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CARBONIZATION CHARACTERISTICS OF BIOMASS/COAL BLEND FOR BIO-COKE

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ABSTRACT

The carbonization characteristics such as char properties and gas release rate of biomass/coal blend have been determined in a batch-type carbonization reactor. The yellow poplar as a biomass is added to a coal with different levels (10, 15, 20, 30 wt%) at various final temperature (500 – 800°C). The carbonization characteristics of biomass/coal blend shows advantages such as increased energy yield and surface area.

INTRODUCTION

The iron and steel making industry is one of the major greenhouse gas emission sources in Korea as well as in the world. In 2007, iron and steel industry released 75 million tons of CO₂ which is about 12 % of total CO₂ emission in Korea (1). The pressure to reduce greenhouse gas emission is increasing for industry since the conventional fossil fuel (coal) is mostly used in coke making and blast furnace. One of the strategies to reduce greenhouse gas in steel making process is to replace the portion of coal with biomass. Biomass is a promising renewable energy source which is 'CO₂ neutral' for capturing carbon dioxide during its growth (2). Bio-coke is the resultant char prepared with the addition of charcoal(biomass) to a coal blend, which can reduce the greenhouse gas emission by replacing the coke in iron making process(3). Recently, research groups such as CanmetEnergy (Canada) and Kinki University (Japan) are intensively studying bio-coke. In CanmetEnergy, the properties of the bio-coke with various levels of charcoal addition to coal blend has been evaluated (4). The biomass addition can interfere with graphitization process, which affects physical and chemical properties of bio-coke. They found that the addition of charcoal enhances the reactivity of the resultant bio-coke. The CO₂ gasification reactivity of bio-coke using TGA was also examined (3). It was observed that the mineral content (alkalinity index) plays an important role in the gasification reactivity since mineral matters acts as a catalyst. In Kinki University, the ignition behavior of bio-coke at high temperature air flow is studied (5). This is to evaluate application of bio-coke to use in stoves and furnaces. The difference in the temperature distribution inside the bio-coke and the rates of change with time induced two modes of ignition (high temperature

and low temperature). They also claimed that 20% of existing coke can be replaced by biomass to satisfy the required calorific value. However, there are sparse studies on bio-coke preparation which includes carbonization process of biomass/coal blend to prepare bio-coke.

In this study, the carbonization characteristics of biomass/coal blend such as resultant char properties and gas release rate with variation of biomass blend ratio (10,15,20,30 wt.%) and final temperature (500 – 800°C) are determined in a batch-type carbonization reactor.

EXPERIMENTAL

Materials

The testing materials used in this study were bituminous coal, biomass, and their blends. The yellow poplar wood (*Liriodendron tulipifera*) was chosen as the biomass sample since it has high production rate and short growth period applicable to wood recycling. The proximate and ultimate analysis of each sample is given in Table 1.

Table 1 The proximate and ultimate analysis of coal and biomass

Samples	Bituminous coal	Yellow poplar
Proximate analysis (wt%, as received)		
Moisture	2.21	5.31
Volatile matter	35.4	81.52
Fixed Carbon	54	11.63
Ash	8.68	1.54
Ultimate analysis (wt%, daf)		
C	81.93	47.66
H	6.04	5.91
O*	9.38	45.58
N	2.11	0.85
S	0.53	0
Calorific value (kcal/kg)	7209	4701

* calculated by difference.

Vacuum-dried sample was milled by laboratory ball-mill machine (Pulverisette 5, FRITSCH) with a particle size below 250 µm to avoid the heat and mass transfer limitations. Each biomass samples were added to the coal to make the weight ratios of 10, 15, 20, and 30 wt% of blends. The biomass/coal blends are then mixed vigorously and pelletized using press. The pellet has a cylindrical shape with diameter of 13mm and height of 6mm. '15B85C-700' indicates 15 wt% of biomass was added to 85 wt% of coal and final carbonization temperature is 700°C.

Apparatus and procedure

The carbonization of the samples was carried out in a batch-type carbonization reactor as shown in Figure 1. The reactor mainly consists of gas inlet part, electric furnace, trap (tar and water), and gas outlet part (wet gas meter and GC analyzer). Each sample (10 g) was put into a crucible and placed inside the electric furnace. The nitrogen gas (1 L/min) was introduced to the reactor by mass flow controller (MFC) and the furnace was heated from room temperature to desired temperature (500 – 800°C) with a heating rate of 15°C/min. After the

furnace reached the desired temperature, it was maintained around 30 min to finish the carbonization. During carbonization, the released gas flows into the traps to remove tar and water. The tar sampler unit has been made according to the “European Tar Protocol” (6). The sampling unit consists of six impinge bottles of which are filled with iso-propanol (IPA) solution which is cooled down to -20 °C. Then, the gas is passed through a particulate filter and water trap for collecting remaining impurities. Band heater and cartridge heater are insulated to avoid the tar and moisture condensation through the gas passage. The outlet gas flow rate was continuously monitored by a digital indicator connected to wet gas meter. The gas was introduced into a GC (HP 6890) and then analyzed with two TCD (Molecular sieve 5A, Porapak Q column) detectors. The analysis results from the GC were stored in real time, and the emitted gases from the GC flew into a hood system.

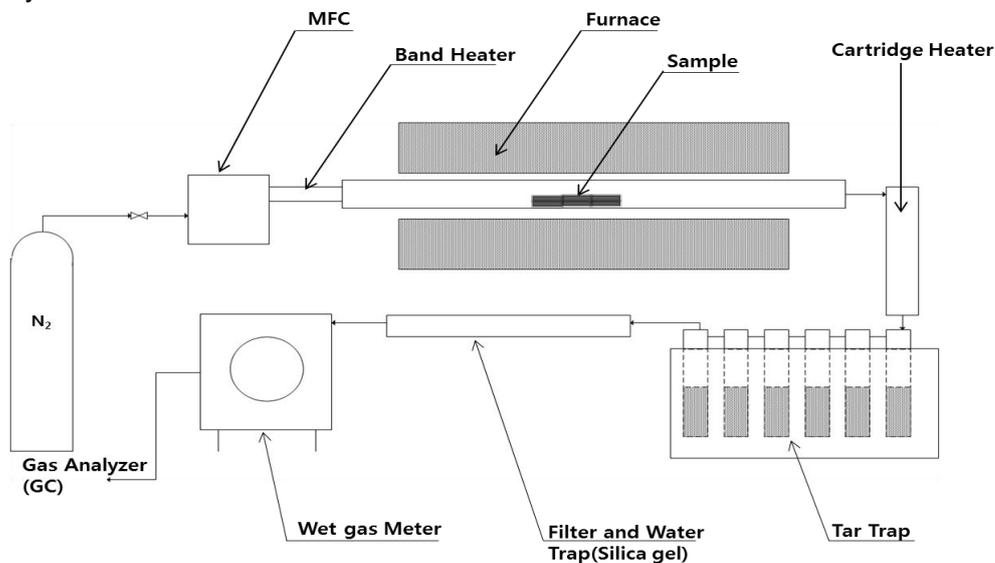


Figure 1 Schematic diagram of experimental apparatus

The resultant char is collected after carbonization. Ultimate and proximate analysis was performed with an ultimate analyzer (Thermo 1112) in accordance with ASTM D3172, D3174, and D3175. Calorific values were measured with a calorimeter (Parr 1261 EA). To determine the surface area and pore properties of the samples, the BET method (Tristar 3000, Micromeritics) was employed. Before each adsorption and desorption measurements, the dried samples were degassed at room temperature overnight.

RESULT AND DISCUSSION

Char characteristics

The pictures of raw and carbonized sample are shown in Figure 2. The biomass/coal blend pellets had a uniform cylindrical shape and size before carbonization. As the biomass blend ratio increased, the size of pellet slightly decreased after carbonization. The fibrous biomass particles attached to the coal particles in well-mixed state and reduced the swelling properties of coal as observed in coal/RDF blends (7). With increasing temperature, more volatile matter released during carbonization so that the diameter and height of pellet seemed to decrease as shown in Figure 2.

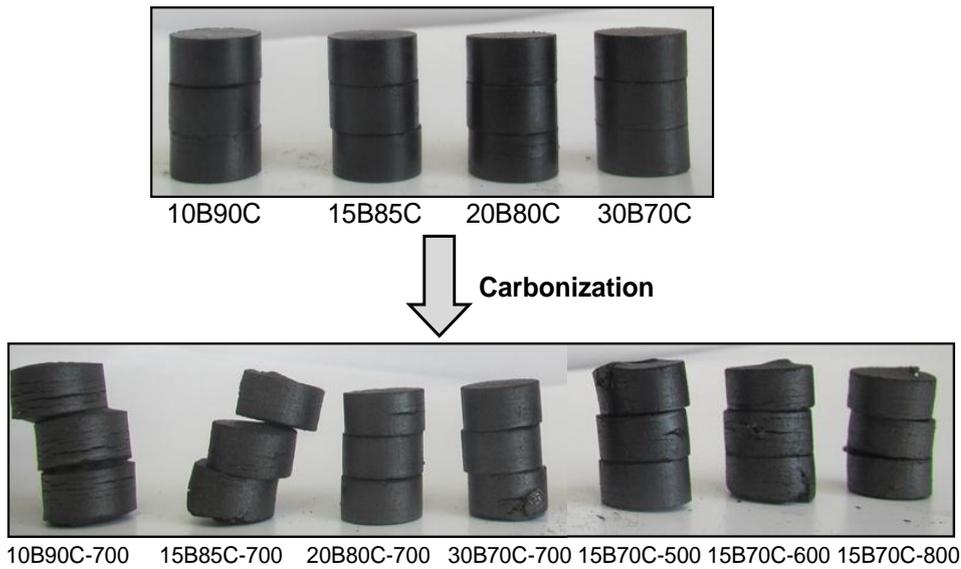


Figure 2 Pictures of raw and carbonized sample

The mass yield (η_M) and energy yield (η_E) of fuel can be represented as (8,9),

$$\eta_M = \left(\frac{W_c}{W_0} \right) \quad (1)$$

$$\eta_E = \eta_M \left(\frac{GCV_c}{GCV_0} \right) \quad (2)$$

where W_0 is the mass before carbonization, W_c is the mass after carbonization, GCV_0 is the gross calorific value of raw samples, and GCV_c is the gross calorific value of carbonized samples. As shown in Figure 3, the mass yield and energy yield decrease with increasing biomass blend ratio at 700°C and final temperature with biomass blend ratio of 15%. As biomass blend ratio exceeded 10%, the energy yield was higher than mass yield indicating that the volatile matter decreased and the fixed carbon as well as calorific value increase during carbonization(8). As temperature increased, the mass and energy yield decreased due to volatile matter release as can be seen in Figure 3 (b).

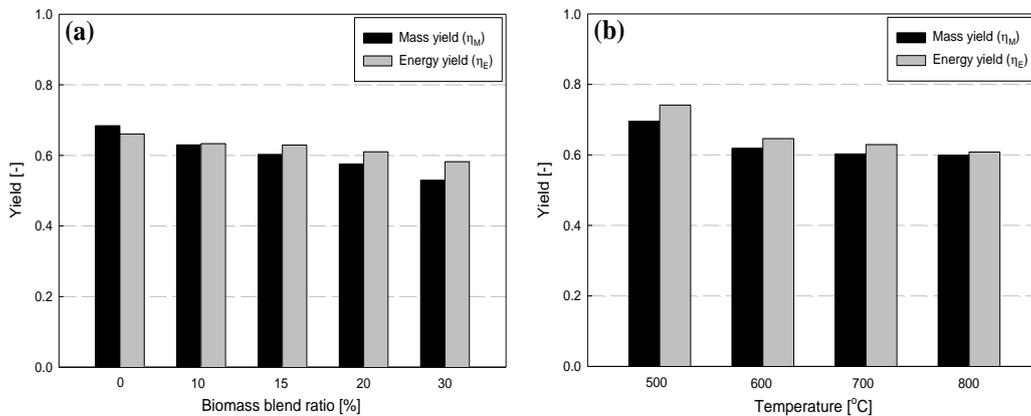


Figure 3 Mass and energy yield of char with variation of (a) biomass blend ratio and (b) temperature.

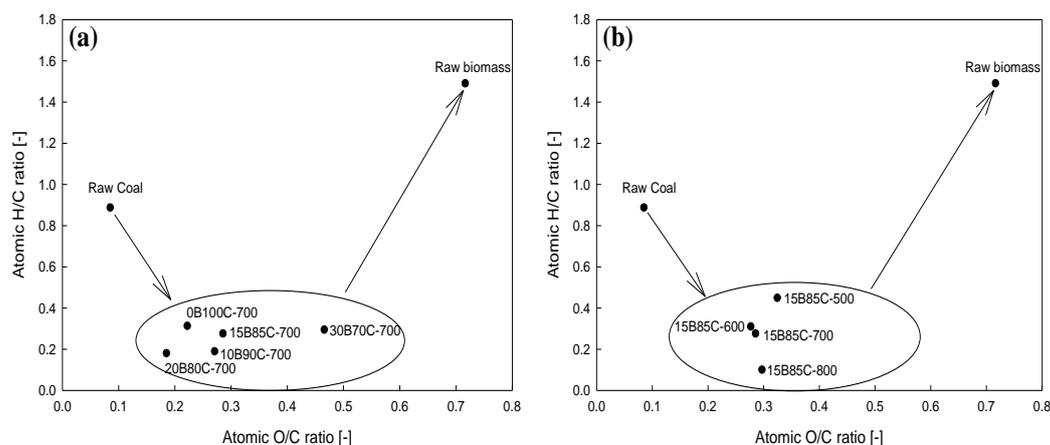


Figure 4 Van Krevelen diagrams of samples with variation of (a) biomass blend ratio and (b) temperature.

The coal-band is an index indicating a coal rank based on the degree of coalification. It can be plotted in a van Krevelen diagram (10) as the relationship between the H/C and O/C atomic ratios from the ultimate analysis of sample as can be seen in Figure 4. As shown in Figure 4 (a), the coal-band moved toward those of biomass at higher biomass blend ratio. This is due to high portion of oxygen in biomass. With increasing temperature, the H/C atomic ratio fell from 0.45 (500°C) to 0.1 (800°C) as can be seen in Figure 4 (b). With increasing temperature, H/C ratio of sample reduced as hydrogen released from the fuel. The values of O/C ratio and H/C ratio prepared in this study ranged 0.19-0.47 and 0.1-0.45, respectively. The value of H/C ratio in this study is lower than that of low temperature carbonized wood (8) and torrefied wood (9).

The specific surface area of samples are presented in Table 2. With increasing biomass blend ratio, the surface area of char drastically increased from 6.09 m²/g (coal) to 110.58 m²/g (biomass blend ratio = 30%). The increased surface area of biomass/coal blend (2) and RDF/coal blend (7) are reported. The increase in surface area can increase the reactivity and combustion behavior of char. With increasing final carbonization temperature, the surface area had the maximum value (41.62 m²/g) at 700°C. This behavior was also obtained from pectin char (11) and sewage sludge char (12). The polymerization occurred and surface area increased with increasing temperature. However, at higher temperature (800°C) the carbonization intermediate melted and decreased the surface area of sample.

Table 2 Specific surface area of samples

Sample name	Biomass blend ratio [%]	Final temperature [°C]	Specific surface area [m ² /g]
0B100C-700	0	700	6.09
10B90C-700	10	700	23.93
15B85C-700	15	700	41.62
20B80C-700	20	700	79.91
30B70C-700	30	700	110.58
15B85C-500	15	500	0.21
15B85C-600	15	600	19.11
15B85C-800	15	800	6.89

Gas release characteristics

The release rate of the most important gas components (H_2 , CH_4 , CO , CO_2) during carbonization is shown in Figure 5. Coal and biomass show different gas evolution characteristics. The main gas components from coal are methane and hydrogen whereas, the high contents of oxygen in biomass release as CO and CO_2 . The coal carbonization starts around $400^\circ C$ with emission of CO_2 with the cracking of bridge bonds with the lowest bonding energy ($-O$ from ether bridge and $-OH$ radical) as can be seen as red line in Figure 5 (13). Then large amount of methane (small aliphatic gas molecule) are formed from recombination among smaller radicals and its reaction with hydrogen. At higher temperature ($> 550^\circ C$), the hydrogenation and hydrocracking of the aromatic clusters released H_2 and CO components. On the other hand, biomass has double-maxima release profile due to its different structure decomposition temperatures (hemi-cellulose: $200 - 375^\circ C$, cellulose: $275 - 380^\circ C$, lignin: $180 - 550^\circ C$). The early release of CO and CO_2 occurs with a first peak around $460^\circ C$, followed by the release of hydrocarbons with peak around $490^\circ C$ (14). Then the second CO peak from lignin decomposition occurs around $670^\circ C$. This behavior is shown with '30B70C-700' sample which contained the highest blend ratio of biomass.

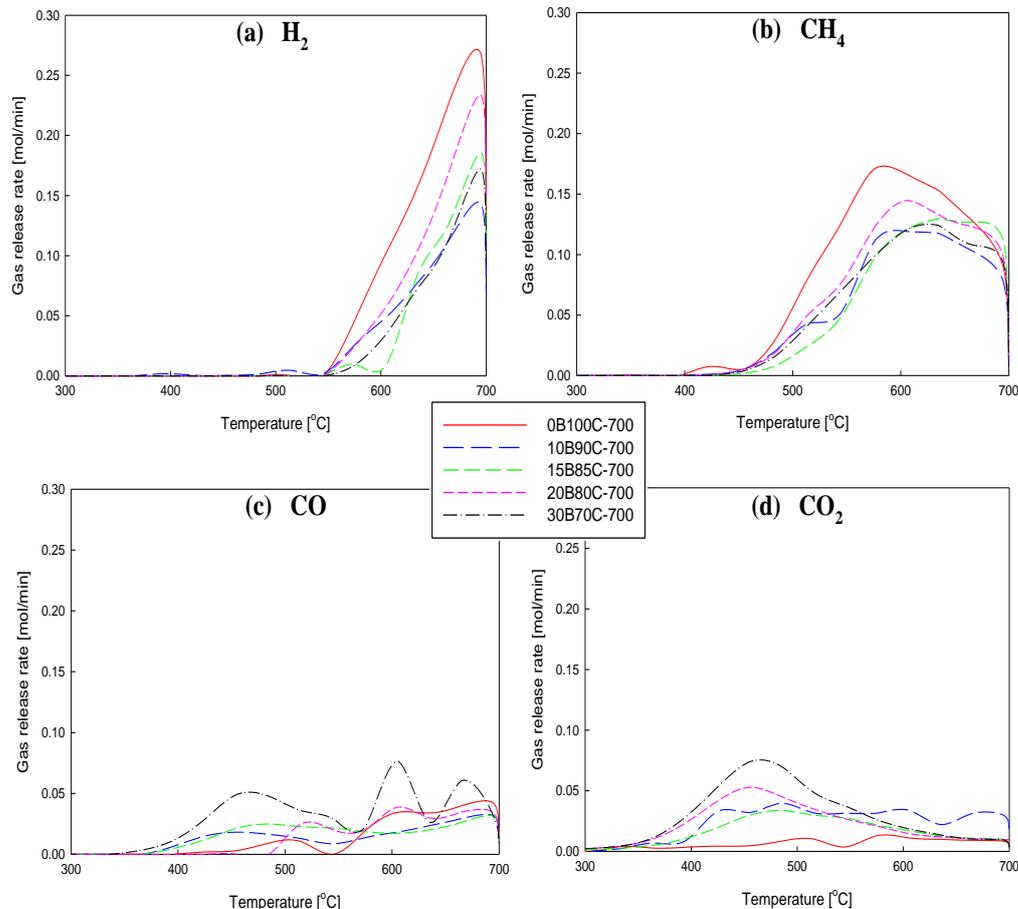


Figure 5 Gas release rate with variation of biomass blend ratio

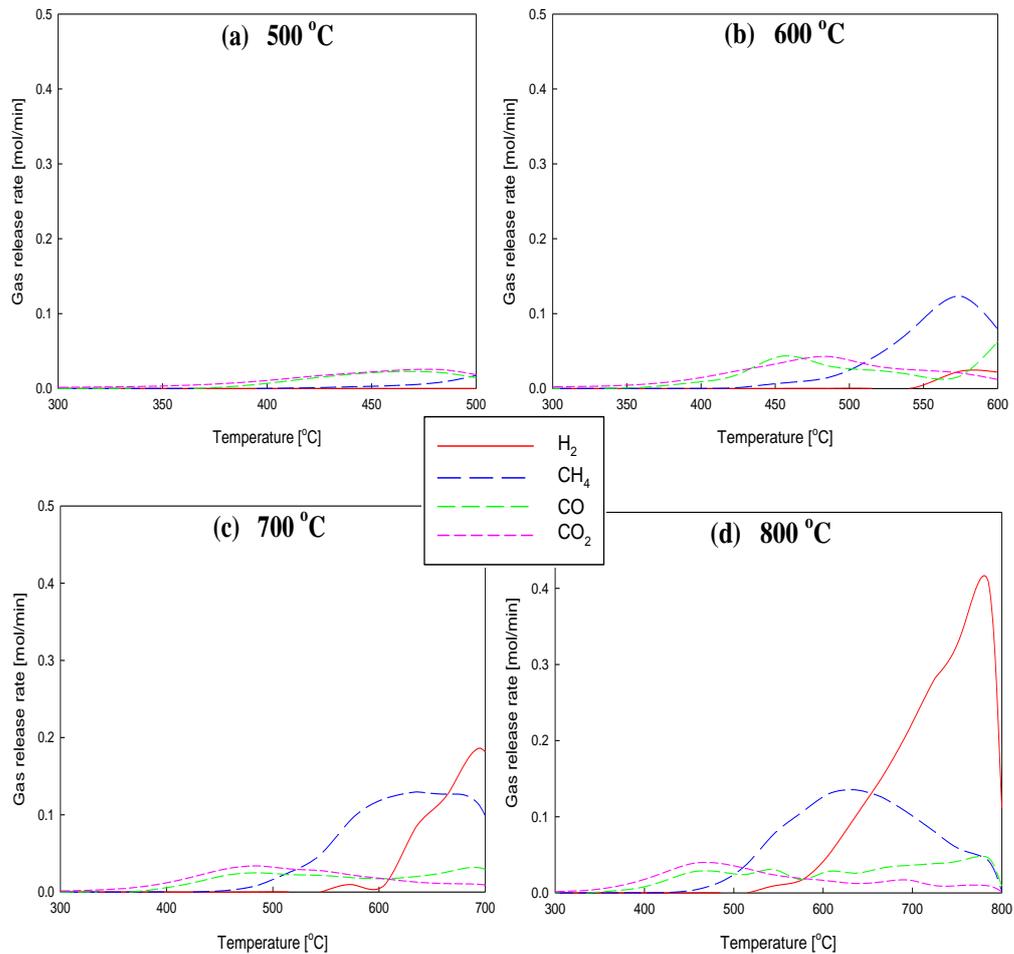


Figure 6 Gas release rate with variation of final temperature

With increasing final temperature, the gas release rate dramatically increased as observed in other reports (15,16). Figure 6 shows the gas release rate at various final carbonization temperatures (500 – 800°C) of biomass/coal blend sample (B15C75). As mentioned earlier, the carbonization of coal and biomass occurs above 400°C. However, the low temperature (500 °C) is not high enough to evolve gases. With increasing temperature, the gas released drastically for H₂ and CH₄. It is also reported that the hydrogen released from biomass had a peak around 800°C (14). This induced the maximum release of hydrogen with 800°C. It is reason for 'B15C75-800' char sample had the lowest H/C atomic ratio as observed in Figure 4 (b).

CONCLUSIONS

The carbonization characteristics such as char properties and gas release rate of biomass/coal blend with different levels (10, 15, 20, 30 wt%) at various final temperature (500 – 800°C) have been determined in a batch-type carbonization reactor. The analysis of resultant char is performed as size measurement, ultimate analysis, mass yield, energy yield calculation, and BET analysis. With increasing biomass blend ratio, the size of pellet decreases and energy yield

increases with increasing surface area. The increase in carbonization temperature is found to be disadvantageous for the char; however more volatile gas (mostly H₂ and CH₄) is released at high temperature.

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