
| With activation at 900°C for 3 hours | 16.77 | 0.2080 | 496.00 | |

Table 2. BET surface area, specific pore volume, and pore size of chars derived from fast pyrolysis of plastic wastes.

Adsorption and desorption isotherms of char obtained from fast pyrolysis of HDPE plastic wastes with and without activation were illustrated in Fig. 3. Both isotherms might be in the type III. These isotherms show large deviation from Langmuir model and explain the formation of multilayer.



Fig. 3. Soprtion isotherm of char obtained from fast pyrolysis of plastic wastes (a) without activation; (b) with activation under air atmosphere at 900°C for 3 hours.

3.3. Application of Char Briquette as a Fuel for a Cook stove

During the combustion process, flame temperature continuously increased to the maximum value (455° C) at the 16^{th} minute and gradually decreased. It required 13 minutes to increase water temperature from room temperature to the boiling point. Average evaporation rate was 1.04 kg/h. Compared to wood fuel, the char derived briquette required a longer time to ignite with the stable flame. The reddish-orange flame occasionally produced smoke with undesirable smell. Unexpectedly, the briquette was melt during burning and flow into the grate. When the stove was cooled down, the melt fuel was solidized and can be re-used.

4. Conclusion

Fixed carbon and volatile matter were the main components in char derived from fast pyrolysis of HDPE wastes (>97%). Carbon, hydrogen, nitrogen, and sulfur contents of the char were 42.62%, 3.06%, 0.43%, and 1.8%, respectively. Calorific value was 4,500 cal/g. Char derived briquette was used as a fuel for boiling water in a cookstove. Such a briquette can make the water boil within 13 minutes with the evaporation rate of 1.04 kg/h. Thermal activation at 900°C for 3 hours caused the larger BET surface area, the greater specific pore volume, and the smaller pore size of the char powder.

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