ASSESSMENT OF CHAR MORPHOLOGY IN HIGH PRESSURE PYROLYSIS AND COMBUSTION

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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) ______________________________

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Glossary, Abbreviations and Symbols

ad or a.d.	Air-dried basis of analysis.
anisotropic	Coal or coke showing directional changes in optical reflectance due to rearrangement of carbon structural units by pressure or heating.
anthracite	Very high rank coal with a carbon content of circa 91 % in vitrite and a volatile matter content of less than 8 % (daf).
ash	The sum of the inorganic matter and the minerals in the coal as determined by proximate analysis (AS1038.3).
bituminous coal	A type of coal between subbituminous coal and semianthracite, including thermal and coking coals.
burnout	Degree of consumption of combustible material in the raw fuel, as a percentage. Percentage burnout is calculated using the ash tracer technique (Chapter 2.7).
Carboniferous	Period of the Geological Time Scale from about 360 million years before present to about 286 million years before present. Named for the rich coal deposits formed in many parts of the Northern Hemisphere during this time.
carbonisation	The heating of coal in the absence of oxygen to produce a carbon-rich solid (e.g. char) and liquid or gaseous products (e.g. coal gas, tars).
char	The completely or partially devolatilised product remaining after pyrolysis of pulverised coal.
clarain	A coal lithotype that has a semi-bright, shiny lustre, is finely laminated, with smooth or irregular fracture and has banding parallel to bedding (Allaby and Allaby, 1990).
coke	The solid formed by carbonisation of coal lumps above 900 °C and utilised in steel making.
combustion	Rapid reaction of coal with oxygen producing heat and light.

	Complete combustion yields CO_2, H_2O, N_2, SO_x and ash as the primary products. Incomplete combustion yields CO, hydrocarbons, tars and carbonaceous residues.
daf or d.a.f.	dry, ash free basis of analysis, without surface water or ash
db or d.b.	dry basis of analysis, without surface water
devolatilisation	Removal of volatile (gaseous and liquid) matter from coal by heating.
dmmf or d.m.m.f.	dry, mineral matter free basis of analysis, without surface water or mineral matter
DTF	drop tube furnace
durain	A coal lithotype which is grey to brownish-black, banded, dull, with a granular and rough surface. Durain is harder than vitrain and more common (Allaby and Allaby, 1990).
EFR	entrained flow reactor
exinite	see "liptinite"
FC	proximate analysis fixed carbon
fixed carbon	The difference between the initial mass and the sum of the volatile matter, ash and moisture content as determined by proximate analysis.
fly ash	Fine inorganic and mixed organic/inorganic particles produced by solid fuel combustion and suspended in the flue gases.
FMRP	Full maceral reflectogram parameter
fuel ratio	Ratio of proximate analysis fixed carbon to volatile matter, used as a classification parameter.
fusain	A coal lithotype which is sooty black, with a silky lustre; it is fibrous and friable like charcoal (Allaby and Allaby, 1990).
fusibility	The capability of coal components to soften and reharden during heating. Fused chars may show vesicles due to degassing, rounding

	of angular edges and development of anisotropy.
gasification	Reaction of organic material with steam and air or oxygen to produce gaseous fuels (e.g. syngas).
Gondwana(n) coals	Coals found in rocks that were part of the Gondwana supercontinent (i.e. Australian, Indian, South African and Antarctic coals formed during the Permian period).
graphitisation	Development of a microstructure dominated by clusters of aromatic layers similar in structure to graphite.
heterogeneous combustion	Reaction of a solid (char, coke) with a gas (oxygen, steam, carbon dioxide) that causes oxidation of the carbon in the solid.
homogeneous combustion	Reaction of gases evolved from coal or char with oxidising gases.
IGCC	Integrated Gasification Combined Cycle.
inertinite	The name of the maceral group containing fusinite, inertodetrinite, macrinite, micrinite, sclerotinite and semifusinite. These macerals are relatively high in carbon due to partial oxidation during the coalification process.
isotropic	Material that shows no visible ordering of optical texture under reflected light.
lignite	Low rank coals characterised by high bed moisture (30-75 % ash free) and volatile matter (60-70 % d.a.f.) contents and calorific values less than 19.3 $MJ.kg^{-1}$.
liptinite	The name of the maceral group containing alginite, cutinite, liptodetrinite, sporinite and sporinite. These macerals are relatively high in hydrogen and volatiles.
lithotype	The name of the coal type (at hand specimen scale), qualitatively assessed and dependent on the original plant structure and coalification path. Types are clarain, durain, fusain and vitrain.
M	proximate analysis moisture

macerals	The microscopically recognisable components of the coal, defined by shape, reflectance, colour, fluorescence, anisotropy, hardness and association. Macerals do not have constant chemical compositions.
microlithotype	The name of the association of different macerals within a minimum area of 50 μm. In this thesis, microlithotypes are determined for whole particles since most particles are smaller than 50 μm in diameter. Types are vitrite, inertite, liptite (monomaceral), clarite, durite, vitrinertite (bimaceral), and trimacerite (trimaceral) depending on the macerals present.
mineral matter	The inorganic fraction of the coal, appearing as included mineral grains within the macerals and excluded mineral grains along fractures and veins within the coal.
moisture content	The amount of water bound to the coal that is released by heating during proximate analysis.
NO_x	Oxides of nitrogen produced during coal combustion.
P	pressure
p.f.	Pulverised fuel - coal ground to pass through a 200 mesh/75 μm sieve, mean particle diameter is about 50 μm.
PDTF	high pressure drop tube furnace
Permian	Period of the Geological Time Scale from about 286 million years before present to about 248 million years before present. Often noted for the extensive glaciation of the southern hemisphere during this time.
petrography	The systematic description and interpretation of rock textures and composition under the microscope and as hand specimens.
proximate analysis	A chemical analytical technique in which a coal sample is treated at various temperatures and under different atmospheres to determine the moisture content, volatile matter, ash and fixed carbon contents.
pyrolysis	Devolatilisation (usually in an inert atmosphere) of moisture, gases

	and tars from p.f. particles during the first tens of milliseconds of residence time in a furnace.
R_{ort}	Mean random telovitrinite reflectance in oil
rank	A measure of the degree of coalification experienced by a coal. Indicates coal maturity in terms of chemical and physical properties.
reflectance	The percentage of light, incident perpendicular to the flat polished surface of a maceral, which is reflected from that surface. Rank determinations using reflectance are carried out upon telovitrinite due to the homogeneity of its reflectance at a particular level of coalification.
reflectance, maximum	The highest reflectance measured when a polished sample is rotated about an axis parallel to the path of the incident plane polarised light. The mean of the total is usually reported.
reflectance, random	The reflectance of a polished sample measured in unpolarised light without sample rotation. The mean of the total is usually reported.
residence time	The length of time a particle takes to pass through the hot zone of a furnace.
semianthracite	Coal between bituminous coal and anthracite in rank. Characterised by low volatile matter contents (8-13.9 % d.a.f.) and high mean random telovitrinite reflectances (about 1.9-2.7 %).
soot	Very fine deposits (10-50 nm in diameter), consisting mainly of carbon from the hydrocarbons that surround the coal particle during heat treatment.
SO_x	Oxides of sulphur produced during coal combustion.
subbituminous coal	Coal between lignite and bituminous coal in rank, with calorific values between approximately 19.3 and 30.1 $MJ.kg^{-1}$. Subbituminous coals do not show any caking properties.
telovitrinite	The vitrinite maceral most often used for rank determinations. Characterised by structure showing preserved cell walls, infilled cell

	cavities and reflectances lower than those of associated inertinites.
turbostratic	Arrangement of layers composed of aromatic carbon rings in stacks. The aromatic stacks are linked by aliphatic chains and non-aromatic groups that hamper further linkage of the stacks.
ultimate analysis	A chemical analytical technique that determines the quantity of elemental carbon, hydrogen, nitrogen, sulphur and oxygen (by difference) in a coal sample.
VM	proximate analysis volatile yield
vesicle	A void within char or coke formed by the expansion of evolved steam or gases.
vitrain	A coal lithotype which is black, with a brilliant, glassy lustre, conchoidal fracture, and cubic cleavage. It is clean and structureless (Allaby and Allaby, 1990).
vitrinite	The name of the maceral group containing tellinite (has visible cell structure), collinite (structureless) and various submacerals. Vitrinite reflectance increases with coal rank and is commonly used as a rank indicator.
volatile matter	The material lost during proximate analysis at high temperatures and under reducing conditions after the moisture content has been removed.

Abstract

Drives to reduce carbon dioxide emissions and improve efficiency make pressurised gasification an attractive option in future coal utilisation technologies. Process conditions in pressurised gasification differ from conventional entrained flow combustion in pressure, atmosphere, peak temperature and heating rate, yet there is sparse literature concerning coal behaviour under pressurised conditions. Previous work suggests that bituminous coals can show enhanced plasticity at high pressures and this phenomenon may not be predicted by standard tests of coking properties.

Previous modelling of char reactivity and burnout in combustion and gasification has failed to take account of the petrographic variability of coals. Current work to improve the predictive capacity of these models requires evaluation of the effects of different macerals and of char preparation pressure on char behaviour. Prior studies of whole coals subjected to high pressure and high temperature conditions have shown that daughter char morphology is influenced by particle heating rate, the size distribution of the feed coal, furnace pressure, feed rate, coal rank and the parent coal petrography.

Chars were produced by pyrolysis at 1100 or 1300 °C and 1, 5, 8, 10 and 15 atm furnace pressure, and by combustion at 1100 °C and 1 atm furnace pressure, from a suite of East Australian bituminous coals. The characteristics of the chars and their parent feed coals were quantified using semi-automated image analysis, as well as petrographic, particle size and chemical analyses. Relationships between the morphology of the chars and properties of the parent coal and furnace pressure were established.

Daughter char morphology and volatile yield was found to be related to the petrographic composition of the parent feed coals, their full reflectance profiles and the char preparation pressure. Chars derived from vitrinite-rich lithotypes and those prepared under high pressure conditions show larger mean diameters, porosities, sphericities and proportions of porous char types. Volatile yield is related to the vitrinite content of the lithotype. A parameter derived from full coal reflectograms proves to be effective for prediction of char morphology and trends in volatile yield. The Carbon Burnout Kinetic model is improved in its predictive value by including parent coal vitrinite content as an input parameter and could be further improved by utilising the full coal reflectogram parameter.