Fundamental gasification characteristics of woody biomass in fluidized bed

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1. Background

The development of renewable energy has attracted a great deal of interest not only because of the limit of fossil fuel reserves, but also because of serious influence on global climate caused by the increased emission of CO_2 from fossil combustion. Biomass is one of the most important energy sources because it is renewable, it is abundant, and it is carbon neutral. It is necessary to improve the technologies for biomass utilizations.

Gasification is one of the most important technologies for biomass utilizations. Gasification converts biomass through partial oxidation into a gaseous mixture of syngas consisting of hydrogen(H_2), carbon monoxide(CO), methane(CH_4) and carbon dioxide(CO_2) mainly. The syngas can be used to generate heat and power like natural gas, synthesize other chemicals and liquid fuels(e.g., $CO + 2H_2 \rightarrow CH_3OH$), or produce H_2[1][2].

Fluidized beds provide many features including high rates of heat and mass transfer and good mixing of the solid phase, so fluidized beds are used for biomass gasification. In the conventional steam gasification of fluidized bed, silica sand is used as fluidizing material, some of fuel is burnt to supply heat for gasification, the product gas is with low heating value because of dilution of combustion gas and nitrogen. Twin fluidized bed gasifiers are being developed to produce high heating value syngas. In the system of twin fluidized bed gasifiers, there are two bubbling fluidized beds, which are used as a gasifier and a combustor, respectively. In the gasifier, steam is used as the fluidizing gas to encourage the shift reaction to generate hydrogen and to encourage carbon-steam reactions. In the combustor, air is used as the fluidizing gas, and the product char is burnt to heat the silica sand which is recirculated to the gasifier. The temperature of gasifier and combustor is maintained by the fluidizing material. Product quality is good from a heating-value viewpoint, but tar in the product gas is undesirable because tar condenses at reduced temperature, thus blocking and fouling process equipments such as engines and turbines. Therefore, the porous alumina is being used as fluidizing material to reduce the tars and modify product gas composition in the twin fluidized bed gasifiers[3] and the tar reduction is apparent. Although the porous alumina can almost completely remove tar, it is expensive. When the ash is removed, the expensive alumina is removed together, so the supplement is necessary, and the running cost becomes high.

2. Study objectives

The basic gasification experiments need to be conducted to find out a way in which we can efficiently get the clean gaseous product with high calorific value by the lowest cost.

3. Experimental section

Sample

Japanese cedar with particle size ranging from 0.5 to 1.0 mm was used as the sample. The sample was dried at 353K for 8h under vacuum prior to the experiment.

Pyrolysis and gasification procedure

A fluidized bed reactor made of quartz was used in this study. The inner diameters of the lower and the upper bed were 48 and 38 mm, respectively. The upper bed can be taken out if necessary. A schematic diagram of the apparatus was shown in Figure 1. The silica sand and porous alumina were used as bed material. The static bed height of silica sand and alumina were 20 mm and 30 mm, respectively. The average particle size of silica sand was 0.1 mm. The porous alumina particles were purchased from Mizusawa Industrial Chemicals Co, Ltd., Tokyo, Japan. The particle size of alumina was 0.075-0.15 mm, their specific surface area was 200 m^2/g, their pore volume was 0.44 cm^3/g. The temperature was maintained at prescribed values by means of an electric furnace. The thermocouple was used to detect the temperature change at all times. Argon gas was used as an inert fluidizing gas. Its flow rate was 1.0 L (STP)/min. The gasifying agent, steam, was supplied by a liquid chromatography pump. The biomass sample (BM) was continuously fed into the pyrolysis zone by a screw feeder (at a feed rate of 0.25-0.3 g/min) and transported downward by argon gas [at a flow rate of 1.0 L (STP)/min]. Cold trap (273K), tar trap (213K) and thimble filter were connected in series at the exit of the reactor to capture steam, tar, and minute particles. The gaseous products were introduced to a high-speed gas chromatography (CP-4900 Varian Inc., CA). The gas flow rate at the exit of the filter was monitored at all times by a flow-meter.

Three patterns of gasification experiment were conducted at 973 K. The experiment of pattern A was conducted to simulate the conventional steam gasification. No catalyst was used in pattern A. The experiment of pattern B was conducted to simulate the gasification where the pyrolysis and gasification reactions occur at the same time. The experiment of pattern C was conducted to simulate the gasification where the pyrolysis reactions occur first, and then the gasification reactions occur.

To confirm the individual gasification characteristics of char and coke, the separate gasification of char and coke were conducted. After pyrolysis at 973 K, the reactor was cooled to ambient temperature, then char and coke were gasified at 1073K, respectively. Kinetic studies of the carbon-steam reaction are of great significance for the design of technical gasification plants. Therefore, the gasification rate of char and coke were investigated separately.
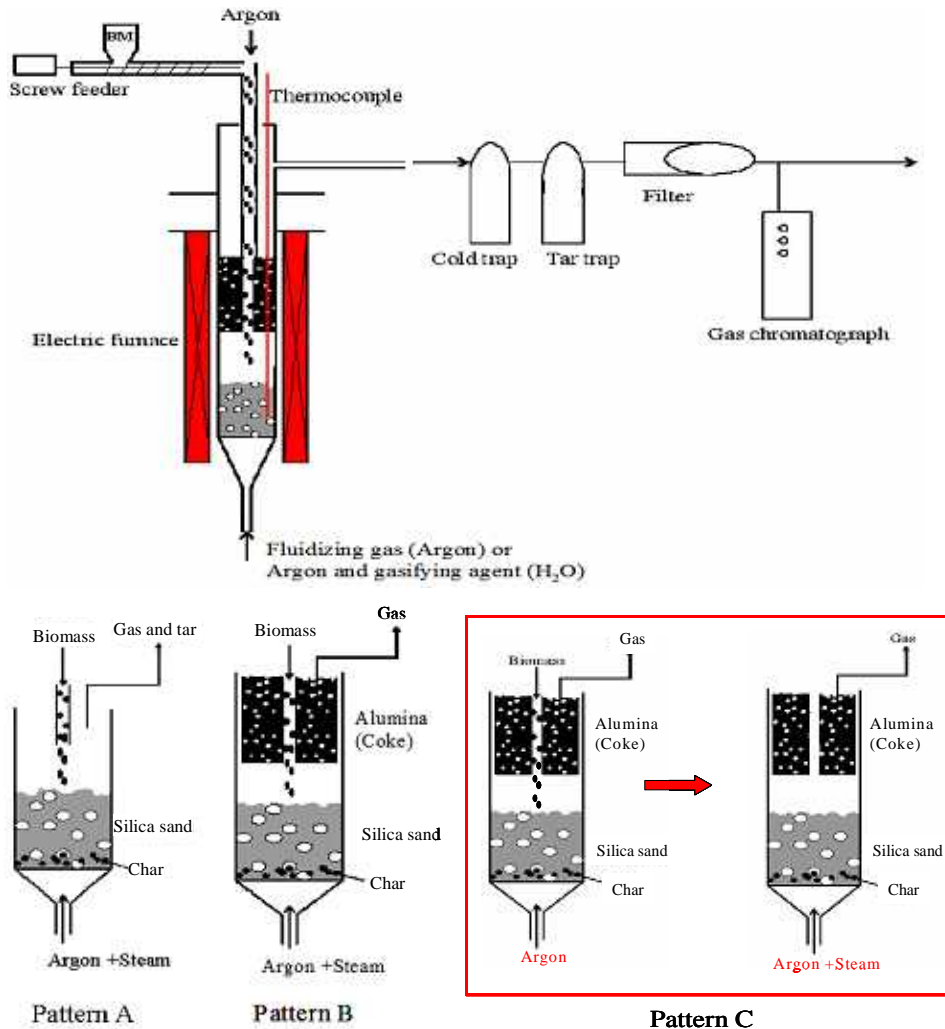

Figure 1. Schematic diagram of the experimental apparatus and the details of the experiment patterns.

4. Results and Discussion

4.1 Gas composition characteristics in pyrolysis

Firstly, pyrolysis was carried out on silica sand. A lot of tar was formed and evacuated from the reactor when pyrolysis was carried out on silica sand, CO and CO_2 were the dominant gases at 873 K (Figure 2-a), CO and H_2 became the dominant gases at 973 K (Figure 2-b). High temperature increased the yield of gaseous products. On the other hand, when pyrolysis was carried out on silica sand and alumina, most of the tar was captured by the alumina, and the amount of evacuated tar was quite small. The tar deposited on the alumina was defined as coke hereafter. The total yield of gaseous products was increased at both 873 K (Figure 2-c) and 973 K (Figure 2-d) by using alumina apparently. The coke was cracked to form H_2 and CO_2 mainly. The thermal cracking of tar was promoted to some extent owing to the temperature increase. Particularly, the yield of H_2 was increased by using alumina at higher temperature.
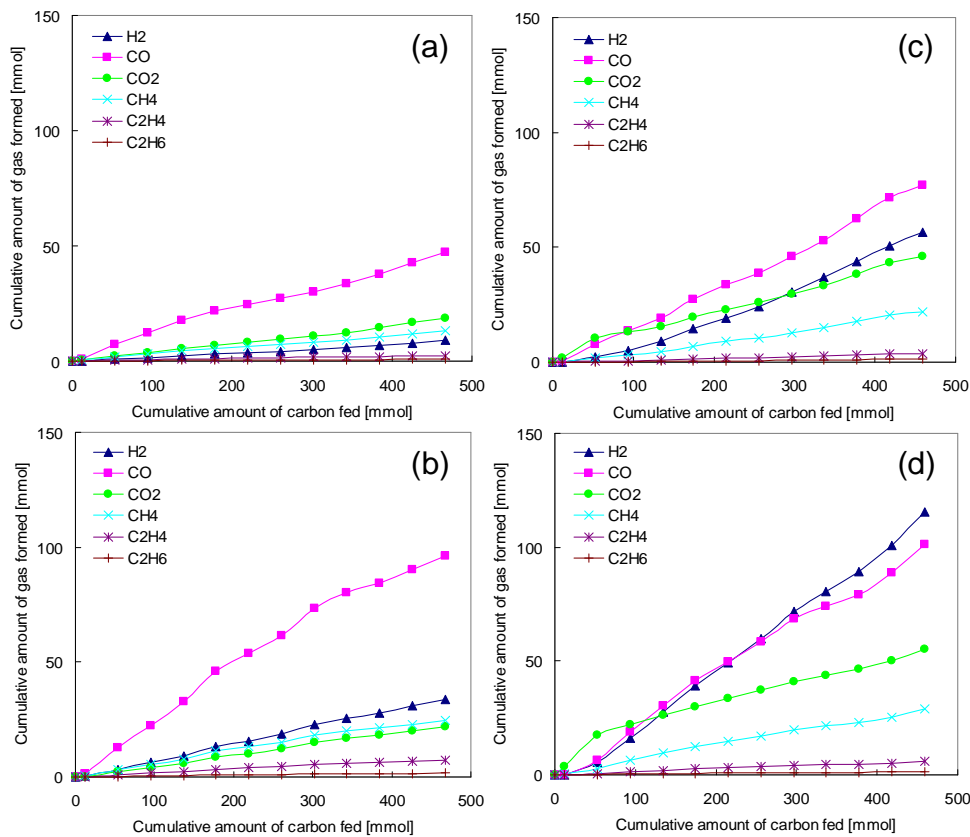
Figure 2. Yields of gas formed during pyrolysis of cedar. (a) bed material, silica sand; 873 K. (b) bed material, silica sand; 973 K. (c) bed material, silica sand and alumina; 873 K. (d) bed material, silica sand and alumina, 973 K.

4.2 Gas composition characteristics in gasification

The results of gasification in pattern A, B, and C at 973 K are shown in Figure 3. Comparing the results of pattern A with pattern B, the total yield of gaseous products was increased by using alumina apparently, besides tar was deposited in the pores of the alumina and thermally cracked, the coke formed was also gasified by the steam. Comparing the results of pattern B with pattern C, little change in the yields of gaseous products containing carbon (CO, CO_2, CH_4, C_2H_4, C_2H_6) was observed, whereas the yield of H_2 was increased in pattern C, because in pattern B steam gasification was inhibited to some extent by volatiles formed from the pyrolysis.

The results of separate gasification of char and coke are shown in Figure 4. The yield of CO in coke gasification was much higher than that in char gasification, and the yield of CO_2 in coke gasification was lower than that in char gasification. The plausible reason[4] is that in coke gasification, the coke was reformed with steam through the following reaction:

$$C(in\ coke) + H_2O(g) \rightarrow CO + H_2$$
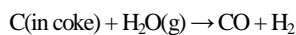
At the same time, coke was thermally cracked into CO_2 and H_2 by alumina.   On the other hand, in char gasification, the char was reformed with steam through the following reaction:

$$C(in\ char) + H_2O(g) \rightarrow CO + H_2$$

$$CO + H_2O \rightarrow CO_2 + H_2\ (water\text{-}gas\ shift\ reaction)$$
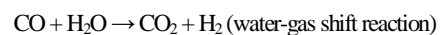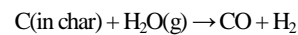
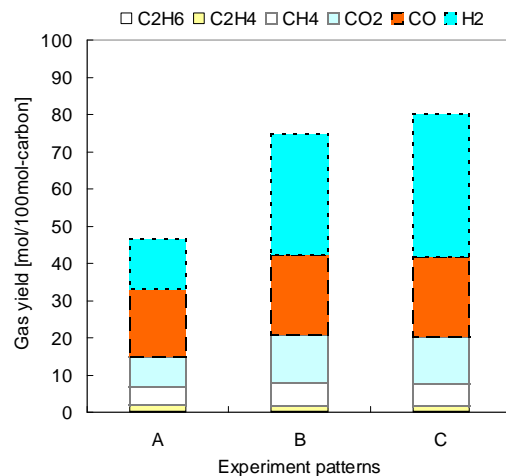The CO formed was consumed in the water-gas shift reaction to some extent.

Figure 3. Gas yield during gasification in different patterns (973 K, steam: 40 vol%)
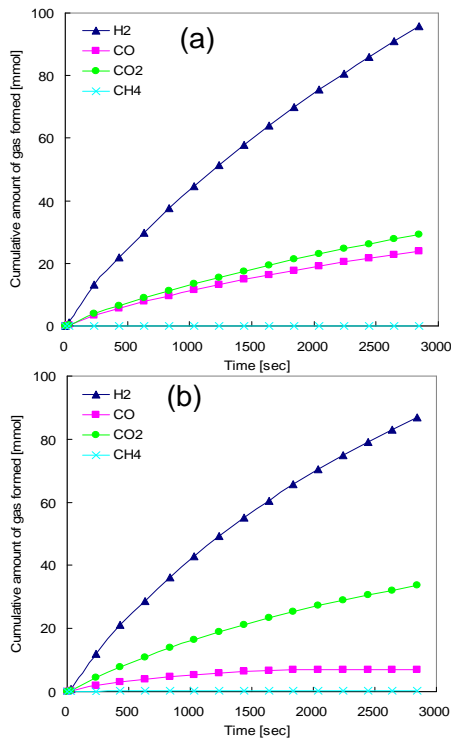
Figure 4. Variation of the cumulative amount of gas formed with time in separate gasification of (a) coke and (b) char.

4.3 Gasification rates of coke and char

The variation of carbon conversion with time during the gasification of coke and char at different temperature and at different steam partial pressure are shown in Figure 5 and 6, respectively. Though not shown here, in the initial 600 seconds of gasification, good linearity was obtained for first-order kinetic plots of the unconverted fraction of carbon in all char and coke gasification under different conditions. It means that the kinetics of steam gasification of coke and char can be described as

$$dX/dt = k(1-X) \quad \dots(1)$$

X: carbon conversion into gas [%];

k: the reaction rate constant [1/sec]; t: time [sec].

$$k = A P_{H2O}^{n} \exp(-E/RT) \quad \dots(2)$$

A: frequency factor, P_{H2O}: steam partial pressure, E: activation energy, R: gas constant, T: thermodynamic temperature, n: steam partial pressure dependence factor.

After E, n and A are calculated, the gasification rates of coke and char can be described by the following equations:

$$k_{char} = 61.575 (P_{H2O})^{0.5973} \exp(-120237.1/RT) \quad \dots(3)$$

$$k_{coke} = 3 \times 10^{6} (P_{H2O})^{0.4323} \exp(-208498.5/RT) \quad \dots(4)$$

Though not shown here, in the first 600 seconds, the value predicted by equation (3) and (4) is in conformity with the data from experiments.
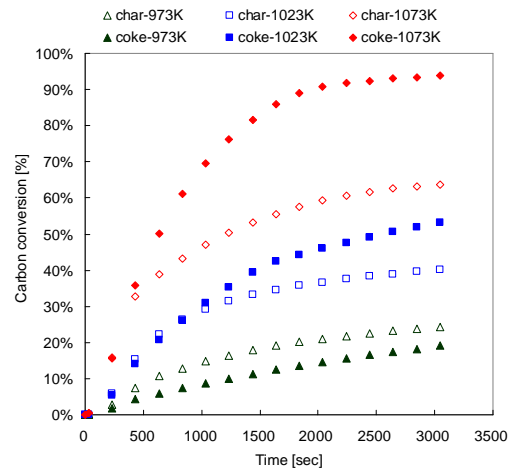

Figure 5. Variation of carbon conversion with time during gasification at different temperature (steam: 40 vol%).
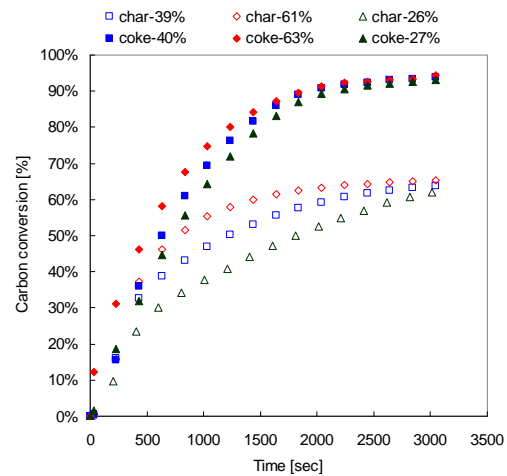

Figure 6. Variation of carbon conversion with time during gasification at different steam partial pressure (1073 K).

5. Conclusion

The gasification where the pyrolysis was conducted first, then the coke and char were gasified was proved to be an efficient method to get the clean gaseous product with composition ratio of 1-2 of H_2 to CO. All of tar could be captured and converted into gas as much as possible during pyrolysis and gasification if enough alumina is used. The gasification rates of coke and char were also clarified.

6. References

[1] Gaseous fuel production from biomass and the energy utilization, (in Japanese) NTS, 2007.10.5 first published. [2] A.V. Bridgwater. Fuel 1995, 74, 631-653. [3] K. Matsuoka; K. Kuramoto; T. Murakami; Y. Suzuki. Energy and Fuels 2008, 22, 1980-1985. [4] K. Matsuoka; T. Shimbori; K. Kuramoto; T. Nanba; A. Morita; H. Hatano; Y. Suzuki. Energy and Fuels 2006, 20, 1315–1320.