A MECHANISTIC STUDY OF COAL SWELLING AND CHAR STRUCTURE EVOLUTION DURING PYROLYSIS—EXPERIMENTS AND MODEL PREDICTIONS

A Thesis Submitted in Fulfillment of
the Requirement for the Degree of
Doctor of Philosophy

By

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I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

(Signed) ______________________________________

(Jianglong Yu)

TO SHUJUAN AND WALTER ...

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Publication

Awards during PhD study:

1. Special Award for Presentation, The Colloquium of Cooperative Research Centre (CRC) for Black Coal Utilization, August 2001, Sydney;
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International Symposium on Combustion:

1. **Yu, J.,** V. Strezov, J. Lucas, G. Liu and T. Wall. *A mechanistic study on char structure evolution during coal devolatilization—experiments and model predictions,* 29th International Symposium on Combustion (International), August 2002, Japan. Combustion Institute. (In press)

Review:

2. Wall, T., **J. Yu,** H. Wu, G. Liu, J. Lucas, D. Harris, "*Effect of pressure on ash formation during pulverized coal combustion and gasification*", Preprints of Symposia - American Chemical Society, Division of Fuel Chemistry (2002), 47 (2), p. 801-806.

Journals:

3. Zhang, Z.D., **J.L. Yu**, J.G. Zheng, I. Skorvanek, J. Kovac, X.L. Dong, Z.J. Li, S.R. Jin, H.C. Yang, Z.J. Guo, W. Liu and X.G. Zhao, *Structure and magnetic properties of boron*-oxide-*coated Fe(B) nanocapsules prepared by arc discharge in diborane*. Phys. Rev. B: Condens. Matter Mater. Phys., 2001. **64**(2): p. 024404/1-024404/5;

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7. **Yu, J.;** Lucas, J.; Strezov, V.; Wall, T., *Swelling and structure of DTF chars from density-fraction samples of pulverized coal*, Energy & Fuel; (Submitted)

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Conference Publications:

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11. **Yu, J.**, J. Lucas, V. Strezov and T. Wall. *"Coal and carbon nano-materials--a review*". 18th Annual International Pittsburgh Coal Conference, 2001, Newcastle, Australia;

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13. **Yu, J.**; V. Strezov; J. Lucas; T. Wall. *"Swelling behaviour of Australian coals during pyrolysis in a single particle reactor",* 4th UK Meeting on Coal Research and its Applications; 2002, London, UK;

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15. Wall, T., **J. Yu**, H. Wu, G. Liu, J. Lucas, D. Harris, *"Effect of pressure on ash formation during pulverized coal combustion and gasification",* 224th ACS Annual Meeting, Division of Fuel Chemistry (2002), Boston, U.S.A.

Presentations:

1. "Project proposal for char formation and devolatilization at pressure", Cooperative Research Centre for Black Coal Utilization (CRC) Colloquium, Newcastle, May 2000;

2. "Investigation of Swelling Behavior of Australian Coals During Pyrolysis", Australia-China Joint Workshop on Clean Power from Coal with Maximized Efficiency, Taiyuan, China, August 2001; (In English)

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Research projects:

1. A Fundamental Investigation of the Thermoplastic Behavior and Porous Structural Evolution of Coke and Char Particles, Australian Research Council Project (large grant), DP0209307, in University of Newcastle, Australia (involved as a PhD student) (2001-2002);

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ABSTRACT

This work presents a systematic study on swelling and char formation during pf coal pyrolysis using both experimental measures and modelling. By using the density fraction samples, i.e. F1.25, F1.30, F1.35, F1.50 and S1.50, prepared using the sink-float method, transient observations using a single particle reactor (SPR) and the analysis of drop tube furnace (DTF) chars prepared at atmospheric pressure consistently reveal the heterogeneity of the pyrolysis behaviour and char structures from pf coal. Particles from light density fractions, i.e. F1.25 and F1.30, experience intensive softening and swelling during heating. Apparent bubbling phenomena have been observed in single particle experiments, which is responsible for the coal swelling. On the contrary, particles from heavy density fraction samples, i.e. F1.50 and S1.50, do not exhibit softening and swelling. Correspondingly, the porosity of DTF chars decrease drastically for heavy density fraction samples. It is observed that Group I chars (porous structure) are mainly generated from two light density fraction samples, while Group III chars (solid structure) are yielded from heavy density fractions. The medium density faction sample contains a mixture of different types of chars. The heterogeneity of char characteristics is attributed to the variations in the raw coal properties among different density fractions. The characters of PEFR (pressurized entrained flow reactor) chars prepared at the elevated pressure of 2.0 *MPa* are examined, and compared with PDTF (pressurized drop tube furnace) and DTF chars. Consistent with previous work, the results suggest that high pressures increase the swelling, the number of bubbles and char porosity, while the population of both cenospheric char and solid char decreases at elevated pressures.

A mathematical model for coal swelling and char structure formation of single coal particles during devolatilization is developed based on a simplified multi-bubble mechanism. The char formation has been considered as two successive steps: the multi-bubble stage followed by a single bubble stage. During the multi-bubble stage, the rupture of bubbles is a rate-controlled process, during which the volatile release is determined by the bubble rupture rate. When the cenospheric char structure is formed, single bubble model applies. During this stage, the bubble rupture is controlled by the wall stress, and the volatiles are released through both bubble ruptures and direct diffusions of volatiles to the particle surface. The sensitivity study has been carried out, based on which the parameters for the present modelling work have been determined. Comparisons of the model predictions with the experimental data show that the present model predicts the experimental trends of the coal swelling and char structure characteristics under different heating conditions. As an advancement of previous work, the model provides a complete description of the char structure evolution process of pf coal during pyrolysis. From the standard parent coal properties of density-fraction samples, the present model predicts the heterogeneity of the char structure in the same coal, and estimates the distribution of char types, i.e., the Group I, II and III chars. The model predicted results agree with the experimental measurements.

Overall, the experimental observations and model predictions from this study consistently reveal the heterogeneity of char characteristics owing to the heterogeneous nature of coal. In addition to the dominant role of coal macerals, the influence of ash level in coal on char formation is identified. In the meantime, heating conditions under which coal is heated have a significant impact on char formation. Smaller particle sizes tend to have a higher swelling under the present experimental conditions, while the model predicts an increase in the swelling for large particle sizes. High heating rates increase the swelling ratio from both experimental observations and model prediction. Pressure plays a significant role in char formation, and favours the formation of foam char structures with a high porosity. An optimum pressure range has been predicted, which is consistent with the literature data.

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NOMENCLATURE

C_b	Molar concentration of volatiles inside the bubble, *mol/m*^{3}
D_e	Effective diffusivity of volatiles through the porous liquid shell, *m*^{2} */s*
D_L,D_g	Diffusivity in liquid phase and in gas phase, *m*^{2} */s*
E_b	Bubble escaping rate, *bubble/s*
ϕ_m	Metaplast content in coal mass, *%*
MW_v	Molar weight of volatile, *kg/mol*
n_b	Total number of bubbles inside of the particle
n_m	Molar mass inside bubbles, *mole*
P_0	The ambient pressure, *MPa*
P_b	Internal pressure of bubbles, *MPa*
R	Gas constant, *8.314N-m/g.mole.K*
ρ_0	The true density of the coal particle, *kg/m*^{3}
r_b	Bubble radius, *m*
R_p, R_{p0}	Particle radius and initial particle radius, *m*
Rt	Devolatilization rate, calculated from CPD, wt%/s
σ, σ_0	The surface tension of the coal melt, *N/m*
Sw, Swc	Wall stress *(MPa)*
t, dt	Time, *s*
T, T_c	Temperature, critical temperature, *K*
Ts, Td	Softening temperature and re-solidification temperature *(K)*
W_{p0}	Particle weight, *g*
yv	Cumulative yield of the volatile, *%wt*
δn_b	Bubble number ruptured at the particle surface
ε, ε0	Porosity of the coal particle, *%v*
μ, μc	The viscosity of coal melt, *Pa.s*

ACRONYMS

a.d.	Air dry basis
C	Cenoshpere
CCSD	Cooperative Research Centre for Coal in Sustainable Development, Australia
CPD	Chemical Percolation Model for Devolatilization
d.a.f.	Dry ash free bassis
d.b	Dry basis
DTF	Drop tube furnace
F	Foam char structure
FG-DVC	Functional Group-Depolymerization, Vaporization, and Cross-linking
IGCC	Integrated Gasification Combined Cycle
L, V, I	Liptinite, vitrinite and inertinite, respectively
MIP	Mercury intrusion porosimetry
MMMF	Moisture mineral matter free basis
NMR	Nuclear Magnetic Resonance
PEFR	Pressurized entrain flow reactor
pf	Pulverized fuel
PFBC	Pressurized Fluidized Bed Combustion
PSD	Particle size distribution
SEM	Scanning electronic microscope
SPR	Single particle reactor
TGA	Thermogravimetry
VM	Volatile matter
WMR	Wire-mesh reactor (also refered to as heated grid, or heating screen)
XRD	X-ray diffraction