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ORIGINAL RESEARCH PAPER

THE PREPARATION OF FIXED CARBON DERIVED FROM WASTE TYRE USING PYROLYSIS

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Abstract: This work was aimed at investigating the influence of heating rate, particle size, pyrolysis time and temperature against the content of fixed carbon and characterizing the carbon black using Analysis of Variance (ANOVA). Pyrolysis technique conducted, employed an unstirred semi-batch reactor with capacity 1.150 L, which was equipped by a condenser and operated at 1 atmosphere as well as flowed by nitrogen gas at 1 L·min^{-1}. The tyre waste used as raw material was 30 g. The research variables used in this study were as follows: heating rate was 10-20 °C·min^{-1} particle sizes were -10/+16 mesh, -16/+20 mesh, and -20/+30 mesh; pyrolysis time and temperature were 30-90 min, 400-600 °C, respectively. It was found that heating rate, particle size, pyrolysis time and temperature significantly affected with respect to the content of fixed carbon and carbon black characterization. The biggest content of fixed carbon was 61.8984 %, which was produced at heating rate of 20 °C; particle size was -20/+30 mesh conducted at 600 °C for 90 min. After performing an ANOVA analysis, the best carbon black obtained (iodine number 315.27 mg·g^{-1}, ash content 3.0983 %) was prepared at heating rate of 10 °C·min^{-1}, particle size -10/+16 mesh. Meanwhile, the highest moisture was obtained at heating rate of 20 °C·min^{-1}, particle size -20/+30 mesh with similar pyrolysis time and temperature.

Keywords: *ANOVA, carbon black, heating rate, particle size, temperature, time*

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INTRODUCTION

Amount of tyre waste expected significantly increases as the number of cars and motorcycles go up every year in Indonesia. The tyre waste, which is synthesized from natural rubber, is mainly composed of carbon (85.16 %), sulfuric substance (1.9 %) and cadmium (2.9 ppm), zinc oxide (2.2 %), chromium (49.9 ppm), and tin (11 ppm) [1, 2]. The tyre is prepared from both of natural rubber (NR) and synthesized rubbers (SR) like butyl rubber (BR), and co-polymer styrena-butadiene rubber (SBR) [3]. The special properties of tyre are high volatile and are naturally degraded in long time [4].

Most of used tyres place in open field and have not yet utilized massively as valuable materials unless they are used as a handicraft and reused by retreading as well as burned-out. Those methods are not a permanent solution to eliminate the tyre waste. The high content of carbon inside tyre waste is possible to recover it becomes carbon black.

Some authors have reported for 10 years that pyrolysis of tyre waste produced some valuable materials; one of them was carbon black. Pyrolysis of used tyre is a decomposing process thermally conditioned without oxygen (inert) and is conducted at high temperature. The rubber arranged by chains of double bond carbon (polymer), is degraded into simple units (monomers). Pyrolysis of waste tyre produces three phase substances, such as, liquid, gaseous and solid products. The solid phase product is called pyrolytic carbon black (PCB). Conversion and yield of pyrolytic product depend on the process and conditions employed.

Investigators studied the pyrolysis of used tyre to analyze the influence of operational conditions toward product yields (liquid and solid). The effect of pyrolysis temperature with respect to the degradation rate and yield was previously reported [5]. Products, oil and carbon black were successfully obtained from the truck tyre waste at 480 – 520 °C in reduced pressure and atmospheric conditions [6]. Optimum condition of pyrolysis technique to produce the pyrolytic carbon black and oil was investigated with performing a fixed bed reactor, which was heated by furnace [7].

The gas obtained from tyre waste was researched intensively by other authors [8]. The results showed that the tyre dust could be converted into gas employing pyrolysis at 500 – 1000 °C by altering the resident time. The more advance method was proposed to recover the liquid product as previously works [9]. The technique introduced the continue pyrolysis of tyre waste into liquid product using a conical spouted bed reactor at 425 – 600 °C and the results were compared to those of employing batch reactor. Meanwhile, other authors explained about the hydrodynamics and heat transfer on conical spouted bed reactor (pilot plant) of pyrolytic process and studied the effect of temperature and the rate of heat transfer in reactor [10].

Reported works, however, mostly investigated the influence of temperature and pyrolysis time versus product yield and mainly recovered liquid product. In reality, pyrolysis is also significantly affected by heating rate, particle size, water content and chemical composition of raw material, which were impacted on product yield and product characterization. Based on problem definition previously mentioned, this work is directed to prepare the carbon black (solid) converted from tyre waste and is focused on the influence of heating rate, particle size, pyrolysis time and temperature toward the content of fixed carbon as well as characterized the product. Fixed carbon was assumed as pyrolytic carbon black.

MATERIAL AND METHODS

Preparation of raw material

The raw material employed in this study was the used tyre, which was obtained from retreaded seller. The tyre waste was washed with water and steel wires were removed. The cleaned tyre was dried under sunlight for hours and milled and continued with screening to obtain particles size of -10/+16, -16/+20 and -20/+30 mesh, which were similar to 1.321, 0.912 and 0.687 mm [11]. The chemical compositions of particles were analyzed by applying an ultimate and proximate method.

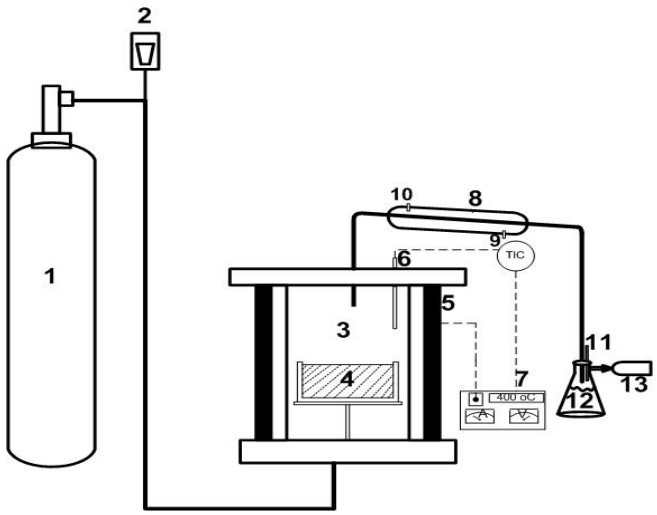

Figure 1. *The diagram of pyrolysis apparatus used in this work (1) - nitrogen tube; (2) – gas flow-meter; (3) - semi batch reactor; (4) - sample place; (5) - electrical heater; (6) - thermocouple; (7) - controlling instrument; (8) - condenser; (9) - cooler water inlet; (10) - warm water outlet; (11) - thermometer; (12) - liquid cross-section; (13) - gas cross-section*

Pyrolysis procedure and analysis

The pyrolysis apparatus was designed and constructed that was adapted from some reports [8, 12] and reactor system was a semi batch whose its temperature and heating rate could be controlled and be conducted at 900 °C as shown in Figure 1. Pyrolysis system is consisted of the main component, unstirred semi batch reactor (1.150 L) made of stainless steel (3) and supportive components, nitrogen tube (1), gas flow-meter (2), sample place (4), electrical heater (5), thermocouple (6), controlling instrument (7), condenser (8), cooler water inlet (9), warm water outlet (10), thermometer (11), liquid cross-section (12) and gas cross-section (13).

The 30 g of particles (-10/+16 mesh, -16/+20 mesh, and -20/+30 mesh) were put inside sample place and it was introduced into reactor. Reactor was closed tightly and nitrogen was flowed to reactor with a rate of 1 $L \cdot min^{-1}$ for ± 40 min purposing eliminating oxygen and impurities from the air. The rate of nitrogen gas was controlled by the gas flow-meter.

Reactor was heated by an electrical heater started at room temperature until 400, 500 and 600 °C, which those were controlled by PID instrument through reading the electrical pulses transmitted from thermocouple inside reactor. Pyrolysis took time for 30, 60 and 90 min and heating rate was set at 10, 15 and 20 °C·min^{-1}. The pyrolysis time was recorded when temperature was attained and then maintained until determined duration as described previously. Nitrogen gas was flowed continually into reactor during pyrolysis.
A condenser was connected to reactor functioning to change the gas- to liquid phase of the pyrolytic product. The gas produced from heating of particles passed through a condensor and was cooled until room temperature, 30 °C. The product, which was condensed, was kept inside a liquid storage while, the vapour that was not changed into liquid, was channelled to gas storage. The pyrolysis process was conducted in atmospheric pressure. The sample (solid) was removed from reactor after pyrolysis completely finished.

The content of fixed carbon and carbon black characterization

Prior to analysis of product, the fixed carbon was assumed as carbon black of pyrolysis product. The fixed carbon obtained was defined as the subtraction of the solid product and carbon black inside raw material (ash, water and volatile matter). The influence of temperature, heating rate, pyrolysis time and size of particle toward the fixed carbon content, was analyzed [ASTM D-5142-09].
The iodine number, ash - and moisture contents of carbon black, were analyzed employing methods, ASTM D4607-94, ASTM D1506-99 and ASTM D1509-95, respectively. Those characterizations purposed at investigating the influence of temperature, heating rate, duration and size of particle against carbon black pyrolyzed.
An ANOVA evaluation was employed to investigate the variance of data obtained and to analysis the influence of research variables (heating rate, size of particles, pyrolysis time and temperature) with respect to fixed carbon represented by parameters, iodine number, moisture and ash contents. It used a design experiment program (design expert) 6 in which experiment design was applied to construct all experiment and to predict statistical parameters and model used in this work was factorial [13]. The first step was determined the model employed and variances, A (pyrolysis time), B (heating rate), C (pyrolysis temperature) and D (particle size), were used as data input. Responds of analysis were iodine number, moisture content, and ash content. The second, results obtained were input into design expert program and then was run by choosing the analysis menu until the program stopped and showed an ANOVA analysis result.

RESULTS AND DISCUSSION

Analysis of chemical composition

Chemical composition of raw material was analyzed with performing methods, ultimate (ASTM D-5373-08), total sulphur (ASTM D-4239-08) and proximate (ASTM D-5142-09). Those calculations were purposed at obtaining the initial chemical composition contained in tyre particles. The results of ultimate analysis to obtain the compositions of

ash, water, C, H, N, S, and O atoms is described in Table 1. It was shown that percentage of carbon was 81.93 % and followed by H, ash and O recorded at 6.27, 4.10 and 3.94 %, respectively. Meanwhile, total sulphur and moisture contents were observed at 2.34 % and 1.41 %. These findings were relatively similar to those reported by other authors [2].

Table 1. *The ultimate analysis of tyre waste*

Components	Composition [%]	Standard Method Analysis
Moisture	1.41	ASTM D-5373-08
Ash	4.10	ASTM D-5373-08
Carbon (C)	81.93	ASTM D-5373-08
Hydrogen (H)	6.27	ASTM D-5373-08
Nitrogen (N)	0.00	ASTM D-5373-08
Total Sulfur (S)	2.34	ASTM D-4239-08
Oxygen (O)	3.95	By difference

The result of proximate analysis (ASTM D-5142-09) of tyre particles is revealed in Table 2. The volatile matters were the highest composition, which was recorded at 59.45 % followed by fixed carbon recorded at 35.00 %. Both of moisture- and ash contents were noted at 4.10 and 1.41 %, respectively, which were much smaller than those of previous ones. These values were comparable to those of previously reported by other investigators [14]. As described that these were an indication, the used tyre could be transformed into valuable substance, carbon black.

Table 2. *The proximate analysis of tyre particles*

Components	Composition [%]	Standard Method Analysis
Moisture content	1.41	ASTM D-5142-09
Volatile matter	59.49	ASTM D-5142-09
Ash content	4.10	ASTM D-5142-09
Fixed carbon	35.00	ASTM D-5142-09

The influences of heating rate, pyrolysis time and temperature versus the contents of fixed carbon for three particle sizes

The heating rates applied in this work were, 15, and 20 °C·min^{-1} and the sizes of particle were chosen at -10/+16 mesh (1.321 mm), -16/+20 mesh (0.912 mm), and -20/+30 mesh (0.6875 mm). The influence of heating rate, pyrolysis time and temperature towards the contents of fixed carbon at various particle sizes, is shown in Figures 2, 3 and 4.
Figure 2 shows that the higher of heating rate and the smaller of particle size were introduced the bigger of percentage of fixed carbon was obtained.
The highest contents of fixed carbon were close to 62 % with heating rate and particle size were of 20 °C·min^{-1} and 0.6875 mm for all sizes. It was indicative that the heating rate and particle size were significantly influenced on heat transfer and thermal decomposition during pyrolysis. The smaller particle increases the convective energy flow on sample so the particles degradation was accelerated. The heat, which penetrated and transferred on sample, was short distance and the degradation was not uniform that caused the decrease of the content of fixed carbon as previously investigated [15].

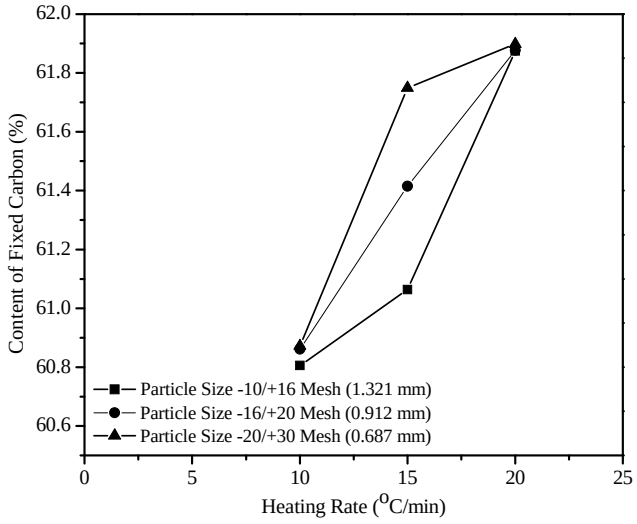

Figure 2. *The influence of heating rate versus the contents of fixed carbon*

Meanwhile, the pyrolysis time in this study took for 30, 60 and 90 min and particle sizes were kept constant as previous variable. The influence of pyrolysis time with respect to the content of fixed carbon for various particle sizes as described in Figure 3.

Figure 3 shows that pyrolysis duration significantly affects on the fixed carbon obtained. The smaller particle size improved the composition of fixed carbon since the surface area was bigger so that the heat absorbed increased. When time needed in pyrolysis reached 90 min, the fixed carbon degraded from tyre particles (0.6875 mm) was 61.8984 %, which was the biggest value recorded. The increase of fixed carbon when the time was inclined, was caused by the heat transfer was enough to degrade carbon double bonds inside tyre into fixed carbon. The smaller particle and enough duration in pyrolysis could increase the decomposition rate of particles into monomer compared with the bigger particles, which were relatively similar to those of previously published [16, 17].

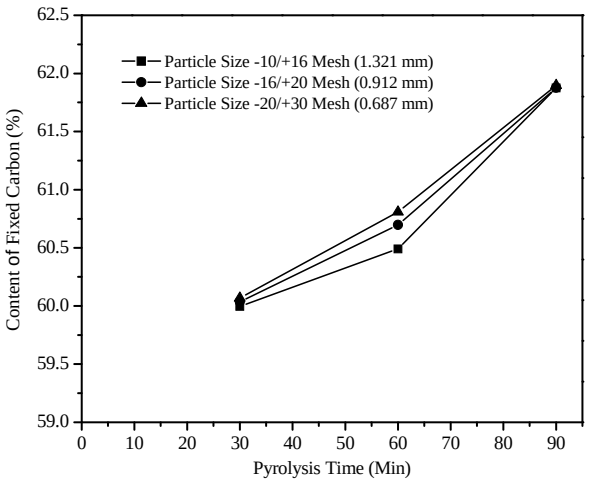

Figure 3. *The influence of pyrolysis time with respect to the content of fixed carbon for various particle sizes*

In this investigation, pyrolysis temperatures used were set at 400, 500, and 600 °C with the similar particle sizes. The content of fixed carbon, which affected by pyrolysis temperatures, is shown in Figure 4.

The result presented in Figure 4 shows that the temperature dominantly influenced the obtained carbon for all particle sizes. The increase of temperature meant that the heat transfer from heater into particles improved that caused the degradation was accelerated. The chemical composition of fixed carbon recovered at 600 °C was 61.8984 %, which was the highest value obtained and the size was of 0.6875 mm. As described previously, the smaller particle employed was the higher content of fixed carbon obtained. The investigated results were comparable with other study as previously published [7, 18].

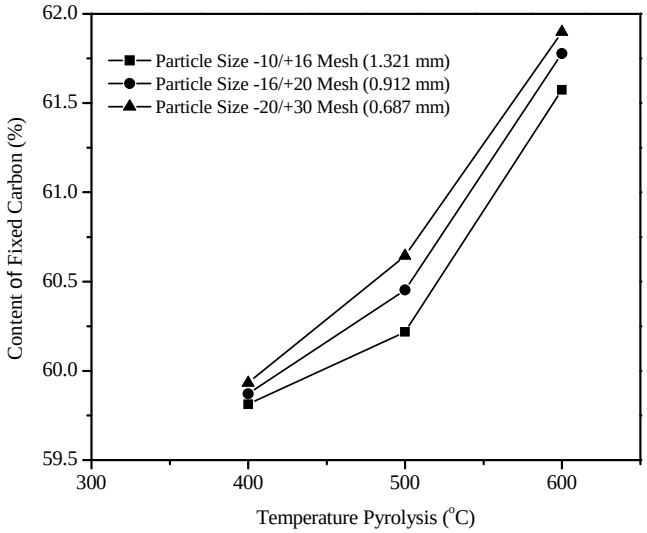

Figure 4. *The effect of temperature against the content of fixed carbon for three particle sizes*

ANOVA analysis

An ANOVA analysis was performed to evaluate the influence of heating rate, size of particles, pyrolysis time and temperature versus characteristics of fixed carbon, which were represented by iodine number, moisture and ash contents. The iodine number was defined as the amount of iodine (in mg) adsorbed by one gram carbon. The higher the iodine number, the bigger the carbon adsorb the dissolved substance. The analysis of iodine number was performed by using an ASTM D-4607-94 method and was conducted on some pyrolysis products.

Referring to the iodine number, the pyrolytic carbon black, which commercially fulfilled the standard carbon black, was pyrolyzed with heating rate 10 and 20 °C·min^{-1}, at 600 °C, particle size -10/+16 mesh (1.321 mm) and -20/+30 mesh (0.6875 mm) for 90 min, which was similar to those of moisture and ash contents analysis. Those conditions generated iodine number at 304.83 mg·g^{-1} and 315.2 mg·g^{-1}, respectively, while the commercial carbon black has the iodine number 301.84 mg·g^{-1}.

The obtained iodine number was tested by using ANOVA employing the design expert 6 programs and the factorial model following the previous study [19]. The objective of ANOVA analysis is to know the variable, which was the most influent on tyre

pyrolysis. Variances A and B represented pyrolysis time and heating rate, meanwhile those C and D were in capacity of temperature and particle size, respectively. The ANOVA result the iodine number of black carbon recovered is shown in Table 3.

Table 3. *The result of ANOVA analysis the iodine number of carbon black*

Source	Sum of squares	Degree of freedom	Mean square	F value	p-Value > F	Remark
Model	63381.30	4	15845.32	22.17	< 0.0001	Significant
A	39305.05	1	39305.05	55.01	< 0.0001	-
B	2311.690	1	2311.690	3.240	0.0995	-
C	20639.63	1	20639.63	28.88	0.0002	-
D	1124.930	1	1124.930	1.570	0.2356	-

The ANOVA testing generated an iodine number, moisture and ash equations as formulated in (1), (2) and (3) as follow:

$$Iodine\ No = -97.46926 + 1.65213\ A + 2.40400\ B + 0.35916\ C - 26.47198\ D \quad (1)$$

$$Moisture\ content = 0.74771 - (2.34104 \times 10^{-3}\ A) - (6.32375 \times 10^{-3}\ B) - (4.25188 \times 10^{-3}\ C) + 0.060399\ D \quad (2)$$

$$Ash\ content = 4.59812 - (6.665979 \times 10^{-3}\ A) - (8.56875 \times 10^{-3}\ B) - (1.49469 \times 10^{-3}\ C) + 0.1748\ D \quad (3)$$

Based on the result showed that pyrolysis time and temperature were the most significant influence of process variables, whose value Prob > F approached zero. Equation (1) shows that values A (pyrolysis time), B (heating rate) and C (pyrolysis temperature), were positive. It was indicative that time and temperature significant affected linearly on iodine number. In contrast, D value was negative, which described an inversely proportional relation between the iodine number and particle size. It was discovered that those findings as previously described were relatively similar to those of moisture and ash contents though equations used were different as shown in equations (2) and (3). All calculations (iodine number, moisture and ash contents) using ANOVA analysis found that the pyrolysis time and temperature were the most significant of variables on tyre waste pyrolysis.

Determination of moisture content employing ASTM D-1509-95 technique was assumed that carbon black only contained volatile substances trapped inside pores.

The moisture contents obtained were of 0.2710 %, 0.2501 %, and 0.2618 %, respectively compared with that of commercial carbon black was of 0.2761 %. The result of ANOVA analysis with respect to moisture content is described in Table 4.

Table 4. *The result of ANOVA analysis toward moisture content*

Source	Sum of squares	Degree of freedom	Mean square	F value	p-Value > F	Remark
Model	0.13	4	0.032	8.42	0.0023	Significant
A	0.079	1	0.079	20.50	0.0009	-
B	0.016	1	0.016	4.15	0.0663	-
C	0.029	1	0.029	7.51	0.0192	-
D	5.856E-003	1	5.856E-003	1.52	0.2432	-

Equation (2) shows that values parameters A, B and C were negative, which attributed to significant variables in pyrolysis. Pyrolysis time and temperature were the most significant parameters in black carbon preparation that were similar to iodine number calculation. The value of D was positive that the bigger particle improved the water content inside sample.

Ash in carbon black generally consists of metal oxide that does not vaporize in pyrolysis. In this work ash analysis was carried out by using ASTM D-1506-99 technique.

The ash content found in pyrolysis was 3.0983 %, which was comparable with that of commercial ash, 3.2055 %. The results showed that ash content did not change significantly at any operational conditions, heating rate, temperature and particle size, those were indicative that samples were not oxidized during pyrolysis

Based on ANOVA analysis as shown in Table 5, the variables significantly influenced on pyrolysis were time and temperature.

Table 5. *The result ANOVA analysis versus ash content*

Source	Sum of squares	Degree of freedom	Mean square	F value	p-Value > F	Remark
Model	1.07	4	0.27	49.53	< 0.0001	Significant
A	0.64	1	0.64	117.75	< 0.0001	-
B	0.029	1	0.029	5.41	0.0401	-
C	0.36	1	0.36	65.9	< 0.0001	-
D	0.049	1	0.049	9.05	0.0119	-

As previously described, pyrolysis time and temperature were more significant than heating rate and particle sizes variables for all calculations. Those results were same to those other works as previously reported investigators [13, 20, 21].

CONCLUSIONS

The carbon black was prepared successfully with employing pyrolysis technique. It was found that heating rate, particle sizes, time and temperature influenced the content of obtained fixed carbon. Based on the iodine and moisture analysis, the highest content of fixed carbon obtained was produced by controlling temperature at 600 °C for 90 min and heating rates were 10 °C·min^{-1} and 20 °C·min^{-1}. After ANOVA analysis, the recovered product fulfilled a requirement of commercial carbon and time and temperature were the most significant influences, meanwhile heating rate and particle sizes slightly affected on carbon black characterizations.

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