

## KINETIC MODELING OF COAL PYROLYSIS IN A LAMINAR-FLOW REACTOR SYSTEM

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### INTRODUCTION

There will soon be an intense competition in the energy marketplace among oil, natural gas, coal, nuclear fission and the newly developing alternatives of solar, wind and waste utilization. The charge to the energy-entrepreneurs is to intensify their search to recognize and exploit the most economical and technically expedient manner of converting these raw energy sources into acceptable forms for the public's use.

Coal will certainly play a leading role in supplying the future energy needs of this nation's industrial and commercial ventures. But coal is an extremely complex heterogeneous material, composed of a number of distinct organic entities, called macerals, and inorganic minerals. Coals from different coal seams and even from separated points in the same seam often behave quite differently in a gasification reactor because of the unique associations of the maceral and mineral species in the coal matrix.

When the coal particle is first injected into the hot gasifier, the associated water is rapidly evolved. This drying mechanism is usually modeled as being independent of the other subsequent reactions; however, intuition says that a severe drying action could alter the particle's surface characteristics which in turn would significantly alter the later devolatilization and gasification reactions. As the dry coal particle is then rapidly heated, bound water, carbon oxides and hydrocarbon fragments are thermally cleaved from the coal's organic matrix and evolves into the surrounding gas phase. The amount and composition of this "volatile matter" are significantly controlled by the heat and mass transfer conditions in that pyrolysis/devolatilization zone. The physical severity of those devolatilization reactions, sometimes resembling mini-explosions, drastically affects the rate of the subsequent char-gasification reactions.

Today's most commercially-successful coal gasification processes completely shatter the coal's organic structure into blends of carbon monoxide and hydrogen, syngas mixtures that can be reassembled into a variety of desired gaseous and liquid products (1). Although proven to be technically and economically feasible in the present energy-market atmosphere, that destruction and reconstruction method of converting coal to useful energy and feedstock forms may not have the highest thermodynamic efficiency compared to other yet-to-be commercialized coal<sup>2</sup>conversion mechanisms. In a return to the controlled destructive distillation of the old coke-making era, research emphasis is now re-examining low-temperature, "mild gasification" methods which can skillfully carve a suite of desirable products from the coal-structure, such as specific specie blends of gaseous feedstocks and/or highly aromatic condensibles, along with specially-formed chars (2).

In order to recognize the most expedient paths to perform these selective coal-radical slicing, one must understand fully the individual pyrolysis/devolatilization reactions of that particular coal. A laminar flow reactor has some advantages in studying coal devolatilization, such as precise control of experimental conditions like the flow rate and composition of the carrier-reactant gas. Also, both the reactor temperature and particle residence time can be easily

varied to evaluate the effects of changes of the heating rate of the coal-particle. There are also disadvantages to analyzing the data from such a laminar-flow reactor system, mainly associated with the need to mathematically compute the particle temperature and then to isolate the chemical reactivity from the mass transfer resistances. Many of the original studies using laminar-flow reactors used rather high temperatures where the particle heatup time was negligible. This permitted the particles to be considered at steady-state temperature for the entire particle residence time in the reactor. However, studies of the coal devolatilization in the 650° to 1100°K range in inert or non-igniting atmospheres reveal significant time-lags before devolatilization weight-loss starts.

In this presentation, experimental weight-loss data from the devolatilization treatment of a Herrin (Illinois) No. 6 coal in a laminar-flow laboratory reactor are examined and the observed reaction behavior are used to outline criteria for a coal-pyrolysis kinetic model.

#### EXPERIMENTAL REACTOR SYSTEM

The concept of the laminar-flow reactor design derives from those used by Badzloch and Hawksley (3), Kobayashi (4), Nsakala et al. (5) and Agreda et al. (6). Modifications were made in the design of the coal-feed inlet and the exiting-solids collector tube to permit a smooth 0.46 gm/min flow of coal solids, to expose the solids to reactor temperatures up to 1073°K with particle residence times up about 400-500 msec, and to collect and quickly quench-cool the coal-char solids immediately as they leave the hot-zone of the reactor. This reactor system, described in detail by Wu (7) and Moslehi (8), is illustrated in Figure 1.

In this reactor system, the hot nitrogen-gas stream enters the top head of the reactor into the shell-annulus surrounding the coal-feeder tip. This gas is then directed down into the main reactor tube chamber through a flow-straightener formed from a 3.8 cm (1.5-inch) thick disk of Corning "Macor" machineable glass-ceramic through which 2.2 mm diameter holes were drilled to form a 38% voidage ratio across the primary gas flow region. The vertical reactor chamber body was formed of a nominal two-inch, Schedule 40, Type 316 stainless-steel tube twenty inches long surrounded by a tube furnace. After passing through the heated reactor zone, the solids enter the throat of the char-solids collector where a cool-flush of nitrogen flowing inward through a permeable sintered stainless-steel tube at the collector tip quickly quench-cools the solid-particle and dilutes the surrounding reactive gases. The solids are separated in mini-cyclones and the condensible and permanent gases collected for quantification and analysis. The collector assembly tube was designed with a slip-joint around its outside diameter so that the uppermost tip of the collector could be positioned at any desired distance below the coal-inlet feeder tip. Thus, the coal particle reaction path-length, which determines the particle residence time, can be varied from almost zero to more than 50 cm.

The Herrin (Illinois) No. 6 coal used in the experiments was extracted from a west-central Illinois underground mine and had a dry-analysis of 43.3% volatile matter, 9.8% ash and 46.9% fixed carbon, along with a 4.2% total sulfur content. The coal was vacuum-dried and ground to an average particle diameter of about 75 micrometers before being fed to the reactor. The operating conditions of the reactor during the processing of this coal are listed in Table 1.

#### EXPERIMENTAL RESULTS AND DISCUSSION

The pyrolysis reactions were examined at three reactor temperatures; 450°, 600° and 800°C; and at three particle flow path lengths; 10, 20 and 30 cm. The

total residence times of the coal-particles, computed using the reactor operating conditions existing at these nine temperature-length combinations, are listed in Table 1, the values ranging from 137 to 473 msec. The overall weight-loss data from these experiments, computed by an ash-content balance and expressed on a dry ash-free basis, are shown in Figure 2. The reasoning and procedures of all the computational analyses have been detailed by Wu (7) and Moslehi (8).

It can be seen in Figure 2 that for a given temperature, the weight loss increases with time almost exponentially, approaching a maximum value. This maximum weight loss value is definitely a function of temperature, with a value in the upper 40% (daf weight loss) approached at 600°C, while the maximum weight loss at 800°C is in the upper 50% range.

Although the five-stage succession of devolatilization reactions detailed by Suuberg et al. (9) is probably the most chemically realistic, the single-reaction first order decomposition model discussed by Howard (10) can be utilized in approximating the coal's devolatilization behavior for quick comparison with those described in previous literature-reported studies. This model is stated as;

$$dW/dt = k ( W^* - W ) \quad 1).$$

where W represents the weight-loss of the coal-particle (expressed on a dry ash-free basis) and  $W^*$  is the weight loss after an infinite exposure time at the reaction temperature, gas flow rate and other operating conditions. Badzioch and Hawksley (3) and other investigators realized that there was negligible weight loss until the dry coal particle was heated to about the 300<sup>o</sup>-to-500<sup>o</sup>C temperature range where the weight loss reactions became significant. They incorporated a particle heating time into their model;

$$\text{Total Time} = \text{Heatup Time} + \text{Reaction Time.} \quad 2).$$

In order to simplify the mathematics, they assumed there to be no reactions taking place during this heatup time, even though the particle would be heating slowly through the entire devolatilization temperature range up to the steady-state temperature of the reactor.

Using the relationships derived by Kobayashi (4) in a mathematical analysis of the temperature and velocity flow in a similar laminar-flow reactor, which were modified and used by Agreda et al. (6) and Felder and coworkers (11) in their studies, particle heatup times were computed to be in the range of 24 to 27 msec for the three experimental reactor temperatures. The values of the pseudo rate constant, k, yielded a reasonably straight line on an Arrhenius plot. This experimental data correlates by the expression;

$$k = k_0 \exp (-E/RT) \quad 3).$$

with the pre-exponential factor,  $k_0$ , being equal to 16035 sec<sup>-1</sup> and the apparent activation energy, E, being equal to 68.12 kJ/mole (16.27 kcal/mole). This activation energy value compares quite well with the results found by Felder et al. (11) who, when devolatilizing a western Kentucky No. 11 coal in a similar reactor system, found the value of the apparent activation energy to be 80 kJ/mole (19.12 kcal/mole).

For use as a comparison with the experimental results of this study as shown in Figure 2, the devolatilization weight loss data reported by Felder et al. (11) for the western Kentucky Seam No. 11 coal is plotted in Figure 3. It

should be noted that the western Kentucky coal Seam No. 11 is believed to have been deposited in the same geological time-period as the Herrin (Illinois) No. 6 seam. The lines sketched in both Figures 2 and 3 are merely to depict a trend-connection of the points, not to suggest a specifically derived model path.

The 450°C and the 600°C weight-loss lines of Figure 2, along with the 600°C line of Figure 3, demonstrate that there is a definite effect of reactor temperature on the heating time of the particle. The mathematical analysis of Kobayashi (4) used to approximate the particle heatup time in this study was originally derived for coal devolatilization at much higher reactor temperatures than those of these experiments. Both the 800°C lines in Figure 2 and 3 could approach zero reaction within the 20-30 msec range predicted by the Kobayashi relationship. At the lower temperatures, however, the onset of devolatilization is much affected by reactor temperature as well as by other reactor operating conditions. The Felder et al. data for the 600°C experiments in Figure 3 indicate that no weight loss occurred for almost 200 msec, while at 600°C in this study, the reactions seem to have started before 100 msec.

Note also that reactor operating conditions, other than the temperature effect, seem to cause differences in the maximum asymptotic weight loss at each reactor temperature. In this study at 600°C, the maximumdaf weight loss was around 40%, while the 600°C line in Figure 3 was leveling in the 15% range. At 800°C the data in Figure 3 demonstrated a maximum weight loss of around 49%, which was about 1.11 times the ASTM Proximate Analysis Volatile Matter of that coal. In the study reported in this paper, the coal's weight loss after 300 msec had reached almost 60% (1.24 times the ASTM Proximate Volatile Matter) and the maximum weight-loss asymptote had not been reached.

An examination of the approached asymptotes of  $W^*$  at the various temperatures suggests the validity of the "multiple reactions" model developed by several investigators and discussed by Howard (10). In Figure 2, the 450°C and the 600°C data appear to be approaching ultimate  $W^*$  values that are very close together, while the 800°C value of  $W^*$  is more than 20% higher. The data of Felder et al. (11) in Figure 3 indicates that the maximum weight loss  $W^*$  at 800°C is almost three times larger than the value of  $W^*$  at 600°C, with weight loss curve at 700°C still increasing after 1000 msec of reaction exposure time. Suuberg et al. (9) in their listing of the five stages of devolatilization states that carbon oxides, hydrocarbons, tar and hydrogen are released in the fourth stage from 700°C to 900°C. It would be logical to suggest that the reactions occurring in this temperature range would be strongly influenced by variations in the mass and heat transfer mechanisms caused by differences between reactor operating conditions. Also, the primary volatile hydrocarbon species being evolved in this temperature range would be susceptible to secondary decomposition and/or cracking reactions. Thus, the pyrolysis reaction chain probably includes a complex mix of both parallel and successive reactions.

#### CONCLUSIONS

A Herrin (Illinois) No. 6 coal was devolatilized in nitrogen in a laboratory laminar flow reactor system. The reactions took place at 450°C, 600°C and 800°C for reaction residence times ranging from 130 to 480 msec at Reynolds Numbers of 235-308. The experimental data can be reasonably approximated by a single reaction decomposition model;  $dW/dt = k(W^* - W)$ ; with the pre-exponential found to be 16035  $\text{sec}^{-1}$  and the apparent activation energy being equal to 68.12 kJ/mole (16.27 kcal/mole). This reactor system stimulates a rather efficient reaction as evidenced by the fact that, after only 300 msec exposure at 800°C, the coal's weight loss had reached almost 60% (1.24 times the ASTM Proximate Analysis Volatile Matter) and the maximum weight-loss asymptote had not been reached.

At the lower temperatures of this experimental study, 450° through 600°C, knowledge of the particle heatup time is quite important. Estimates by previous investigators of the time-period before the "onset of devolatilization weight loss" occurs were substantially smaller than the actual experimental values observed in this study. There is considerable evidence that the particle heating rate and the flow conditions within the reactor system have a significant bearing on not only the pyrolysis rate, but also on the maximum weight loss of the coal which could be achieved at each reactor exposure temperature. Also, implications are that the overall devolatilization is both a parallel and a successive series of reactions, each influenced by the interrelated mass and heat transfer mechanisms occurring in that specific reactor system.

A predictive model useful in representing the reactive behavior of high-volatile coal at relatively low temperatures must incorporate a consideration of the very complex mix of mass and heat transfer effects. The development of such a model is the next stage of this continuing investigation.

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TABLE 1  
EXPERIMENTAL REACTOR OPERATING CONDITIONS

Reactor Temperature	REACTOR TEMPERATURE		
	723 K (450°C)	873 K (600°C)	1073 K (800°C)
Dried Coal Feed Rate (gm/min)	0.46	0.46	0.46
Nitrogen Gas Flow Rate (L/min at 20°C, 1 atm)			
Main Gas Stream	20	20	20
Solids-Carrier Gas Stream	1	1	1
Combined Gas Velocity, (m/sec)	0.412	0.497	0.574
Total Gas Flow Reynolds Number	308	274	235
Coal-Solids Residence Time, msec			
Particle Flow Path Length			
10 cm	186	155	137
20 cm	336	280	227
30 cm	473	393	318

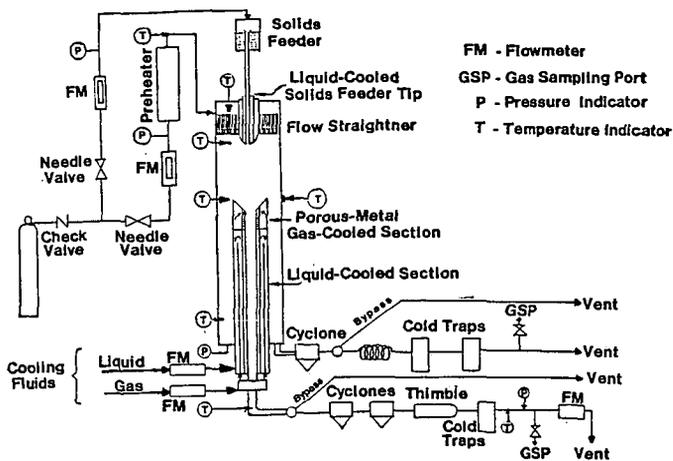


Figure 1. Experimental Laminar-Flow Reactor System

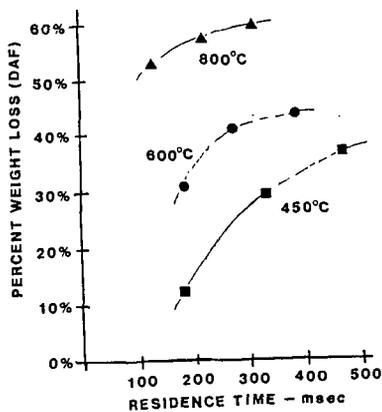


Figure 2. Weight-Loss (DAF) Versus Time, Herrin (Illinois) No. 6 Coal, This Study

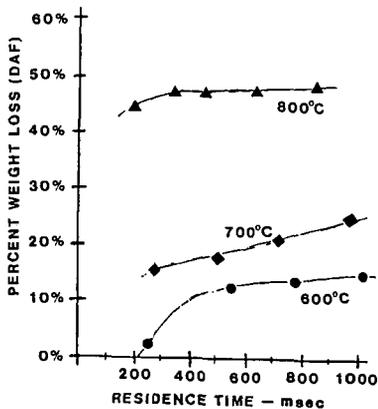


Figure 3. Weight-Loss (DAF) Versus Time, Western Kentucky No. 11 Coal, Felder et al. (Reference 11)