

# Characteristics of Fast Pyrolysis and Char Product of a Low-Rank (Sub-bituminous) Coal in High Temperature Drop Tube Furnace (HT-DTF)

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**Abstract:** In this study, fast pyrolysis characteristics of a sub-bituminous (SB) coal were investigated using a high temperature drop tube furnace (HT-DTF). Effect of pyrolysis temperature (850, 1000 and 1300°C) on product distribution (char, soot and gas yield) as well as the gas composition was investigated. The product chars were characterized for the intrinsic combustion reactivity under isothermal condition at 550°C using a TGA and for surface properties using BET analysis and SEM. The results showed that, with increasing temperature, char yield decreased while gas and soot significantly increased especially at above 1000°C, suggesting the occurrence of secondary reactions. The disappearance of hydrocarbon gases (CH<sub>4</sub> + C<sub>2</sub> HC gases) and sharp decrease of CO<sub>2</sub> with a significant increase of CO and H<sub>2</sub> at above 1000°C strongly suggests the reactions of hydrocarbon fractions with CO<sub>2</sub> and steam. The DTF char prepared at 1300°C gave the highest intrinsic combustion reactivity at 50% char conversion with R<sub>50</sub> and t<sub>50</sub> of 66 × 10<sup>-4</sup> s<sup>-1</sup> and 80 s, respectively. This might be due to its high surface area and highly porous structure. However, the char prepared at lower temperatures had lower burnout time, t<sub>b</sub>, which may be due to the difference in pore structural change with conversion.

**Keywords:** Fast pyrolysis, sub-bituminous coal, drop tube furnace, coal, char.

## 1. Introduction

The demand of coal in Thailand is still increasing every year and is used mainly for power utilities and industrial sector such as cement, paper and textile industries [1]. Over 53% of total coal consumed is imported mostly from Indonesia and is of sub-bituminous (SB) type. In Thailand, coal is combusted in pulverized coal combustion boilers or fluidised bed combustion boilers for steam and power generation. So far, the combustion behavior of low rank coals (sub-bituminous coal and lignite) is less investigated when compared to high rank coals. To achieve high efficiency, in-depth understanding of combustion behavior of coal used is therefore necessary. Pyrolysis is an important early step of combustion, which strongly influences the subsequent combustion reaction. Pyrolysis characteristics in terms of product distribution, product gas composition and char properties are useful information to understand the behavior of the overall combustion process.

In this study, fast pyrolysis of sub-bituminous (SB) coal was carried out in a high temperature drop tube furnace (HT-DTF). Effect of pyrolysis temperature (850, 1000 and 1300°C) on product distribution (char, soot and gas yield) and product gas composition was investigated. In addition, the char was analyzed using a TGA under an isothermal condition for the intrinsic combustion reactivity, BET surface area measurement and SEM for the char morphology.

## 2. Material and methods

Sub-bituminous (SB) coal was ground and sieved to the particle size less than 106 µm. Before use, it was oven dried at 110°C for 6 hr. The proximate and ultimate analyses and heating value of the SB coal are shown in Table 1.

Pyrolysis of SB coal under N<sub>2</sub> atmosphere at different temperatures (850, 1000 and 1300°C) was conducted in a high temperature drop tube furnace (HT-DTF). The schematic diagram of DTF is illustrated in Fig. 1 with the specification and pyrolysis conditions used in this study. Drop tube furnace (DTF) is a useful device that can closely simulate the reaction conditions in a large-

scale reactor [2]. The HT-DTF consists of three electrical heaters which were individually controlled to ensure a uniform temperature distribution (as also presented in Fig. 1). After heating the furnace to the required temperature, the pulverized coal was continuously fed with constant feed rate of 47.8 g/hr for 30 min. During testing, pyrolysis gas was characterized by using the online-micro GC equipped with TCD detector with the interval time of 2 min. Main gaseous product detected included H<sub>2</sub>, CO, CH<sub>4</sub>, CO<sub>2</sub>, C<sub>2</sub>-hydrocarbon gases. After finished each run, the pyrolysis char so-called "DTFchar" was collected from char pot and weighed to determine the char yield. Particles adhering to the inner wall of reactor were also collected and weighed to determine the "soot" fraction. The gas yield was calculated from the gas composition determined by micro GC and N<sub>2</sub> balance, while the other fraction which is likely to contain mainly heavy tars, light tars and water was determined by difference.

Intrinsic combustion reactivity of char was analyzed using a thermogravimetric analyzer (Shimadzu model TA50) under isothermal condition at 550°C. 2-3 mg of the DTF char powder was heated up with heating rate of 20°C min<sup>-1</sup> to 550°C under N<sub>2</sub> flow (100 mL min<sup>-1</sup>). After the weight stabilized, air was introduced at the same flow rate to replace N<sub>2</sub> and the temperature was maintained until the combustion was complete. Under such condition, the mass transfer limitation may be assumed negligible. Conversions of char, X, and char reactivity, R<sub>x</sub>, were determined by Eq. (1) and (2), respectively.

$$X = \frac{m_0 - m}{m_0} \quad (1)$$

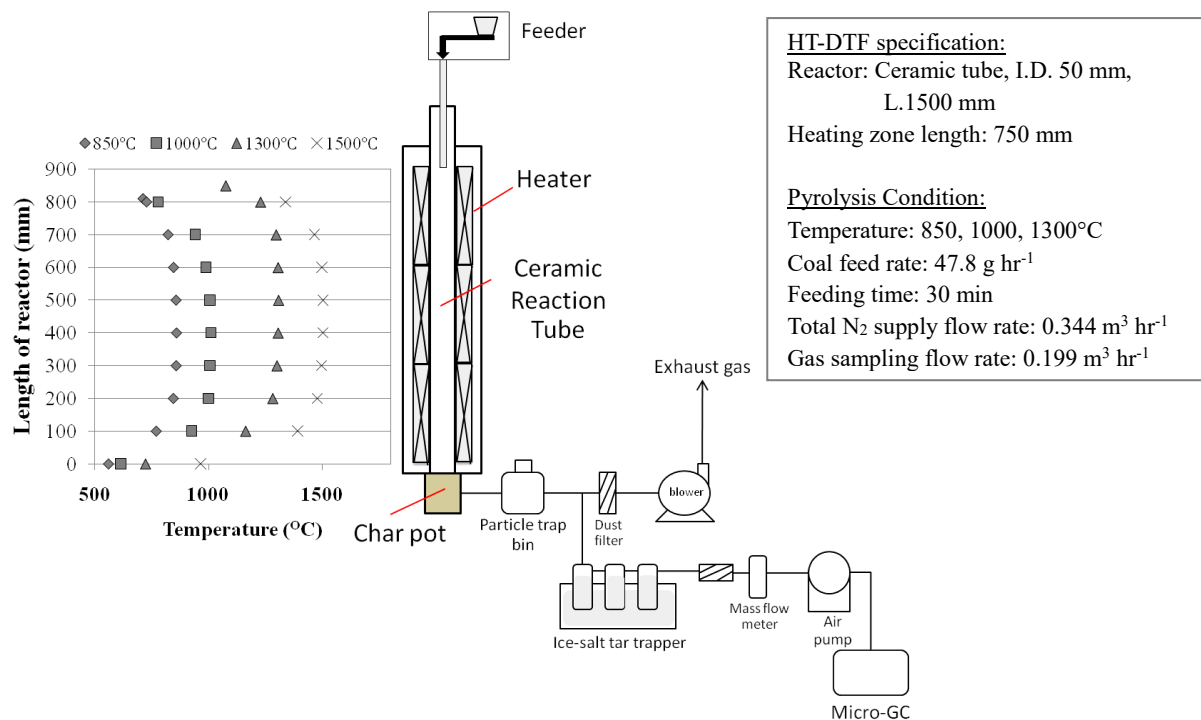
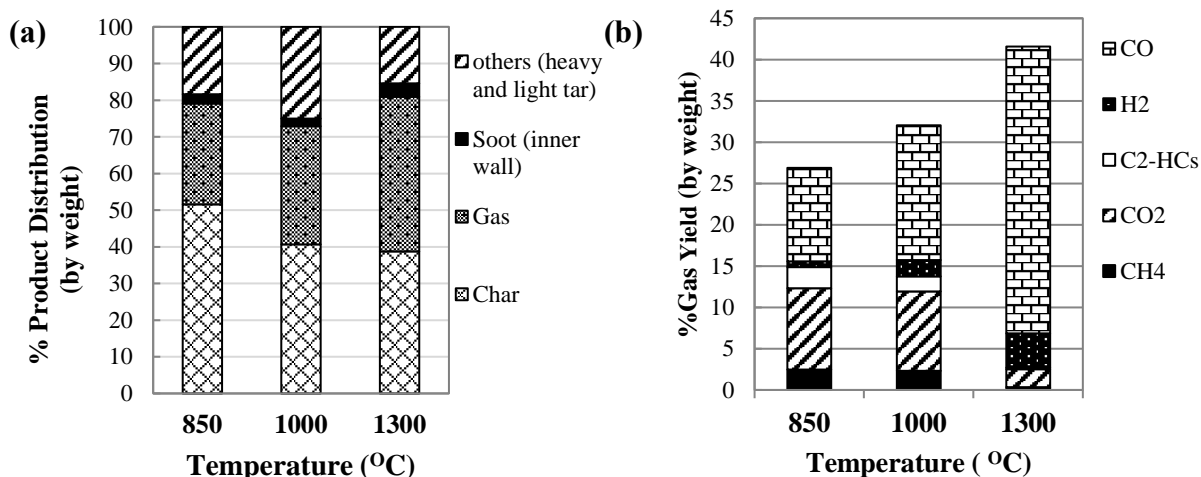
$$R_x = -\frac{1}{m_0} \left( \frac{dm}{dt} \right)_x \quad (2)$$

where m and m<sub>0</sub> were the weight of char at any time (t) and initial weight of char on dry-ash-free basis, respectively. The surface area and pore structure of the DTF char were characterized by Brunauer-Emmett-Teller (BET) analysis and the morphology was characterized by using Scanning Electron Microscope (SEM) (JEOL model JCM-6000).

**Table 1.** Proximate, ultimate and heating value analyses of the sub-bituminous (SB) coal.

	moisture (wt% as received)	Proximate analysis (wt% dry basis)			Ultimate analysis (wt% dry ash free basis)					HHV (MJ/kg dry coal)
		ash	volatile matter	fixed carbon	C	H	N	S	O*	
SB coal	19.5	3.9	51.4	44.6	62.6	5.3	1.2	0.5	30.4	25.5

\* by difference

**Figure 1.** Schematic diagram of the high temperature drop tube furnace (HT-DTF), temperature profile along the reactor height and pyrolysis condition used in this study.**Figure 2.** Effect of pyrolysis temperature on (a) product distribution and (b) Gas product composition from the pyrolysis of SB coal.

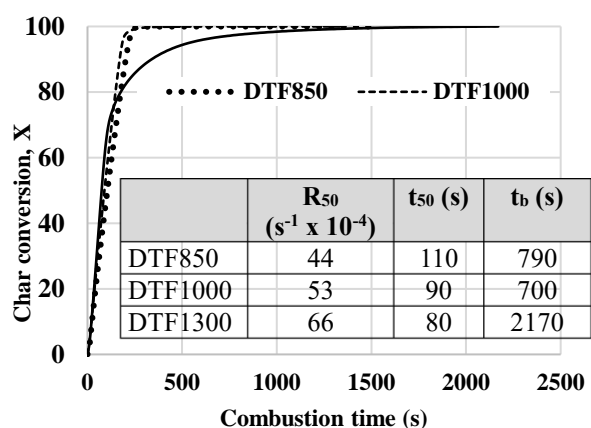
### 3. Results and Discussion

Product distribution from fast pyrolysis of SB coal at different temperatures is shown in Fig. 2(a). It was observed that, as temperature was increased, char yield decreased and started to level off after 1000°C indicating the end of devolatilization. The fraction of (tar+water) initially increased with temperature and started to decrease after 1000°C. This observed decreasing trend coincided with the significant increase of gas and soot generation,

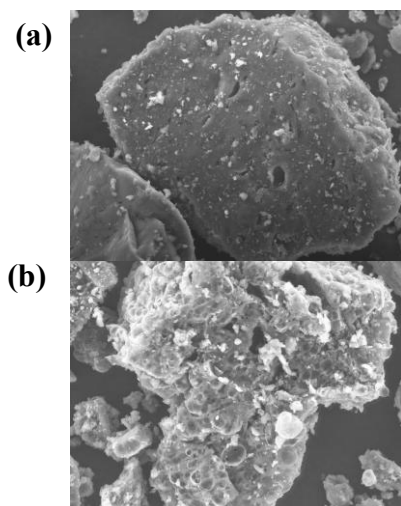
suggesting that secondary reactions occurred at sufficiently high temperature. The formation of solid carbon so-called coke or soot from the volatiles produced during the initial devolatilization at high temperature above 1000°C is well known [3]. The change of product gas composition as shown in Fig. 2(b) was also an evidence of secondary reactions. The disappearance of hydrocarbon gases (CH<sub>4</sub> + C<sub>2</sub>-HC gases) and sharp decrease of CO<sub>2</sub> with double amount of CO and H<sub>2</sub> at 1300°C as compared to 1000°C strongly suggests the reactions of hydrocarbon fractions with CO<sub>2</sub> and

steam at that temperature range. Previous studies similarly found that reforming of gaseous hydrocarbons by CO<sub>2</sub> and pyrolytic steam was promoted at high temperature [4-5].

Char conversion and char reactivity profiles with respect to time are shown in Fig. 3. The combustion reactivity of char and the time to achieve 50% conversion ( $R_{50}$  and  $t_{50}$ ) as well as the burnout time ( $t_b$ ) were also estimated. At 50% conversion, the char prepared at higher temperature tended to have a higher reactivity, e.g. the char prepared at 1300°C (DTF1300) had the highest reactivity of  $66 \times 10^{-4} \text{ s}^{-1}$  and the lowest  $t_{50}$  at about 80 s. These phenomena were confirmed by BET surface area measurement and SEM analysis as shown in Table 3 and Fig. 4, respectively. DTF1300 had the highest BET surface area (i.e.  $222.9 \text{ m}^2 \text{ g}^{-1}$ ) and highly porous structure as compared to DTF850. However, as conversion further progressed, the reactivity of char prepared at lower temperature overtook the high temperature ones, which resulted in the lowest  $t_b$  for DTF850 (i.e. 790 s). This may be caused by the difference in pore structural change with conversion as found in earlier studies [6].



**Figure 3.** Char conversion profile with time of the combustion of DTF char derived from different pyrolysis temperature.



**Figure 4.** SEM images of (a) DTF850 and (b) DTF1300 (700X magnification).

**Table 3.** BET surface area of the DTF chars prepared at different temperatures.

	BET surface area ( $\text{m}^2 \text{ g}^{-1}$ )
DTF850	2.66
DTF1000	106.00
DTF1300	222.89

#### 4. Conclusion

Fast pyrolysis of a sub-bituminous (SB) coal was carried out in a high temperature drop tube furnace (HT-DTF) to investigate the effect of pyrolysis temperature (850, 1000 and 1300°C) on product distribution (char, soot and gas yield), gas composition and char properties. With increasing temperature, char yield decreased while gas and soot significantly increased especially at above 1000°C. The results suggest that secondary reactions occurred at such high temperature including soot formation and reforming reactions of hydrocarbon fractions with CO<sub>2</sub> and steam. Char prepared at 1300°C gave the highest intrinsic combustion reactivity at 50% char conversion but the longest burnout time. This may be caused by the difference in pore structural change with conversion of different chars.

#### Acknowledgement

This work was performed under the frameworks of the Japan-Thailand joint research program called Science and Technology Research Partnership for Sustainable Development (SATREPS), Project: Development of clean and efficient utilization of low rank coals and biomass by solvent treatment. The authors would like to thank PTT public company, the Higher Education Research Promotion and National Research University Project of Thailand, Office of the Higher Education Commission to provide the financial support.

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