

## Pyrolysis of Coal at High Temperatures

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### Introduction

Pyrolysis of coal at high heating rates is the initial step in its utilization by combustion, gasification or liquefaction. This involves the thermal decomposition of the coal's organic structure and the release of volatile products, which may account for up to 70% weight loss of the coal. Knowledge of the behaviour of the many volatile species liberated during pyrolysis is warranted, since their composition, rate of release and secondary reactions will have an important influence on such practical considerations as ignition, rate of combustion and trace gaseous and particulate emissions.

For many coals the condensed volatile species, or tar, comprise a major part of the volatile yield in coal devolatilization(1). They have been suggested as an important source of soot during coal combustion(2,3), and they have potential as models of coal structure. Thus an understanding of secondary reactions of tars is necessary for a complete model of coal devolatilization to be developed. The tars can crack to form soot, char and gases. Secondary reactions of the char involving ring condensation and gas evolution (mainly CO and H<sub>2</sub>) will influence reactivity of the char towards gasification or combustion.

This paper presents data on the pyrolysis of a subbituminous coal and of tar produced by the rapid pyrolysis of this coal in a small fluidised bed reactor and in a shock tube. Kinetic parameters for light gas formation from secondary reactions of the tar have been determined. The results also provide evidence that secondary reactions of the tar are a source of polycyclic aromatic hydrocarbons (PAH) observed during pyrolysis. Data are also presented to show the effect of preparation conditions on the combustion kinetics of chars produced by rapid pyrolysis.

### Experimental

The design and operation of the fluidised bed pyrolyzer has been described previously(1,4,5), as has the shock tube used for the high temperature cracking (6,7). Light gases were analyzed by gas chromatography. Tar components were recovered from the fluidised bed pyrolyzer by filtration through a Soxhlet thimble held at liquid nitrogen temperature, extracted with dichloromethane and analyzed by high resolution gas chromatography(5). Millerran subbituminous coal was used for all experiments (analysis wt%; C, 79.1; H, 6.5; N, 1.2; S, 0.6; O (diff.), 12.6).

Chars for the combustion studies were prepared, using a large-scale fluidised bed pyrolyser at temperatures of 540, 600 and 800°C. The product char was separated hot from the pyrolyser product gas, cooled, sampled, and then sieved to give size-graded fractions. The combustion reactivity of the char was determined using a flow reactor, and an ignition apparatus(10). The char samples contained appreciable amounts of volatile matter, the 600°C material having a standard VM yield of 16.6% (daf), and a hydrogen content of 4.0%.

### Results

#### Kinetic parameters for secondary cracking of tar

Pyrolysis reactions of the coal under rapid heating conditions were separated from decomposition reactions of the tar to allow the vapour phase cracking reactions to be investigated free from influences of the original coal or char. This was

achieved by linking a fluidised bed pyrolyzer, operating at a low temperature (600°C) to minimise secondary reactions, to a shock tube capable of providing temperatures up to 2000K and residence times of 1-2 ms.

Arrhenius parameters for the rates of formation of  $\text{CH}_4$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_3\text{H}_6$ ,  $\text{C}_6\text{H}_6$  and  $\text{CO}$  were determined and are presented in Table 1. Rates of production of  $\text{C}_2\text{H}_4$  and  $\text{C}_3\text{H}_6$  yielded activation energies of 230 and 260  $\text{kJ mol}^{-1}$  respectively and are thus in excellent agreement with typical Arrhenius parameters obtained for the pyrolysis of long chain gaseous hydrocarbons(11,12). Thus the likely precursors of these alkenes are long chain n-alkyl groups. Recent studies(13) have shown that Millmerran flash pyrolysis tar contains at least 23 wt% n-alkyl groups of which about 40% are present as free alkanes and alkenes and the balance are bound to other structures, probably as substituted aromatics. Yields of  $\text{C}_2\text{H}_4$  and  $\text{C}_3\text{H}_6$  observed from the tar cracking are in excellent agreement with this n-alkyl content.

Kinetics for the lumped disappearance of long chain alkanes and alkenes have also been determined for pyrolysis in the fluid bed reactor. These results are presented in Fig. 1 and give an activation energy of 237  $\text{kJ mol}^{-1}$  in good agreement with literature values for the decomposition of n-octane(11) and n-hexadecane(12).

Activation energies for the formation of  $\text{CH}_4$ ,  $\text{C}_6\text{H}_6$  and  $\text{CO}$  from the tar cracking are low and in the range 110 - 140  $\text{kJ mol}^{-1}$ . This implies that many different functional groups in the tar contribute to the formation of these species with very different rates leading to a low apparent activation energy.

#### Formation of Polycyclic Aromatic Hydrocarbons (PAH)

Tar reactions have been identified as a source of the soot produced in both pyrolysis and combustion systems(2,3). Recent results(5) have also shown that the predominant components of the tar produced at temperatures greater than 800°C in the fluid bed reactor are PAH with up to five rings.

Mechanisms postulated for the formation of PAH in the combustion of simple hydrocarbons in flames include both ionic(14) and free radical(15) processes. The species observed, and which are regarded as important intermediates in the formation of the larger aromatic species, include phenylacetylene, styrene, indene, naphthalene and acenaphthalene. The free radical mechanisms involve addition reactions of aromatic radicals (predominantly benzyl and phenyl) to unsaturated aliphatics such as acetylenic species and stabilisation of the adduct by the formation of six-membered rings. Recently Homann(16) has shown that these species occur in approximately equivalent relative amounts in flames burning a very wide variety of fuels.

The predominant species produced from coal pyrolysis at high temperatures where tar cracking is important are remarkably similar to those found in the flame studies. Fig. 2 shows yields of phenylacetylene, styrene and indene obtained from the pyrolysis of Millmerran coal in the fluid bed reactor. Analysis of the tar by FTIR shows that acetylenic species have also undergone addition reactions with the larger aromatic species.

The similarity of the species distribution observed for the coal pyrolysis products and the flame products strongly suggests that a common mechanism is responsible for the formation of PAH in these two systems. Thus in addition to their importance for soot formation, secondary reactions of volatiles are an important source of PAH formed in combustion.

#### Char reactivity

The combustion reactivity of the three chars determined in the flow reactor (production temperatures 540, 600 and 800°C respectively) is given in Fig. 3(a). At a

combustion temperature of  $\sim 700^{\circ}\text{C}$  the reactivities of the chars show an inverse relationship to their preparation temperature the lower the preparation temperature the higher the reactivity(17). At  $1000^{\circ}\text{C}$  these differences have largely disappeared.

The question then arises as to the relative contributions to the observed reactivity by the consumption of the volatile and solid components of the char. The data in Fig. 3(a) were determined using a flow reactor when the particles and hot gas were mixed some distance before the burning suspension passed the positions in the reactor where rate measurements were made. There is some indication(17) that the volatile matter is evolved rapidly, and that the burning rate data are for the consumption of the solid char after the volatiles have been released.

Support for this view is given by Rybak *et al.*(10) where the reactivity of the  $600^{\circ}\text{C}$  char was determined from a measurement of particle ignition temperature. It was found that the ignition temperature was affected by the volatile content of the char - the more times the char was cycled through the heated ignition reactor (in the absence of oxygen), the higher the ignition temperature ultimately measured. Fig. 3(b) shows that the reactivity of the char reduces with increasing heating time (increasing number of cycles through the reactor) in a manner similar in reactivity to the reactivity change with pyrolysis temperature shown in Fig. 3(a). After eight cycles the reactivity is close to that measured in the flow reactor (and in a quite different reactor at the Sandia Laboratories(18)).

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Table 1 Kinetic parameters for formation of products from tar cracking in the shock tube.

Species Formed	A/s <sup>-1</sup>	E <sub>a</sub> /kJ mol <sup>-1</sup>
CH <sub>4</sub>	7 x 10 <sup>6</sup>	110
C <sub>2</sub> H <sub>2</sub>	5 x 10 <sup>9</sup>	220
C <sub>2</sub> H <sub>4</sub>	2 x 10 <sup>12</sup>	230
C <sub>3</sub> H <sub>6</sub>	5 x 10 <sup>13</sup>	260
C <sub>6</sub> H <sub>6</sub>	7 x 10 <sup>6</sup>	110
CO	2 x 10 <sup>8</sup>	140

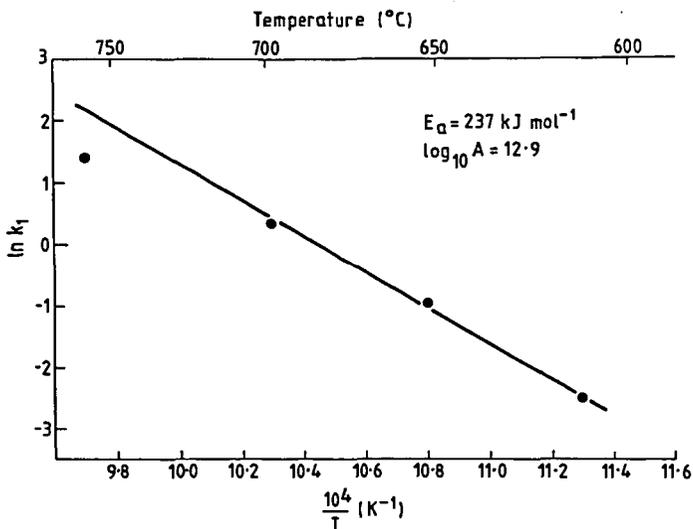


Fig. 1 Arrhenius relationship for polymethylene disappearance in fluidised bed reactor.

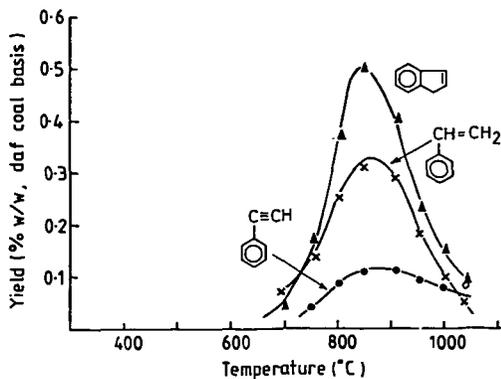


Fig. 2 Yields of indene, styrene and phenylacetylene as a function of temperature for pyrolysis of Millmerran coal.

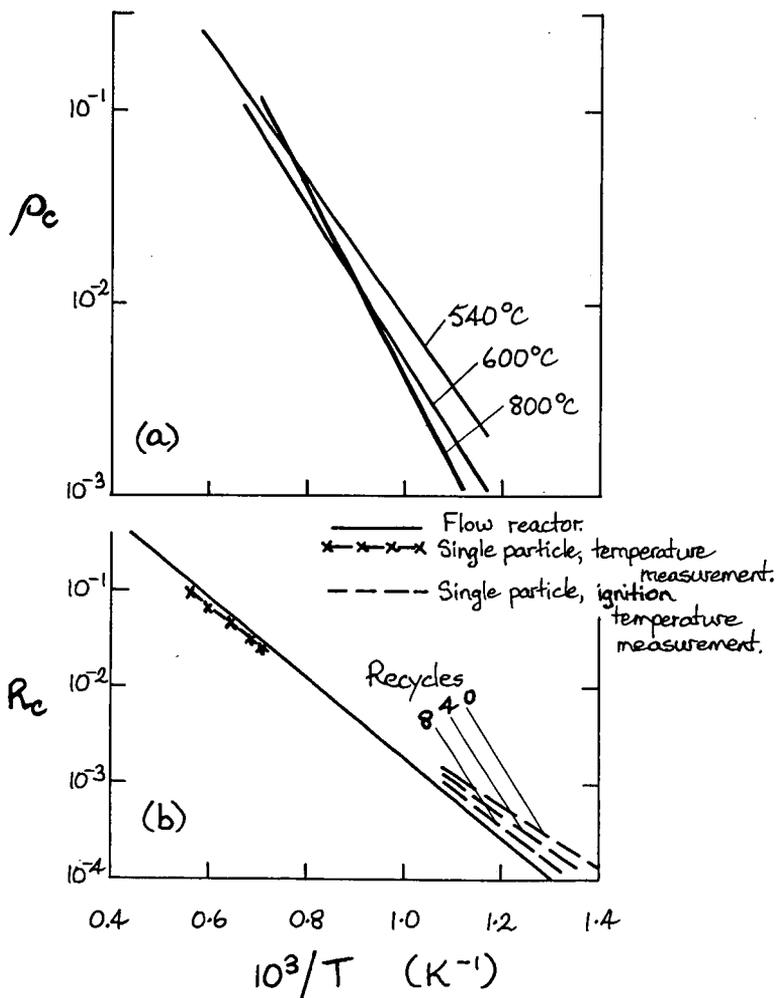


Fig.3. Reactivity of Sub-bituminous Coal Char: (a) as a function of pyrolysis temperature; (b) by various techniques, showing effect of heating time.