

## Short Communication

### Devolatilization of large coal particles at high pressure

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Devolatilization times of large (0.1 and 0.2 g) Utah hvBb and North Dakota lignite coal particles, in the range 15–30 s, were measured in air at 101 and 507 kPa, at air temperatures of 900 and 1200 K in a convective flow reactor. Visual observations indicated infrequent heterogeneous ignition of the lignite prior to devolatilization and occasional explosion of bituminous coal particles during devolatilization. Devolatilization times were correlated with temperature, pressure and particle size. Power-law exponents for tests at 101 kPa and 900 K were determined to be 2.5 for Utah hvBb coal and 2.2 for North Dakota lignite. At 507 kPa and 900 K, exponents decreased to 1.6 for both Utah and North Dakota coals. At 101 kPa and 1200 K, exponents were 1.9 for Utah coal and 1.6 for North Dakota lignite. Copyright © 1996 Elsevier Science Ltd.

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Particle size, combustion conditions and structural and compositional characteristics of coal have a large impact on its devolatilization behaviour. Unravelling the complex nature of the devolatilization process has been the focus of much fundamental and applied research. Reviews<sup>1–9</sup> have presented past experimental and modelling work in coal devolatilization. The majority of previous devolatilization studies were on pulverized coal, but there is a recognized need for studies on large coal particles. In the US Clean Coal Technology (CCT) programme, advanced fixed-bed gasifiers, which make use of large coal particles in the range 3–25 mm, have been adopted for air-blown, integrated gasification–combined cycle power generation using Lurgi technology and for mild gasification of lump coal in air at atmospheric pressure to obtain liquid and solid products<sup>10</sup>. Fluidized-bed combustors and gasifiers, which make use of coal particles in the range 2–3 mm, are increasing in commercial use and are the basis for several other CCT processes<sup>10</sup>. Yet few data have been reported for devolatilization times of large coal particles at atmospheric or elevated pressures and high temperatures.

In a landmark study of large-particle pyrolysis, Essenhigh<sup>11</sup> combusted coal particles between two horizontal heating coils. He measured the devolatilization times of 80 mg to 10 µg particles of 10 different coals. Using a power-law relation of the form  $t_{\text{dev}} = k d_i^n$ , he obtained values of  $n$  between 1.8 and 2.6. Pillai<sup>12</sup> investigated devolatilization times of

large (6–15 mm diameter) Pittsburgh No. 8 and Rufford coals in a fluidized bed combustor with the oxygen content of the inlet gas maintained at 13 vol.% and the bed temperature at 1170 K. Particle temperatures were measured with 2 mm diameter thermocouples inserted into 3 mm diameter holes drilled into the particles and held in place with high-temperature refractory cement. Temperature traces showed initial rapid heating to 500–620 K followed by a period, evidenced by the volatiles flame, in which the particle temperature continued to increase, though at a much lower rate, up to ~1060 K. Devolatilization times were visually determined as the duration of a luminous flame in the freeboard or bed. The effect of initial particle diameter on devolatilization time was correlated with a power law. Exponents were determined to be 1.8 for the Rufford coal and 0.8 for the Pittsburgh coal.

Convective flow tests in an atmospheric pressure drop-tube furnace were performed by Ragland and Yang<sup>13</sup> to determine devolatilization times for large (5.3–9.9 mm diameter) high-volatile C bituminous coal particles in air at temperatures of 900–1200 K. Correlation of the devolatilization time with original particle diameter yielded a power-law exponent of 1.7. Devolatilization times decreased with increasing air temperature from 900 to 1100 K, but no further decrease was noted when the temperature was increased to 1200 K (see Figure 1). The effect of Reynolds number on devolatilization time was negligible.

Zhang *et al.*<sup>14</sup> determined devolatilization times of large (5–50 mm diameter) eastern Canadian coals (Evans coal from Cape Breton and Minto coal from New Brunswick) in a fluidized bed held between 1023 and 1173 K, using atmospheric pressure air as a fluidizing gas. Devolatilization time was determined visually as the duration of the volatiles flame. Power-law correlations yielded exponents between 1.5 and 1.6. Studies of the devolatilization behaviour of large coal particles have mainly used fluidized bed systems characterized by high heat transfer rates and vigorous agitation at atmospheric pressure. Large-coal-particle devolatilization models have been presented by Fu *et al.*<sup>15</sup> and Adesanya and Pham<sup>16</sup>, but these authors do not discuss the effect of pressure.

The effect of pressure on devolatilization has received little attention, especially for large particles. Recently, Griffin *et al.*<sup>17</sup> studied effects of pressure (0.1–1.0 MPa) and temperature (750–1230 K) on pyrolysis of pulverized Pittsburgh No. 8 bituminous coal in a helium atmosphere, using an electrical screen heater reactor. They found that volatiles yields increased dramatically with increasing temperature between 750 and ~1000 K, above which the temperature had little effect. Volatiles yields reached an apparent asymptote as the temperature was increased above 1000 K, signifying the conclusion of devolatilization under these conditions. Also, volatiles yields decreased slightly with increasing pressure, which effect was more pronounced at higher temperatures.

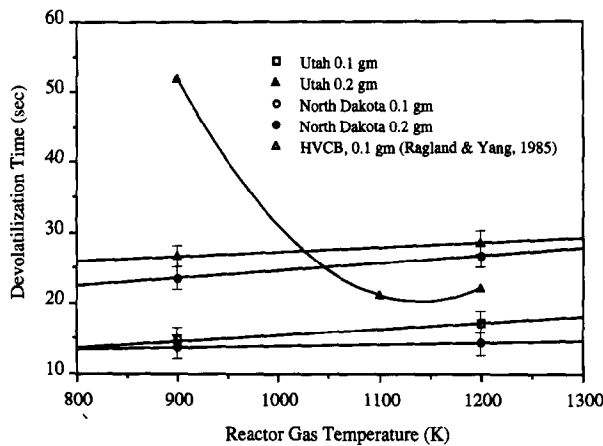


Figure 1 Effect of reactor temperature on devolatilization time for Utah hvBb coal and North Dakota lignite (0.1 MPa). Error bars represent 90% confidence intervals of the mean

Table 1 Analyses of Utah Blind Canyon hvBb coal and North Dakota Beulah Zap lignite used in tests

	Blind Canyon	Beulah Zap
Proximate analysis (wt% as-received)		
Moisture	8.7	32.2
Ash	8.2	6.6
Volatile matter	37.2	30.5
Fixed carbon	45.9	30.7
Ultimate analysis (wt% db)		
C	73.6	68.4
H	4.8	4.6
N	1.12	1.14
S	0.51	0.67
O	11.7	18.6
Gross calorific value (MJ kg <sup>-1</sup> db)	26.86	21.44

Table 2 Summary of test conditions

Fuel type: Utah Blind Canyon hvBb coal and North Dakota Beulah Zap lignite
Pressure: 101 and 507 kPa in air
Gas temperature: 900 and 1200 K
Reynolds number (based on particle diameter): 63 and 126
Particle mass: 0.1 and 0.2 g (~5.5 and 7.0 mm diameter)
Particle support: platinum screen

Below 970 K, pressure had little effect on yields.

A recent comprehensive review of coal pyrolysis by Solomon *et al.*<sup>5</sup>, which includes pyrolysis data for small particles from seven different studies, performed on heated grids in inert atmospheres at heating rates of 103 K s<sup>-1</sup>, indicates that the devolatilization process was essentially complete at ~1000–1100 K under these test conditions. These results agree with those of Griffin *et al.*<sup>17</sup>, also for small particles. Also, Anthony and Howard<sup>1</sup> state that devolatilization continues until, if maintained for an extended time, a temperature typically ~1200 K is reached. However, at very high heating rates (10<sup>5</sup> K s<sup>-1</sup>), effects of temperature on devolatilization time extend to much higher temperatures (e.g. 2100 K), at least for small, pulverized

coal particles in inert atmospheres, since there is insufficient time for the devolatilization process to be completed at the lower temperatures<sup>8</sup>.

The objective of the present study was to establish devolatilization times of large coal particles for two coals at various temperatures and pressures in convective air in a new, high-pressure reactor.

EXPERIMENTAL

An innovative high-pressure drop-tube furnace (referred to as the high-pressure control profile—HPCP—reactor) described in Monson and Germane<sup>18</sup> was modified<sup>19</sup> to study large (0.1 and 0.2 g) coal particle combustion at elevated pressures. The HPCP reactor allowed for convective flow of

air at pressures from 0.1 to 1.52 MPa with controlled gas temperature. It also provided for optical viewing through ports and was equipped with a video camera and a laser-based optical pyrometer for measurement of particle temperature. The sample was introduced horizontally through an attachment to one of the optical access ports<sup>19</sup>. Bateman *et al.*<sup>19</sup> discuss the operation of the reactor for large particles and the accuracy and reproducibility of the test results and report the first results from this facility for oxidation of large char particles for pressures up to 0.75 MPa. The device can be used for the study of both coal devolatilization and char oxidation.

Test results for the coal devolatilization phase are reported and analysed here. Tests were completed using two coals, Utah Blind Canyon high-volatile bituminous B (hvBb) coal and North Dakota (Beulah Zap) lignite (L). Both are prominent US coals included in the Argonne National Laboratory premium coal suite and differ substantially in characteristics<sup>9</sup>. Properties of the test coals are given in Table 1 and a summary of test conditions in Table 2. Extensive data on the detailed structure of these two coals are provided by Smith *et al.*<sup>9</sup>.

The two particle masses or sizes were prepared by fracturing a lump of coal into several pieces. These pieces were then formed, using pliers, to resemble spheres. The mass of each particle was either 0.20 g (~7 mm diameter) or 0.10 g (~5.5 mm diameter). A total of 89 tests were conducted, of which 50 tests yielded devolatilization time data. Other tests were vitiated by phenomena such as particle fragmentation or premature ignition, so that the duration of the volatiles flame could not be determined. Devolatilization time was determined visually as the duration of the luminous volatiles flame. It is likely that the evolution of volatile matter is slightly longer than this, particularly for the lignite, since devolatilization is initiated before ignition of the volatiles cloud<sup>20</sup>. Also, towards the end of devolatilization, rapid evolution of hydrogen and carbon monoxide occurs<sup>5</sup> which produces a flame of relatively low luminosity. However, the duration of the luminous flame is a convenient reference for devolatilization time and consistent with other investigations<sup>14,21,22</sup>.

RESULTS AND DISCUSSION

General observations

The video record showed that, in the majority of tests, extremely abrupt homogeneous ignition of the volatiles cloud was evident. However, the video revealed a few tests that exhibited heterogeneous ignition, as the coal particle began to glow before volatiles ignition occurred<sup>19</sup>. This heterogeneous ignition

process was an uncommon occurrence, being observed in only six of the tests, all with the lignite, and all at the lower gas temperature of 900 K. Another fascinating observation relating to coal type was particle explosion during devolatilization. In seven tests on the Utah bituminous coal only, the particle suddenly exploded<sup>19</sup>. Fragmentation of smaller (<1.5 cm diameter) bituminous coal particles during devolatilization in a fluidized bed was noted by Chirone and Massimilla<sup>23</sup>, who attributed it to the buildup of pressure in the pore network of the coal. Dacombe *et al.*<sup>24</sup> also observed fragmentation of 1–6 mm anthracite particles in a drop-tube furnace. The fragmentation or explosion noted in this study, presumably caused by internal volatiles pressure, was not otherwise correlated with any test condition and was never observed in the lignite. The moderately plastic behaviour of the bituminous coal may fuse pores, preventing volatiles escape and causing pressure buildup and fragmentation.

#### Effect of temperature

Figure 1 suggests a slight increase in devolatilization time with increasing gas temperature for the large particles between 900 and 1200 K. This unusual observation is not consistent with behaviour for small coal particles in inert atmospheres, where it has been commonly observed that mass loss increases markedly while devolatilization time decreases sharply in this temperature range<sup>25</sup>. This result is also contrary to the findings of Ragland and Yang<sup>12</sup> at lower temperatures, which showed, with very limited data, a dramatic decrease in devolatilization time between 900 and 1100 K from 52 to 21 s for 5.3 mm diameter particles. However, from 1100 to 1200 K they reported that the devolatilization time changed little, increasing from 21 to 22 s. As can be seen from Figure 1, no devolatilization times above ~30 s were measured, even for 0.2 g (7 mm diameter) particles. A gas temperature effect on devolatilization time is absent in these tests probably because the particle temperature is primarily determined by heat transfer from the volatiles flame surrounding the particle. The surrounding combustion gas flame temperature is not significantly dependent on the initial test gas temperature or on the test pressure. Results of large-particle devolatilization studies performed in fluidized beds, where volatiles combustion occurs on the bed surface rather than surrounding the particle, show a decrease in devolatilization time with increasing temperature<sup>20</sup>. No significant effect of air flow rate on devolatilization time was noticed, consistent with the results of Ragland and Yang<sup>13</sup>, further evidence that heat transfer rate from the hot convecting gas was not a controlling factor.

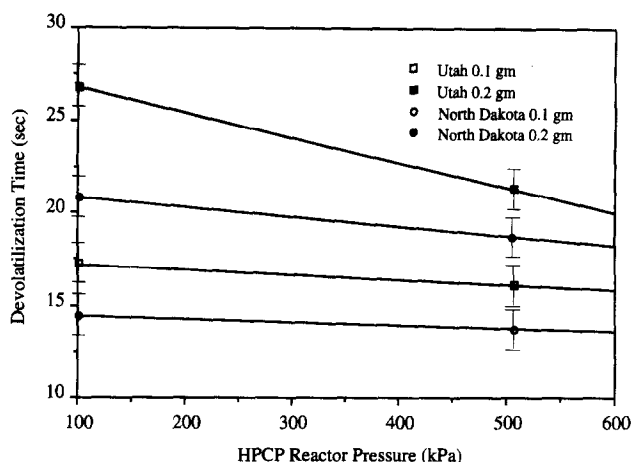


Figure 2 Effect of reactor pressure on devolatilization time for Utah hvBb coal and North Dakota lignite (1200 K). Error bars represent 90% confidence intervals of the mean

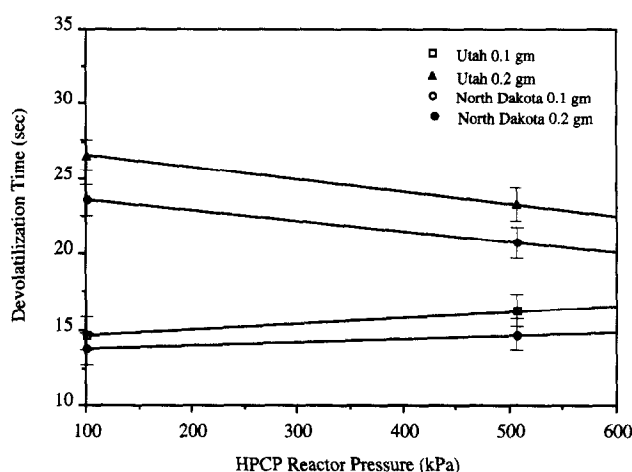


Figure 3 Effect of reactor pressure on devolatilization time for Utah hvBb coal and North Dakota lignite (900 K). Error bars represent 90% confidence intervals of the mean

#### Effect of pressure

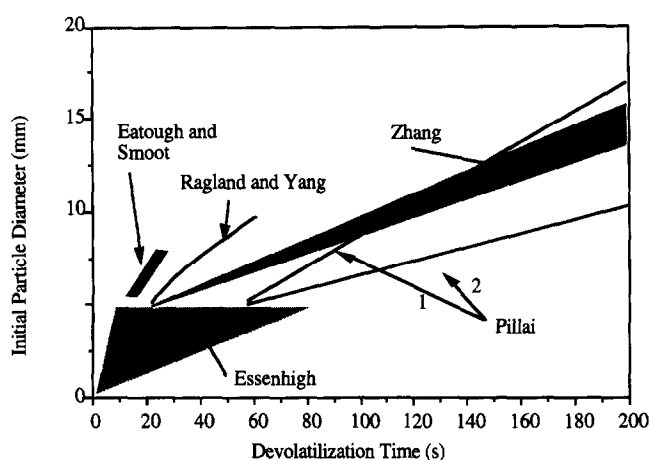
Test data in Figure 2 show that at 1200 K, devolatilization time decreased modestly with increasing pressure. This decrease was somewhat more pronounced for the larger particles. Figure 3 shows that at 900 K, there was a slight decrease in devolatilization time with increasing pressure for 0.2 g particles but a slight increase for 0.1 g particles. The interpretation of these findings is confounded by the complex interaction between pressure and volatiles behaviour. As pressure is increased, the transit time of volatiles within the particle increases<sup>9</sup>; therefore condensation and secondary repolymerization reactions of volatiles on char surfaces are more likely to occur, resulting in lower yields<sup>5,9</sup>. Also, as pressure increases, the molecular weight distribution of released volatiles shifts toward lighter components<sup>5</sup> which have higher molecular diffusivities<sup>26</sup>. These effects may explain a decrease in total volatiles emission time with increasing pressure.

Since 900 K is lower than the temperature at which devolatilization is complete,

tightly bound tars are more likely to be retained in the char or released slowly. The difficulty in releasing these tars is compounded by increasing the pressure<sup>5</sup>. The smaller particles may allow the release of more of these tars, due to shorter intraparticle residence times<sup>2</sup>, but at a slower rate as pressure is increased<sup>2</sup>, effectively increasing the devolatilization time. This may account for the slight increase in devolatilization time with pressure for the smaller particles at 900 K. However, this issue cannot be resolved without data on mass loss and product distribution. Nevertheless, the net effect of pressure on volatiles release rate for large coal particles is modest and involves complex interactions among competing effects which have not yet been well characterized.

#### Effect of particle size

The effect of initial coal particle size on devolatilization times in this study was determined using a power law<sup>11,12,14</sup>. For tests at 101 kPa and 900 K, exponents were determined to be 2.5 for Utah bituminous coal and 2.2 for



Summary of experimental conditions

Investigators	Coal Type	Reactor Type	Temperature, K	Pressure, kPa
Eatough and Smoot (this study)	Utah hvBb and North Dakota Lignite	Convective flow furnace	900 and 1200	101 and 507
Essenhigh, ref. 11	10 coals	Heated coil furnace with quiescent atmosphere	Particles present during reactor heat-up	101
Pillai 1, ref. 12	Rufford	Fluidized bed	1173	101
Pillai 2, ref. 12	Pittsburgh #8	Fluidized bed	1173	101
Ragland & Yang, ref. 13	hVcb PSOC #273	Convective flow furnace	1200	101
Zhang et al., ref. 14	Evans HVBB and Minto HVAB	Fluidized bed	1023-1173	101

Figure 4 Measured effect of initial particle size on devolatilization time

North Dakota lignite. At 507 kPa and 900 K, exponents decreased to 1.6 for both Utah and North Dakota coals. At 101 kPa and 1200 K, exponents were 1.9 for Utah coal and 1.6 for North Dakota lignite. The measured effect of initial particle size on devolatilization time is shown in Figure 4, where shaded areas indicate the range of results from various investigators. The effect of particle size on devolatilization time decreases with increasing pressure and temperature. Particle devolatilization time is controlled by heating rate in large particles. For external heat transfer control, the devolatilization time of a spherical particle is related to the heating rate, which is proportional to the square of the diameter<sup>26</sup>. For kinetic control, devolatilization time is exponentially dependent on temperature and independent of size<sup>5</sup>. For volatiles convective transport control, the devolatilization time is related to the distance that volatiles must travel to escape from the interior of the particle as well as the resistance of the pore structure, and is therefore related to the particle diameter<sup>26</sup>. As the particle heating rate increases, the mechanism controlling devolatilization time moves from heat transfer toward kinetics, decreasing the effect of particle size.

#### Effect of coal type

An effect of coal type on the behaviour and duration of the volatiles flame was noted. The bituminous coal exhibited discrete flamelets or jets venting from the particle surface, whereas a uniform flame cloud characteristically surrounded the lignite particles. Figures 1–3 show that

under nearly all reactor conditions, luminous flame times were longer for the bituminous coal than for the lignite. The bituminous coal has a higher volatiles yield and the softening nature of the coal slows transport of volatiles to the particle surface. Also, the lignite produces more gaseous volatiles<sup>5</sup> (e.g. CO, CO<sub>2</sub>, HC) prior to ignition.

#### Multiple-particle effect

Two 0.1 g Utah coal samples were set on the same platinum mesh with particles touching. Results were compared with those for a single particle of the same total mass, 0.2 g. During devolatilization, the particles began to swell and fuse together, thus reducing the total surface area of the two particles, which initially differed by ~25% from that of the larger single particle. The results showed that the two 0.1 g particles and the single 0.2 g particle had similar devolatilization times, being more dependent on total mass than on surface area. All tests of single vs. multiple particles exhibited this same general result.

#### CONCLUSION

Devolatilization times of large, 0.1 and 0.2 g (~5.5 and 7.0 mm diameter) Utah hvBb coal and North Dakota lignite particles in the range 15–30 s were measured by monitoring the visible volatiles combustion in air at 101 and 507 kPa, 900 and 1200 K, and Reynolds numbers of 63 and 126 in the HPCP reactor. Heterogeneous ignition of the lignite was clearly, through infrequently, observed prior to devolatilization. Bituminous coal particles occasionally

exploded during devolatilization, but no explosion of lignite was observed. The volatiles flame was uniform surrounding the lignite particles but emitted as distinct jets at localized points surrounding the bituminous coal particles. No significant effect of gas flow rate on devolatilization time was noticed. Devolatilization times were longer for the bituminous coal.

Between 900 and 1200 K, no significant effect of gas temperature on devolatilization time was observed. The dominance of heat transfer from the volatiles flame of nearly constant temperature probably accounts for this insensitivity. At 1200 K, devolatilization times for both the 0.1 and 0.2 g particles decreased slightly with increasing pressure, possibly due to the increased tar retention in the char. At 900 K, the devolatilization time decreased slightly with increasing pressure for the 0.2 g particle but increased slightly for the 0.1 g particle. Volatiles retention may account for the decrease for the large particles, while secondary reactions are not so prevalent in the smaller particles. The slower volatiles release rate due to increased pressure probably accounts for the slight increase in devolatilization time for the smaller particles.

Particle size effects on devolatilization time were correlated using a power law. For tests at 101 kPa and 900 K, exponents were 2.5 for Utah hvBb coal and 2.2 for North Dakota lignite. At 507 kPa and 900 K, they decreased to 1.6 for both Utah and North Dakota coals. At 101 kPa and 1200 K they were 1.9 for Utah coal and 1.6 for North Dakota lignite. Longer devolatilization (i.e. luminous flame) times were noted for the bituminous coal than for the lignite, which may be due to the greater volatiles yield and the softening nature of the bituminous coal, which causes pores to fuse, blocking volatiles transport. Two 0.1 g particles placed next to each other exhibited a devolatilization time similar to that of a single 0.2 g particle, being more dependent on total mass than on surface area.

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