

## A ROLE OF DEVELOPING PORES FOR ORGANIC SULFUR RELEASE IN HYDROPYROLYSIS OF COAL

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### INTRODUCTION

In our previous papers [1-4], we examined the dynamic behavior of sulfur forms during hydrolysis of coal, changing heating rates from 40 K/min (fixed bed pyrolyzer, 1 atm hydrogen pressure) and 10 K/min (fixed bed pyrolyzer, 30 atm hydrogen pressure) to 6000 K/s (free fall pyrolyzer, 1 atm hydrogen pressure). The desulfurization feature was characterized by a kinetic model as shown later, and the simulation of observed results was successful by applying the volume reaction model. We noticed that the extent of sulfur release from solid depended on the operating hydrogen pressure and on the heating rate. As for the organic sulfur in solid, it efficiently decreased when a rapid pyrolysis condition was adopted [4]. We pointed out that the release rate of volatile organic sulfur to tar and gas increased with increasing the release rate of volatile matter and with increasing the internal surface area at an initial stage of heating. The purpose of the present paper is to elucidate a role of developing pores which facilitate the organic sulfur release during rapid hydrolysis of coal.

### EXPERIMENTAL

Table 1 shows the proximate, ultimate (daf basis), and sulfur form (% of total sulfur) analyses of sample coals: PSOC-830 (Indiana), Rosebud (Montana). A schematic diagram of the free fall pyrolyzer is shown in Fig.1. Coal particles (ca. 0.5 mm) were supplied from the hopper into the reactor at a feed rate of 0.2 g/min. The heating section length was controlled by changing the number of heating blocks from one to five as seen in the figure. Hydrogen gas flowing upwards (2.0 l/NTP/min) encountered the coal particles and flowed out with gaseous products and tar. Volatile matter was determined by the difference of the weight of coal supplied and that of char received at the bottom of reactor. Hydrogen sulfide in gaseous products, the sulfur forms in coal and char were analyzed quantitatively [4]. The internal surface areas of the coal and char were measured by applying the Dubinin-Polanyi equation to CO<sub>2</sub> adsorption isotherms at 273 K.

## KINETIC MODEL FOR DYNAMIC BEHAVIOR OF SULFUR FORMS

We proposed a kinetic model as illustrated in Fig. 2 where C and D were assumed firstly [2] to be present in void and later [4] in pores. Based on the Dusty Gas Model [5], we assume here that C represents organic sulfur in tar in macropores and D hydrogen sulfide in gaseous products also in macropores. Micropores would play an important role for the surface reaction of reactants in solid. Decomposition of organic sulfur in coal, A into C and D, occurs at an initial stage of heating with volatile matter release. C and D in macropores could be reattached to solid phase, however, pressure increase in macropores with the evolution of volatile matter would facilitate the release of C and D to outside of a particle. As a consequence, we assume that only D forms refractory organic sulfur B at a later stage of heating where the remarkable evolution of volatile matter almost ends. Rate constants are the 1st order for  $k_1 - k_3, k_6 - k_8$ , the 0.5th order for  $k_4$ , and the 2nd order for  $k_5$ . Further reduction of iron sulfide F is negligible in the atmospheric treatment [4]. The release rates of C and D from macropores to outside of a particle are assumed to be the 1st order to their concentrations in macropores and the rate constants to be equal to the observed 1st order rate constant  $k$  for volatile matter release [4].

## EXPERIMENTAL RESULTS AND DISCUSSION

The top section of Fig. 3 shows a calculated curve of particle temperature  $T_c$  for PSOC-830 coal along with the distance from the coal hopper  $X$ . A set of simultaneous differential equations derived from the momentum, heat, and material balances for a particle were solved iteratively to give the relations of  $T_c$  and  $X$  and particle residence time  $t_R$ . Details of the calculation method are the same as in the reference [4]. A vertical dashed line denotes the point where the temperature begins to rise: particle residence time  $t_R$  was set to be 0 at  $X = 56$  cm. Another calculation was also conducted for Rosebud coal which kept a larger apparent density in the pyrolyzer. The particle residence times  $t_{RS}$  were 0.17, 0.25, 0.33, 0.41, 0.49 s for PSOC-830 coal, and 0.16, 0.24, 0.30, 0.36, 0.42 s for Rosebud coal, respectively, with the heating section lengths of 30 ( $X=116$ ), 60 (146), 90 (176), 120 (206), 150 (236) cm. The middle section demonstrates change in internal surface area: a drastic change for PSOC-830 coal and a moderate increase for Rosebud coal. It should be noticed that the dynamic feature was quite different within the order of 100 ms even if the final value attained nearly the same. The bottom section of Fig. 3 represents the observed relation between volatile matter released  $V$  and the distance from the hopper  $X$ . Dashed lines are the calculated values with Eqs. (1) and (2):

$$dV/dt_R = k_0 \cdot \exp(-E/RT_c) \cdot (V^* - V) \quad (1)$$

$$V = 0 \text{ at } t_R = 0 \quad (2)$$

where  $V^*$  means the ultimate value. A smaller value of the activation energy for PSOC-830 coal, 18 kcal/mol, would relate to the rapid development of micropores, compared with a larger value of 30 kcal/mol for Rosebud coal.

Figures 4 and 5 are observed changes in the sulfur forms distribution with  $X$  or  $t_R$  for PSOC-830 and Rosebud coals, respectively. Simulation curves are also drawn with one boldfaced and three lightfaced lines in each figure. The part below the boldfaced line in the figure indicates inorganic and organic sulfurs in solid. One can see that the organic sulfur content in solid in PSOC-830 coal decreases more rapidly and efficiently than Rosebud coal. When we concentrate our attention on the sulfur behavior at an initial stage of heating, i.e.  $t_R < 0.2$  s, we can evaluate the reaction characteristics of organic sulfur in solid with the rate constants,  $k_1 - k_3$ . The simulated values at 1233 K are as follows:

	$k_1$ [1/s]	$k_2$ [1/s]	$k_3$ [1/s]	$k$ [1/s]
PSOC-830	10.1	12.6	25.2	27.7
Rosebud	6.9	4.0	10.1	19.2

Calculated values of the rate constants for volatile matter release with Eq.(1) and (2) are also included. The data suggest that the role of developing micropores is very important for efficient release of organic sulfur from solid.

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Table 1 Ultimate, proximate and sulfur form analyses

Sample	C	H	N	S	Diff.	VM(daf)	FC(daf)	Ash(dry)	FeS <sub>2</sub>	SO <sub>4</sub> <sup>2-</sup>	Organic
PSOC 830	71.0	4.4	1.1	1.3	22.2	40.7	59.3	5.6	13	7	80
Rosebud	72.9	4.5	0.9	0.9	20.8	44.3	55.7	10.2	32	3	65

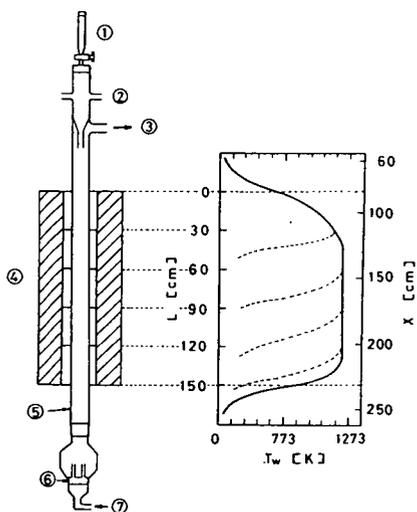


Fig.1 Schematic diagram of free fall pyrolyzer and longitudinal wall temperature profiles of reactor.

- 1, coal hopper
  - 2, entrained gas inlet
  - 3, gas outlet
  - 4, furnace(5 blocks, 30 cm per block)
  - 5, reactor (fused silica tube, 36 mm i.d.)
  - 6, glass filter
  - 7, gas inlet
- L, length of furnace  
X, distance from coal hopper

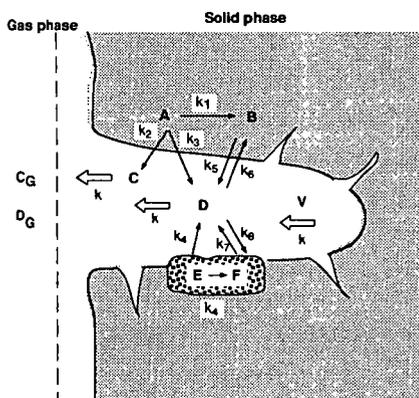


Fig.2 Image of desulfurization of coal.

- A : (Sorg)coal
- B : (Sorg)char
- C : (Sorg)tar
- D : SH<sub>2</sub>S
- E : SFeS<sub>2</sub>
- F : SFeS
- V : Volatile matter

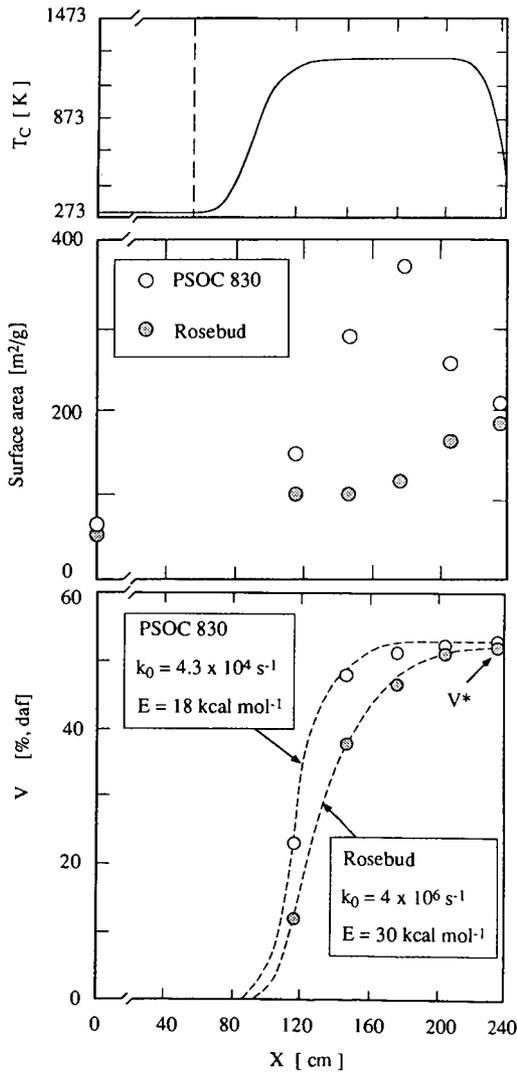


Fig.3 Estimated particle temperature  $T_c$ , internal surface area observed and volatile matter released  $V$  with simulation curve along with distance from coal hopper  $X$ .

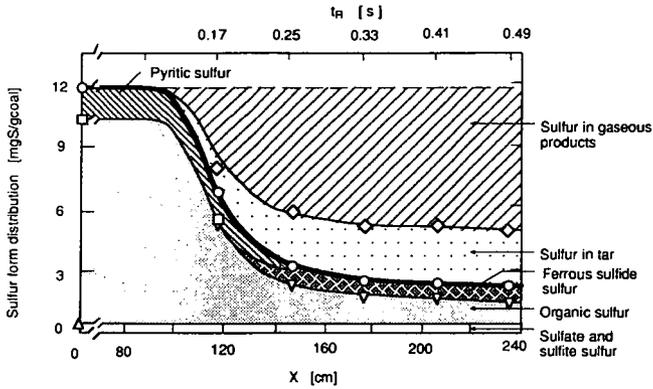


Fig.4 Change in sulfur form distribution with distance  $X$  from coal hopper or with particle residence time  $t_R$  for PSOC-830 coal.

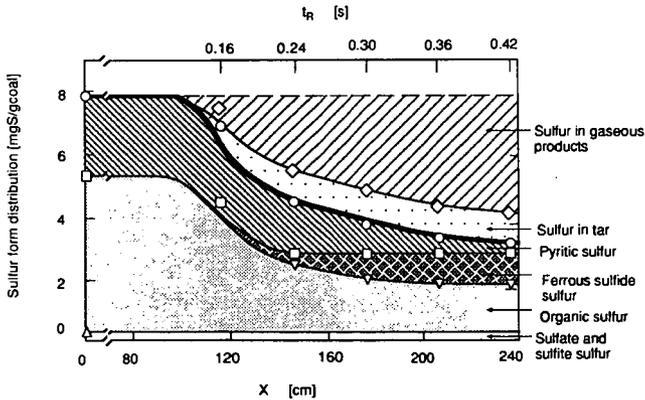


Fig.5 Change in sulfur form distribution with distance  $X$  from coal hopper or with particle residence time  $t_R$  for Rosebud coal.