



## IN-SITU OBSERVATIONS OF DEVOLATILISATION OF COAL

Vladimir STREZOV<sup>1</sup>, John A. LUCAS<sup>1</sup>, Steve R. OSBORN<sup>2</sup>, Les STREZOV<sup>2</sup>

**Abstract.** Coal devolatilisation phenomena were observed in-situ during heating. A single particle of coal of approximately 1 mm diameter was placed on a stainless steel strip heated by an alternative current source. The behaviour of the coal particle was recorded at 100 times magnification through an arrangement of a long focal distance microscope attached to a CCD camera. The two different coal types examined (thermal and coking coal) exhibited significant differences during heating. At about 460°C, during the plastic stage, the coking coal showed rapid swelling and formation of bubbles within the liquid. Unlike the coking coal, the thermal coal showed very little swelling, although devolatilisation (predominantly tars for both coals) was taking place. The volatiles were diffusing to the surface of the particle through the pores in the char, without any significant swelling. At temperatures above 600°C, significant shrinking was observed with the coking coal, while in both samples, evolution of hydrogen was monitored. These observations were compared to the measured specific heats for these coals. The specific heats showed significant differences between the samples associated with a very complex behaviour following the onset of softening. While the coking coal exhibited predominantly exothermic reactions coinciding with the observed swelling phenomena, the thermal coal showed a sequence of endothermic and exothermic reactions. The changes in the specific heats also correlated well with the observed evolution of hydrogen (and shrinking for the coking coal) at higher temperatures.

**Key words:** coal, swelling, devolatilisation, tars, specific heat, reactions.

---

### INTRODUCTION

Most processes of coal utilisation require continuous heating of coal in the absence of oxygen. The heat treatment of coal leads to devolatilisation, which is a complex phenomenon comprising of chemical and physical changes within the coal structure. Coal decomposition has been described as a three-stage process (Serio *et al.*, 1987), where during the first stage coal undergoes bond breaking, melting and formation of metaplast. The metaplast is a plastic liquid which, during the second stage, decomposes upon heating, forming char and evolving tars and primary gases. The temperature at which the plastic material is eliminated from the structure is termed as resolidification. During the third stage, gaseous products continue to react evolving secondary gases, mainly carbon monoxide and hydrogen, while undergoing condensation of the carbon rings.

An attempt was made by Strezov *et al.* (2000) to distinguish the reactions involved during the different stages of the devolatilisation on a number of coals. Significant differences in the thermal properties were observed between the coals with good coking abilities and the thermal coals. These differences were observed when coal reached the plastic stage with strong exothermic heats of reactions being involved during heating of the coking coals. In the current study, the devolatilisation of two coals was visually observed with a long distance focal microscope and the images were compared with the thermal behaviour of each coal. The volatiles were also analysed under the same heating conditions.

---

<sup>1</sup> Department of Chemical Engineering, University of Newcastle, University Drive, Callaghan, 2308, Australia; e-mail: strezov.vladimir.v@bhp.com.au

<sup>2</sup> Centre for Metallurgy and Resource Processing, BHP Research & Technology Development, Newcastle Laboratories, PO Box 188, Wallsend, NSW 2287, Australia

## EXPERIMENTAL TECHNIQUE

The experimental apparatus shown in Figure 1 was used to heat a single coal particle. The particle was placed on the surface of a thin steel strip, which was constrained on the sides by brass electrodes. The heat was produced by passing AC current through the electrodes and the steel strip. The temperature was monitored using a K type thermocouple with insulated junction spot-welded on the bottom surface of the steel strip. The temperature was displayed on a monitor at a frequency of 1 Hz using a data logger and video module. In the current study, the temperature was controlled manually with an average heating rate of about 90°C/min. The particle was kept under inert atmosphere using nitrogen. A long focal distance microscope was used to obtain 100 times magnification of the coal particle. The video image was recorded during the heating with a CCD cam-

era and video recorder. Each image was later captured from the video tape using a video-grabber.

The evolution of the volatiles and tars of the coal samples was analysed with Thermogravimetric and Fourier Transform Infrared analysis (TG-FTIR). The apparatus and experimental procedure for this analysis have been described elsewhere (Solomon *et al.*, 1990).

Two coal samples with different coking abilities were chosen for this study. The proximate and ultimate analysis, plastic properties and swelling index for the samples are detailed in Table 1. While C01 is thermal coal, C04 is good coking coal with high swelling ratio. The coal samples were crushed to a particle size of approximately 1 mm.

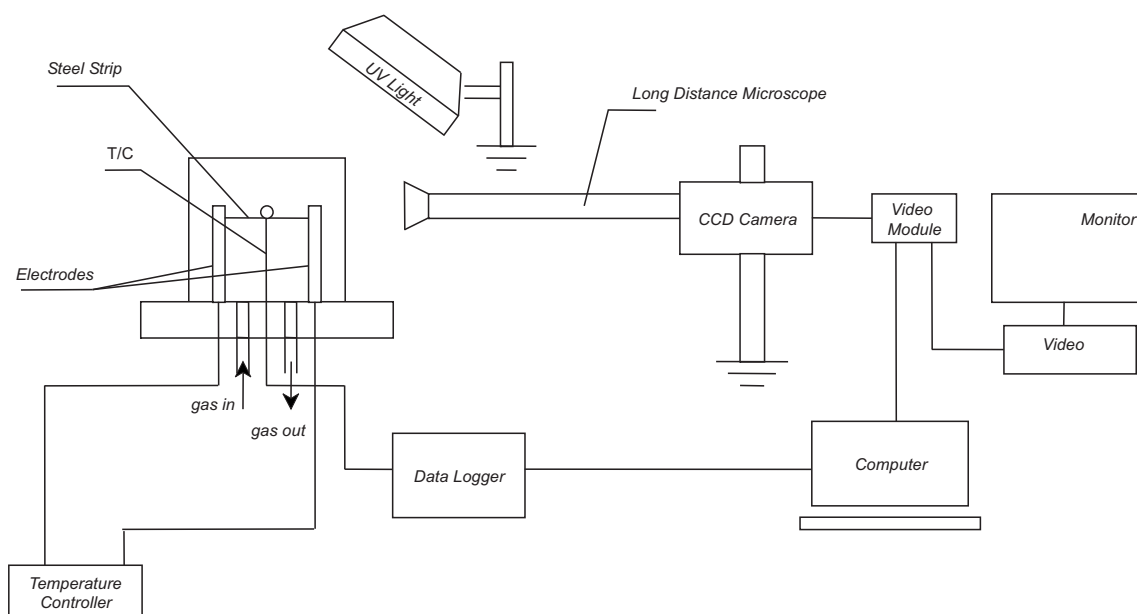


Fig. 1. Experimental arrangement for optical observation of single coal particle

## RESULTS

Selected images of the thermal behaviour of the two different coal samples at a number of temperatures are displayed in Figure 2. Below the softening temperature, the two samples did not exhibit any changes. When reaching the plastic stage, the coking coal C04 started to melt and swell. The formation of gas bubbles was also observed within the liquid. The most pronounced swelling commenced at around 460°C, reaching a maximum rate of bubble growth at the maximum fluidisation temperature (Table 1). The swelling and bubble formation completed at around 700°C with some contraction observed at higher temperatures.

Contrary to the coking coal, the thermal coal C01 showed very little swelling. It is likely that the volatiles were diffusing to the surface of the particle through the pores in the sample. Some bubbles were also formed within the liquid although in much smaller number.

The TG-FTIR analysis of the volatile release and evolution of tars (Figs. 3 and 4) showed maximum rate of devolatilisation in the temperature region where coal reached the plastic stage. The maximum evolution of tars occurred at around 450°C for C01 and 500°C for C04.

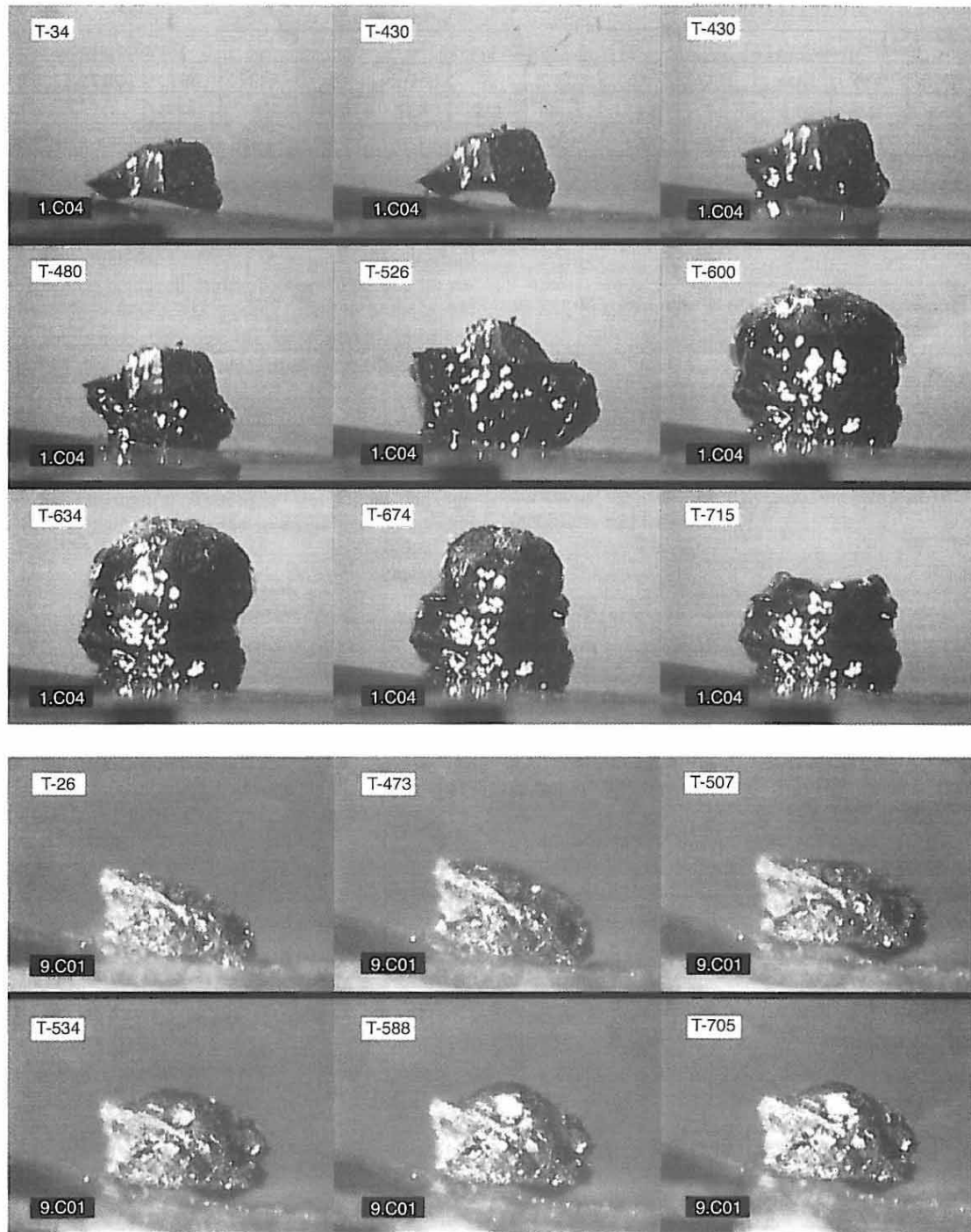


Fig. 2. Long Distance Microscopic observation of the thermal behavior of coking coal C04 and thermal coal C01

Table 1

## Coal analysis

	Proximate analysis [%]				Ultimate analysis [%]					Gieseller plastometer				
	FC	VM	Ash	H <sub>2</sub> O	C	H	N	O	S	CSN	IST	MFT	MF	RT
C01	55.8	32.2	9.2	2.8	84.1	5.16	1.92	8.18	0.64	1	420	435	5	450
C04	68.7	20.7	9.5	1.1	88.5	5.06	1.92	3.95	0.57	81/2	420	470	350	500

CSN — Crucible Swelling Number, IST — Initial Softening Temperature (°C), MFT — Maximum Fluidity Temperature (°C), MF — Maximum Fluidity (ddpm), RT — Resolidification Temperature (°C)

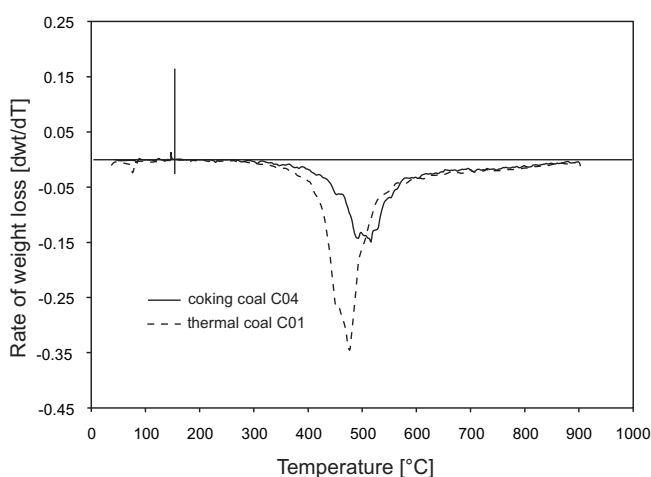


Fig. 3. Rate of weight loss from the TGA analysis for the two coal samples

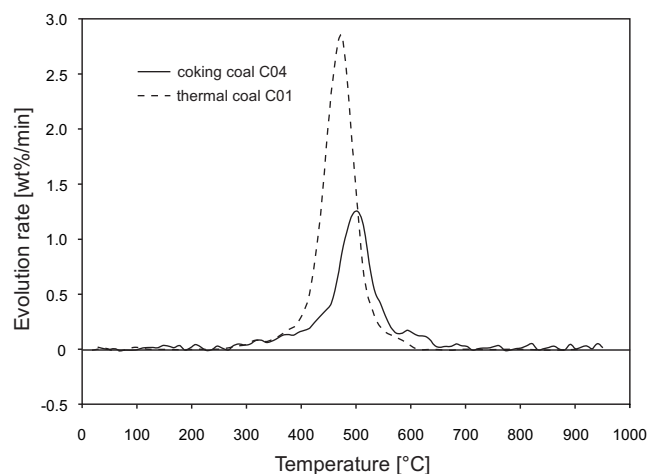


Fig. 4. Evolution rate of tars for the two coal samples

The apparent and real specific heats of the two samples have been determined elsewhere (Strezow *et al.*, 2000) and are shown in Figure 5. The real specific heat was measured accord-

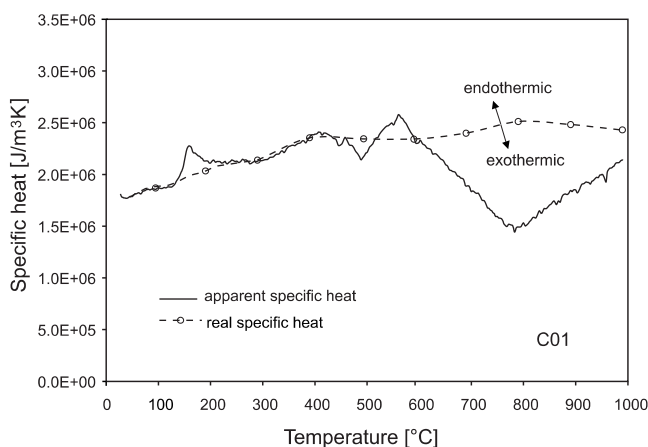
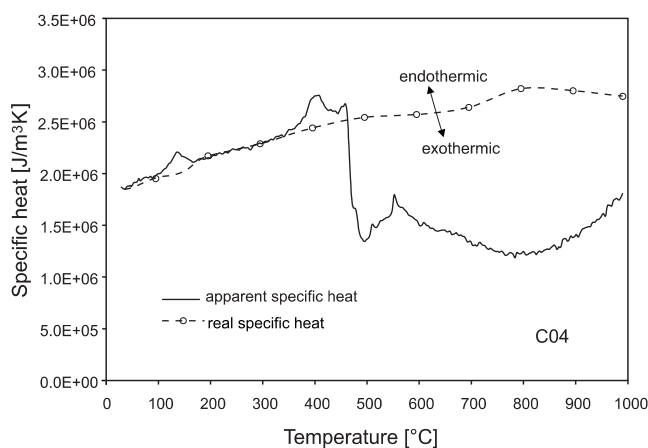


Fig. 5. Apparent and real specific heat of coking coal C04 and thermal coal C01

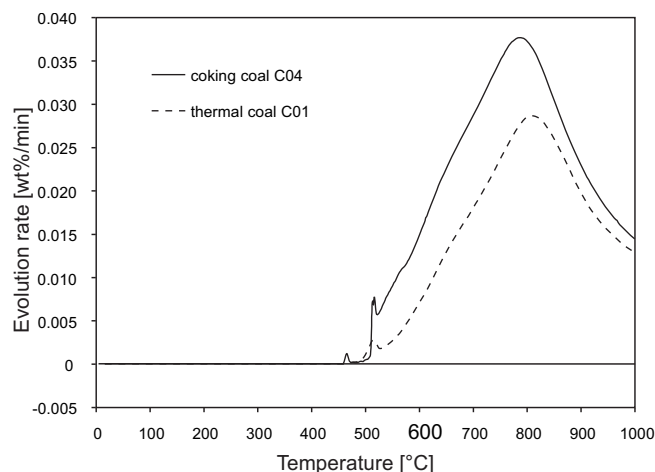
ing to the methodology described by Tomczek and Palugniok (1996). The difference between the apparent and real specific heat was attributed to the heats of reactions involved during the devolatilisation of the coal. The coking coal exhibited mainly exothermic heats for the temperatures above 460°C/min while the thermal coal showed a series of endo and exothermic reactions.

The reactions occurring in the region where coal undergoes maximum plasticity were identified as resolidification reac-

Fig. 6. Evolution rate of hydrogen for the two coal samples

tions. In this temperature region the rate of the devolatilisation was at its maximum. The evolution of the tars also reached maximum in this temperature range with thermal coal C01 exhibiting significantly higher evolution of tars. Its non-swelling behaviour was attributed to the porous structure allowing diffusion of the tars through the surface. Consequently, very small exothermic reaction occurred during this process. The tar release during heating of the coal C04 was followed by a significant bubble formation. Although the tar content was much smaller than C01, the reaction process during the plastic stage was strongly exothermic.

The most pronounced reaction for the two coals at temperatures above 600°C was the exothermic contraction reaction. In this temperature region the C-H bonds break evolving hydrogen, reflecting the formation of stronger C-C bonds. The evolution of hydrogen for the two coals was monitored with Prima



600 mass spectrometer and is shown in Figure 6. The hydrogen release in case of C04 was more pronounced reflected in the higher exothermic reaction. The contraction was also observed during the optical analysis of the two samples with higher effect in the case of coal C04.

## DISCUSSION AND CONCLUSION

The temperatures at which major changes occurred during the optical and thermal investigations were comparable. The beginning of the swelling for the coking coal C04 was in the same region as the sharp decrease in the heats of reactions. The exothermic trough was observed at around 500°C. Swelling occurred throughout the entire exothermic region and was completed at about 700°C.

The swelling of the thermal coal C01 was negligible most likely due to diffusion of the volatiles through the pores of the particle. More volatiles were released than the coal C04, but the

reaction heats associated with the devolatilisation in this region were smaller.

The contraction within the carbon planes was related to the hydrogen release commencing at about 500 to 600°C. Stronger carbon bonds were formed during the release of hydrogen. This process was associated with strong exothermic reaction having a trough at around 800°C, which coincided with the maximum rate of hydrogen evolution, indicating the commencement of the graphitisation process. The hydrogen evolution and subsequent graphitisation coincided with the observed physical shrinkage of the coal sample.

## REFERENCES

- SERIO M.A., HAMBLIN D.G., MARKHAM J.R., SOLOMON P.R., 1987 — *Energy & Fuels*, **1**, 138.
- STREZOV V., LUCAS J., STREZOV L., 2000 — Proceedings of the ISS Belton Symposium: 399–408. Sydney.
- SOLOMON P.R., SERIO M.A., CARANGELO R.M., BASSILAKIS R., 1990 — *Energy & Fuels*, **4**, 319.
- TOMEK J., PALUGNIOK H., 1996 — *Fuel*, **75**, 1089.