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Effect of Wood Biomass Addition on the Char Making Process of Waste Plastic for Controlling the Combustion Efficiency

Abstract: After Kyoto protocol, many companies and institutions in the industrialized countries focused on the energy saving and the utilization of waste heat and materials widely for reducing the CO_2 emission. In such a circumstance, it is key technology for reducing CO_2 emission by using the waste materials efficiently such as a plastic and wood biomass.

In this paper, a method for improving the reactivity of plastic char using wood biomass was investigated. The XRD analysis was performed for elucidating the carbon structure change by addition of wood to PE (polyethylene) and reactivity test with O_2 gas was carried out to clarify the reaction rates of the mixtures of PE and wood.

It was found that the crystallization degree of char decreased continuously with the addition of wood to polyethylene, which meant that the reactivity of polyethylene char increased.

Keywords: biomass, char making process, combustion efficiency

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1 Introduction

Pulverized coal (PC) injected into blast furnace (BF) through tuyere is rapidly heated and a volatilization of volatile matter occurs simultaneously. In the course of the combustion process, some of coal turns to a form of char. Since the residence time of PC is not long enough, the char, which is called as "unburnt char", would be ejected from the raceway without undergoing a complete combustion. Then, the unburnt char will be consumed by the reaction with FeO slag and with molten metal (carburization) in the lower part of BF and also by the gasification reaction ($C + CO_2 = 2CO$) in the upper part of BF below reserve zone. When the amount of the unburnt char increased, the accumulation within the BF would be significant. As the BF condition become unstable owing to the decrease of gas permeability according to its accumulation, the pulverized coal injection (PCI) [1] operation has some limit fatally.

Recently, an alternative injected material into BF, which is a waste plastic [2], is focused on in terms of low carbon emission. However, the plastic also generates a char. The direct observations of combustion behavior of plastic char in the raceway suggested that the reactivity of plastic would be inferior to that of pulverized coal [2]. The amounts of waste plastic injection are thus also limited by such accumulation of unburnt plastic char more seriously than PC injection.

On the other hand, the decrease of CO_2 emission is very important issue in the global level, recently. Furthermore, the price of resources and energy would continuously increased, even though the recent economic crisis put a brake on the trend, the potential of China and India would be still large.

In addition to the price of PC, the problem of CO_2 emission is significant for the industrial countries. As the waste plastic can not be counted on the CO_2 emission, its effective utilization would be noteworthy. From these backgrounds, it is important to improve the reactivity of char from plastic.

The relationship between graphitization degree and reactivity of carbon was presented by Kashiwaya, *et al.* [3] on the coke gasification reaction, in which the graphitization degree was classified into two group and kinetic analysis has been performed. In the case of coke, the carbon crystals are rather than close to graphite structure in comparison with char from low rank coal or wood, generally. On the other hand, analysis of char's reaction has been presented by Lu *et al.* [4–6]. Lu *et al.* have suggested that crystallinity of char would be one of the important factors

and indicated the method to evaluate the amount of amorphous carbon using *X*-ray diffraction (XRD) analysis. Basically, both of them represent that a carbon having low crystallization degree shows high reactivity. In the case of actual coking process, many kinds of coal are blended to get optimum coke properties. There would be an interaction between different kind of coals (for example, bituminous coal and coking coal) during coking process. Although such kind of interaction is considered empirically, a quantitative understanding is not attained. Moreover, in a char making (charring) process, there is no study on the interaction of charring process between different kind of materials.

Based upon the considerations above, this study was aimed at testing a possibility to control the char structure by the addition of wood to polyethylene in order to improve the reactivity of plastic char. In Figure 1, the concept of interaction on the charring process in this study is illustrated. It was defined that the char from PE (polyethylene as a representative material of waste plastic)) consisted of C′(crystallized carbon) + A′(amorphous carbon), while wood char consisted of C″ + A″. In general, the reactivity of A(amorphous carbon) is higher that that of C(crystallized carbon) [3–6]. When a char was made from a mixture between wood and PE, the obtained char would consist of C‴ and A‴, so that the C‴ and A‴ might show intermediate properties between wood char (C″ + A″) and PE char (C′ + A′). However, just a mixture of wood char and PE char, which means a mixing after charring, could be considered as a mixture of (C′ + C″) + (A′ + A″) not (C‴ + A‴). The char (C‴ + A‴), which was made from the mixture before charring, was called as 'Mixed char' for convenience.

In the present study, with respect to the control of the crystallinity of char, an attention was focused on the 'Mixed char'. The chemical (reactivity) and physical (crystallinity) properties were studied through a combustion experiment with O_2 and XRD analysis, respectively.

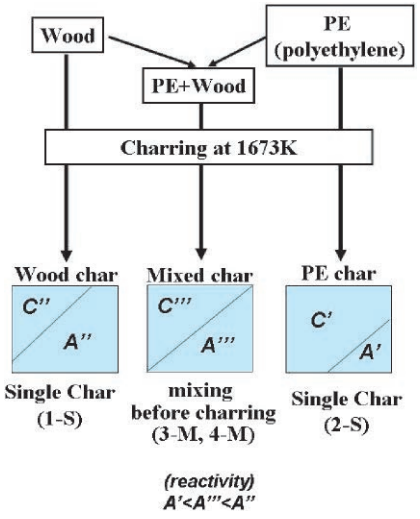

Fig. 1: Difference of nature of char with Charring condition
A: amorphous carbon, C: crystallized carbon.

2 Experimental

2.1 Preparation of chars and *X*-ray diffraction (XRD) analysis

The starting materials are Japanese cypress powder (<1 mm diameter), and reagent-grade polyethylene (PE, plasticizer-free). Wood and PE were mixed at the ratios given in Table 1, are pressed into steel die of 12 mm in diameter, and dried at 343 K for 12 hours.

The resulting pellets were heated rapidly to 1673 K by dropping them into a magnesia crucible heated in a high-frequency induction furnace for 14 min under argon atmosphere (1000 cm^3/min (at STP)) and kept for 14 minutes. As shown in Table 1, the mixed chars are

	Sample code	Composition of raw materials used for char-making (pct by wt.)		Temperature of char-making (K)	Fraction of amorphous carbon, X_{am}	
		wood	polyethylene			
Graphite	0-G	–	–	–	0	
Single Char	1-S	100	0	1673	$X_{am,(1-S)}$	0.61
	2-S	0	100	1673	$X_{am,(2-S)}$	0.14
Mixed Char	3-M	50	50	1673	$X_{am,(3-M)}$	0.36
	4-M	25	75	1673	$X_{am,(4-M)}$	0.23

Table 1: Samples used for experiments.

named as '3-M' and '4-M' for (50%wood + 50%PE) and (25%wood + 75%PE), respectively, while the single chars using wood and PE separately are named as '1-S' and '2-S', respectively.

The chars thus obtained were crushed, sieved to –100 mesh, and submitted to XRD and reactivity test. Using the results of XRD analysis, a crystallinity of chars obtained was examined and a fractions of amorphous carbon, X_{am} were estimated using the technique reported by Lu *et al.* [7].

2.2 Measurement of char reactivity

The combustion reactivity of chars was measured by using a fixed bed reactor, which is schematically illustrated in Figure 2. About 0.2 g of sample was placed on a porous quartz board fixed at an adequate position in a quartz reaction tube, and the height of bed of char was from 1 mm to 2 mm, in which a change of gas composition could be negligible. The sample temperature was measured by a type-R thermocouple which located just below the porous quartz board. A resistance furnace was equipped with the fixed bed reactor, and the furnace temperature was controlled with another thermocouple located in the space between the furnace and reaction tube. The sample was heated under a nitrogen flow to about 400 K. After the temperature was stabilized, an oxygen gas was introduced into the nitrogen flow to be a reaction gas with a composition of 80% N_2 + 20% O_2. The total flow rate was adjusted to 500 cm^3/min at STP. It is important to note that the reaction gas is once go up through the hot zone before entering the reaction bed, that the reaction gas can be preheated to the reaction temperature.

When an oxygen gas introduced into the inlet gas, the reaction between char and oxygen started, and then the content of CO and CO_2 in produced gases in the outlet gas increased. The variation of those gases were determined quantitatively by an infrared gas analyzer and recorded every 1 second by computer. After the gas compositions reached stable values, the furnace temperature was increased by 15 K. This stepwise heating-up was continued until the CO_2 content in the outlet gas reached 0.2 vol%, which meant the spontaneous combustion reaction occurred. Figures 3(a) and (b) show typical experimental results of the sample temperature and the variation of concentrations of CO and CO_2, respectively, obtained during an experimental run using wood char. A stable value was obtainable within 100 seconds after moving to the next step of temperatures.

The char/oxygen reactions can be expressed as the following equations;

$$\langle C\rangle + (1/2)\,(O_2) = (CO) \quad (1)$$

$$(CO) + (1/2)\,(O_2) = (CO_2) \quad (2)$$

$$\langle C\rangle + (O_2) = (CO_2) \quad (3)$$

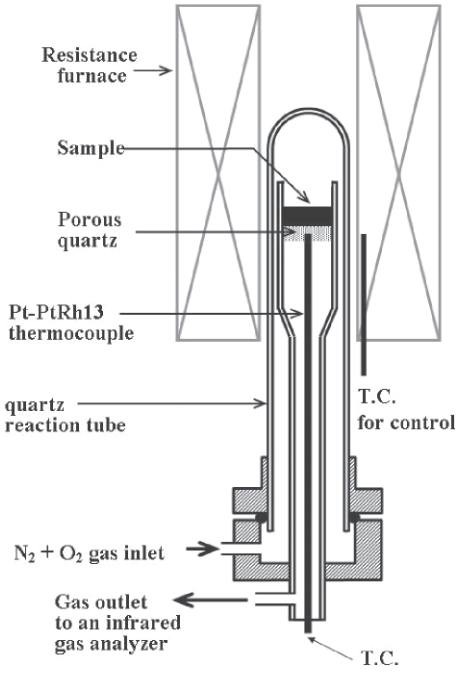

Fig. 2: Experimental apparatus for measurement of chars reactivity.

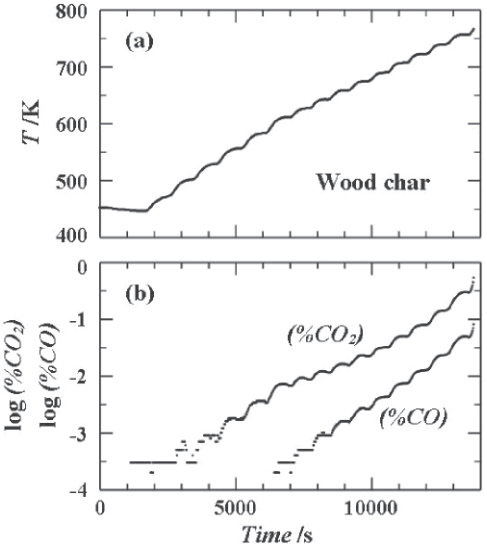

Fig. 3: Variations of temperature and gases (CO and CO_2) in outlet gas during experiment.

Those reactions can be related by Eq. (1) + Eq. (2) = Eq. (3). The reaction mechanism has been examined and discussed with many researchers in terms of a kind of carbon and experimental conditions [8, 9, 10]. In this study, however, the apparent combustion rate was defined by the gas composition change resulted by the reactions through Eqs. (1) and (3).

The apparent reaction rate of carbon consumption at a time t, (dm_C/dt) (g/s), can be calculated as;

$$(dm_C/dt) = 12 \times ((\%CO)/100 + (\%CO_2)/100)Q_{out}/60/22{,}400, \quad (4)$$

where $(\%CO)$ and $(\%CO_2)$ are the volume pct of CO and CO_2, respectively in outlet gas with flow rate of Q_{out} (cm^3/min) at STP. Thus, the apparent rate constant at time t, ρ_m (s^{-1}), can be determined as;

$$dm_C/dt \equiv \rho_m\left(m_C^\circ - \int_0^t (dm_C/dt)\, dt\right) \quad (5)$$

$$\rho_m = (dm_C/dt)/(m_C^\circ - m_C{}^t), \quad (6)$$

where m_C° and $m_C{}^t$ $(= \int_0^t (dm_C/dt)\, dt)$ are the weight of char at $t = t_0$ and $t = t$, respectively.

3 Experimental results and discussion

3.1 X-ray diffraction of Mixed char

Figure 4 shows the XRD patterns of chars used in this experiment and graphite used for the comparison. Hexagonal net plane of (002) in graphite crystal appears around 25° of 2θ ($Cu\ k\alpha$). According to the graphitization degree, the peak of (002) become sharp and the inter planner distance converge to 3.35 Å ($2\theta = 26.61°$) [3, 7]. The broad peak of char from wood (1-S) means that the structure is close to amorphous carbon and contains relatively large amount of amorphous carbon (Fig. 4(a)), while the char from PE (2-S) shows rather high graphitization degree (Fig. 4(d)). It could be understood that the reactivity of PE char was lower than that of wood char only from the shape of XRD pattern, roughly. The peaks of Mixed chars (Fig. 4(b)3-M and (c)4-M) are continuously changed from PE char to wood char in accordance with the content of wood. The results would indicate that an interaction between wood and PE occurred during charring process.

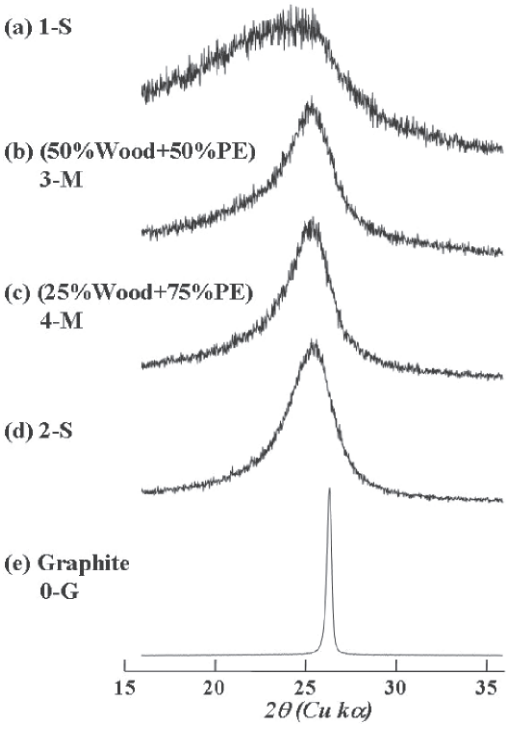

Fig. 4: Results of XRD for chars which were mixed before charring in comparison with single chars and graphite.

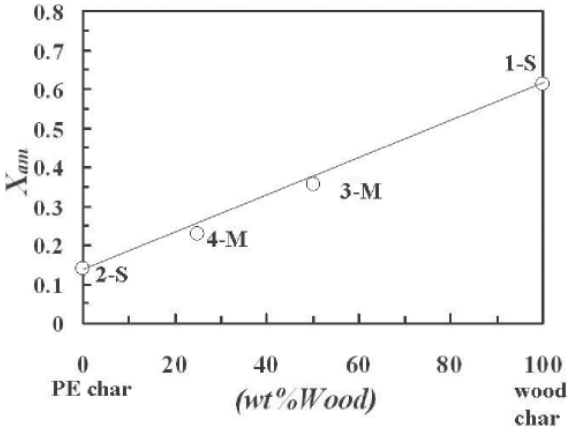

Fig. 5: Relationship between fraction of amorphous carbon and percentage of wood addition to PE.

Using the method of Lu, *et al.* [4–7], fraction of amorphous carbon in char, X_{am}, were determined. The values for X_{am} are summarized in Table 1, and Figure 5 shows X_{am} plotted against wood concentrations within raw materials in percent by weight. As shown in Figure 5, X_{am} increased linearly with an increase in the wood content in the Mixed char.

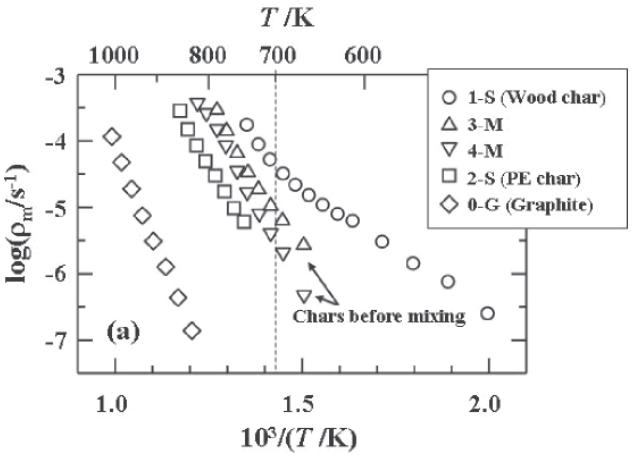

Fig. 6: Variations of apparent rate constant of chars.

3.2 Apparent rate constants and temperature dependences from combustion experiment

Using Eq. (6), the apparent rate constants, ρ_m, were obtained and compared in Figure 6. The values of ρ_m for graphite (0-G: $X_{am} = 0$) was extremely small and was about 1.3×10^{-10} s^{-1} at 700 K, which can not plot in the Figure 6, and 3.3×10^{-8} s^{-1} at 800 K. On the other hand, the lowest value in char samples used in the present study was the one for PE (2-S: C′ + A′) and was 4.1×10^{-7} s^{-1} at 700 K and 4.1×10^{-5} s^{-1} at 800 K, which were larger than that of graphite about three order of magnitude. The value of wood (1-S: C″ + A″) showed highest one and the values of Mixed char (3-M and 4-M: C‴ + A‴) showed the intermediate values between PE and wood.

The temperature dependences of apparent rate constant, ρ_m. were estimated and expressed from Eq. (7) to Eq. (12). The rate constant of wood (1-S) has shown relatively low linearity. Then, the temperature dependence of rate constant for wood was divided into two region below 700 K and over 700 K, which corresponded to Eq. (9) and Eq. (10), respectively.

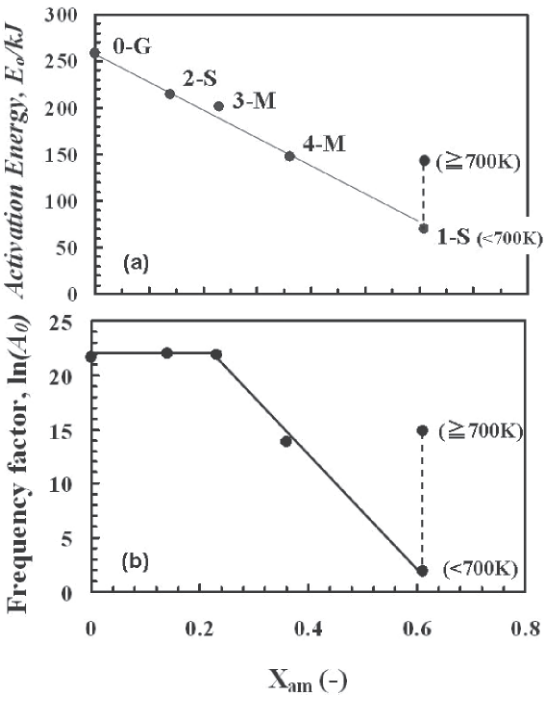

Fig. 7: Activation energies and frequency factors in terms of amorphous carbon, X_{am}.

The activation energies and frequency factors of each char obtained in this experiment were plotted in Figure 7 and summarized in Table 2.

$$\text{0-G (Graphite): } \ln(\rho_m) = \frac{-258400}{RT} + 21.64 \quad (7)$$

$$\text{1-S(Wood (>= 700 K)): } \ln(\rho_m) = \frac{-144600}{RT} + 14.8 \quad (8)$$

$$\text{1-S(Wood (<700 K)): } \ln(\rho_m) = \frac{-71100}{RT} + 1.95 \quad (9)$$

$$\text{2-S (PE): } \ln(\rho_m) = \frac{-214000}{RT} + 22.03 \quad (10)$$

	Sample code	Activation energy (kJ)	Frequency factor ln(A_0)
Graphite	0-G	258	21.64
Single Char	1-S(<700)	70	1.95
	1-S(>=700)	145	14.8
	2-S	214	22.03
Mixed Char	3-M	148	13.85
	4-M	201	21.83

Table 2: Activation energies and frequency factors obtained.

$$\text{3-M; } \ln(\rho_m) = \frac{-148000}{RT} + 13.85 \text{ (50\%wood + 50\%PE)} \quad (11)$$

$$\text{4-M; } \ln(\rho_m) = \frac{-200900}{RT} + 21.83 \text{ (25\%wood + 75\%PE)} \quad (12)$$

The activation energy of graphite in this experiment was 258 kJ. It is in good agreement with other researchers [8]. The ones for Mixed chars, (3-M, 4-M) were 148 kJ and 201 kJ, respectively, which were in the close values to Brown coal char and Activated carbon [9]. The temperature range was selected for comparison of the results among different kinds of chars and the activation energies were decided in the temperature range from 700 K to 800 K, because the ones were slightly changed in low temperature range (<700 K) and high temperature range (>800 K), although the correlation factor was more than 0.99 in the wide range of temperature. Especially, the activation energy of wood near 700 K was 70 kJ, which is closed to the value of subbituminous coal [9].

The activation energies of Mixed chars (3-M and 4-M) were an intermediate one between PE char (2-S) and wood char (1-S) as shown in Figure 7(a). The activation energies among 0-G, 2-S and 1-S showed in excellent linearity in terms of the content of amorphous carbon. On the other hand, the frequency factors showed the good linearity in the relatively high region of amorphous carbon content from 0.2 to 0.6, and was almost constant ($\ln(A_0) \approx 22$) in the low amorphous carbon content region. These tendencies must be related to reaction mechanism concerning to the carbon structure, furthermore, the combustion reaction itself should be analyzed through more precise reaction mechanism. For example, the elementary processes for the formation of CO and CO_2 gases must be different whose reactions are initiated from the adsorption of O_2 on the surface of carbon and the carbon structure will affect the state of adsorption not only reaction gas but also produced gases.

It must be quit complicate reactions between different kinds of carbons having different reactivities. Further study will be performed by authors near future.

4 Conclusions

Using wood and polyethylene (PE), several kind of mixture was prepared and charred at 1673 K. The reactivity of the obtained char with $N_2 + 20\%O_2$ was examined and rate constant was calculated. The obtained results are as follows;

1. Form XRD analysis, it was found that the structures of chars were continuously changed from PE to wood in accordance with the wood addition to PE, which meant the reactivity of PE char could be controlled by the addition of wood.
2. The amount of amorphous carbon increased linearly with the addition of wood to PE.
3. The obtained activation energy for PE, 214 kJ, was in the range of the carbons reported by reference, while the activation energy of wood char was very low and 70 kJ in low temperature range less than 700 K and 145 kJ more than 700 K.
4. Temperature dependences of the apparent rate constants for Mixed char have relatively good linearity, which were in the intermediate value between Wood char and PE char.

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References

[1] K. Yamaguchi, H. Ueno and K. Tamura; *ISIJ International*, 32(1992), No. 6, pp. 716–724.
[2] M. Asanuma, T. Ariyama, M. Sato, R. Murai, T. Nonaka, I. Okochi, H. Tsukiji and K. Nemoto; *ISIJ International*, 40(2000), No. 3, pp. 244–251.
[3] Y. Kashiwaya and K. Ishii; *ISIJ international,* 31(1991), pp. 440–448.
[4] L. Lu, C. Kong, V. Sahajwalla and D. Harris; *Fuel*, 81(2002), pp. 1215–1225.
[5] L. Lu, V. Sahajwalla, C. Kong and A. McLean; *ISIJ International*, 42(2002), No. 8, pp. 816–825.
[6] L. Lu, V. Sahajwalla and D. Harris; *Metallurgical and Materials Transactions B*, 32B(2001), No. 10, pp. 811–820.
[7] L. Lu, V. Sahajwalla, C. Kong and D. Harris; *Carbon*, 39(2001), pp. 1821–1833.
[8] Ian W. Smith; Fuel, 57(1978), pp. 409–414.
[9] A. Cuesta, A. Martinez-Alonso and J. M. D. Tascon; Energy & Fuels, 7(1993), pp. 1141–1145.
[10] E. A. Gulbransen, K. F. Andrew and F. A. Brassart; J. Electrochemical Society, 110(1963), pp. 476–483.