OVERCOMING PROBLEMS OF USING CHARCOAL AS A SUBSTITUTE FOR COAL AND COKE IN IRON AND STEELMAKING OPERATIONS[1]

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Abstract

The substitution of charcoal for coal and coke is being investigated as a way to reduce the net CO_2 emissions from iron and steel making operations. The particular properties of charcoal such as high reactivity, low ash and sulphur content and controllable chemical properties, e.g. volatile matter, makes it suitable for many steelmaking applications. However, other properties such as low density and a high propensity to absorb water from the atmosphere are problems which could restrict the future utilisation of charcoal. The density of charcoal is the main topic of this study and is an important property to optimise in order to minimise transport and handling costs as well as control charcoal reactivity and strength. Investigations into charcoal density included comparisons between pyrolysed dense biomass fuel (DBF) wood pellets and pyrolysed conventional Australian Eucalypt wood chips. The resulting properties of dense charcoal made from DBF pellets were compared to conventional charcoal made from wood chips. The comparisons showed that the true density of charcoal particles increased with pyrolysis temperature. There was little difference between the true density of conventional charcoal made from wood chips and dense charcoal made from DBF pellets. However, the apparent density of charcoal made from DBF pellets was about 80% higher than that of conventional charcoal. Charcoal porosity was found to increase with pyrolysis temperature. The porosity of dense charcoal from DBF pellets was about half the porosity of conventional charcoal. The bulk density of dense charcoal from DBF pellets was about 120% higher than the density of charcoal made with wood chips. Making charcoal from dense wood pellets was shown to be a convenient and effective way to increase the density of charcoal for possible application in steel-making.

Key words: Charcoal; Density; Dense biomass fuel pellets; Wood chips; Pyrolysis.

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1 INTRODUCTION

A collaborative research project between the Australian steel industry, represented by OneSteel and BlueScope Steel, and the CSIRO aims to reduce the net CO_2 emissions from iron and steelmaking operations through the substitution of fossil carbon for renewable carbon, or charcoal, derived from biomass. This work is part of Australia's contribution to the WorldSteel CO_2 breakthrough program. The aim is to improve the greenhouse performance of the industry by sourcing carbon derived from sustainable biomass supplies. The particular properties of charcoal, such as low sulphur and ash levels and controllable chemical properties such as reactivity and volatile content make charcoal an attractive source of carbon for many iron and steel making operations. Other properties such as low density and a high propensity to absorb moisture from the atmosphere are likely to add to biomass processing costs and restrict the rate of charcoal use in existing iron and steelmaking processes. The density of charcoal is an important property to control in order to minimize specific transport and handling costs as well as control charcoal reactivity and strength.

Recent experimental work in this project has been concerned with the densification of charcoal as a way of reducing handling costs and improving the application of charcoal to the operations of iron ore sintering and cokemaking. One possibility of increasing the density of charcoal is to use dense biomass fuel (DBF) pellets as a biomass source. This is a bulk material used in Europe and North America as a source of renewable fuel for electricity generation and domestic heating. The experimental work reported in this paper examined the density of charcoal made from DBF pellets and compared the results to charcoal made from conventional hardwood wood chips. Initially a small gram scale (30 g) thermo-gravimetric apparatus (TGA) was used to carefully control the pyrolysis conditions and ensure that the DBF pellets were able to withstand the stresses involved in the pyrolysis process. The resulting charcoal was then compared to charcoal made in a kilogram-scale retort using both DBF pellets and wood chips as biomass sources.

This work is part of a larger experimental program on the densification of charcoal. Other work on pyrolysis under pressure and the briquetting of charcoal will be published at a later date.

2 MATERIALS AND METHODS

2.1 Materials

Two types of wood were used in the experimental work. The first was a Eucalypt hardwood from Central New South Wales, Australia, called Blackbutt (E. Pilularis). This wood was supplied as coarse chips from an export wood chipping facility. The second type of wood was compressed pellet form called dense biomass fuel (DBF) pellets. These pellets were sourced from an export supply in Albany, Western Australia which used a variety of hardwoods as feedstock material. Table 1 shows the proximate and ultimate analysis of the two types of wood.

Table 1: Proximate and ultimate analysis of the Blackbutt and DBF wood pellets

	Proximate analysis (% db*)			Ultimate analysis (% db*)					
Wood type	Ash	Volatile matter	Fixed carbon	C	H	N	Cl	S	O
Blackbutt wood chips	0.08	78.9	21	50.4	6.0	<0.01	<0.01	0.001	43.5
DBF wood pellets	0.66	79.3	20	50.5	6.1	0.03	0.01	0.01	42.7

**db = dry basis.*

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Both the Blackbutt wood chips and DBF pellets were pyrolysed at the kilogram scale in a modified rotary furnace. The DBF pellets were also pyrolysed at the 30 gram scale, for comparison, in a TGA device fitted to a vertical tube furnace. This apparatus allowed careful control of the pyrolysis parameters of heating rate and temperature.

2.2 Equipment and Procedure

2.2.1 Kilogram-scale pyrolysis

The rotary furnace was able to process about 5 kg of wood chips and up to 15 kg of DBF pellets in a batch operation. A schematic of the furnace and associated equipment is shown in Figure 1. The furnace was heated by electrical resistance elements. A PID controller adjusts the power input to the elements and hence controlled the furnace temperature. A control thermocouple was located between the outer and inner shells.

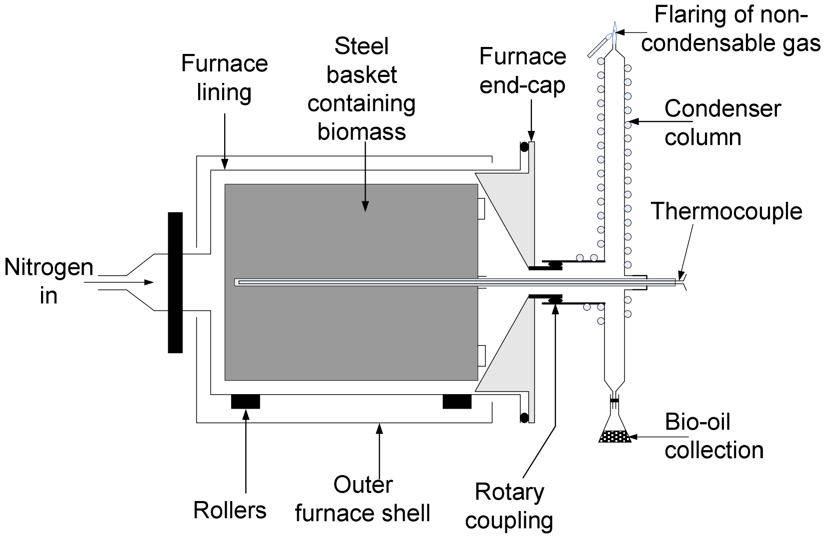

Figure 1: Schematic diagram of the rotary furnace and ancillary equipment used in the kilogram scale pyrolysis experiments.

A sheet metal basket made from perforated steel was used to contain the dried biomass during test runs. The basket was approximately 25 cm in diameter and 50 cm in length. The inside of the basket was separated into four segments, with a hollow tube in the centre into which a thermocouple is placed.

Nitrogen gas flowed into the rear of the furnace and passed through and around the basket before being exhausted from the front and up the brass condenser tube. The condenser tube has an inside diameter of approximately 7 cm and its main purpose is to condense heavy fractions in the fume. A rotary coupling connected the condenser with the rotating furnace shell.

The following procedure was used in the kilogram scale pyrolysis experiments.

- the basket was filled with dried DBF pellets or wood chips and weighed before being closed and sealed in the furnace. Before heating, the furnace contents were purged with a minimal flow of nitrogen (about 5 L/min) for several hours. While the furnace was purged, the gas pilot light was lit, the cooling water for the condenser tube was turned on, and the inner shell of the furnace was allowed to rotate at approximately 5 rpm.
- the furnace temperature controller was programmed to ramp from ambient temperature to 150°C at 10°C/min, and then to reach the final temperature at

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2°C/min. The furnace temperature was held at the required temperature until the sample temperature started to plateau (for about 15 minutes), and then the heating elements were turned off.

- the condensate collected in the beaker at the bottom of the condenser tube was weighed along with the final weight of the basket and its contents.
- the charred DBF pellets were removed, weighed and sent for analysis.

2.2.2 Gram-scale pyrolysis

Small scale pyrolysis experiments using DBF pellets were performed using the TGA device in conjunction with a vertical tube furnace. Figure 2 shows a schematic diagram of the experimental setup. The pellet sample, of about 30 g, was contained in a small sealed steel container of 36 mm diameter and 71 mm in length. A small hole with a diameter of 2 mm at the base of the crucible allowed the evolved fumes and gases to escape. The crucible was suspended in the constant temperature zone at the centre of the furnace. The top end of the suspension wire was connected to an electronic balance. This balance measured the weight loss of the crucible and hence indicated the progress of pyrolysis.

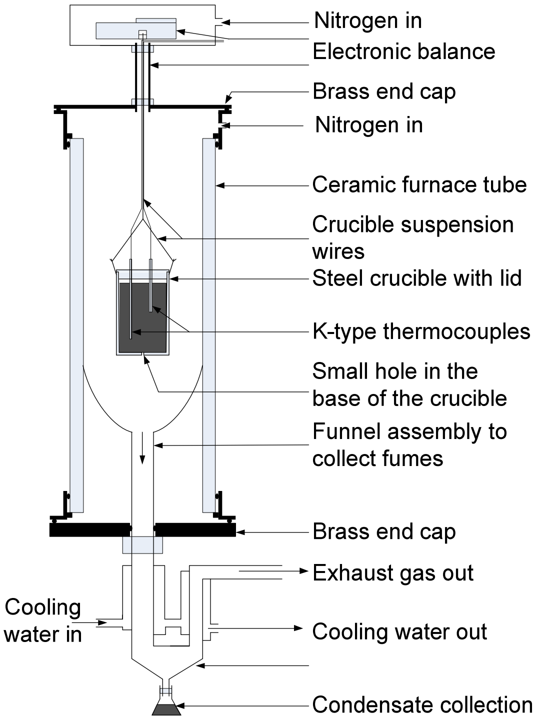

Figure 2: Schematic diagram of the experimental apparatus used in the gram scale pyrolysis experiments.

Nitrogen gas was used to remove oxygen from the balance enclosure and furnace tube. Two nitrogen input ports were used: one through the balance enclosure and the other through the top end cap. This arrangement ensured the flow of gas was to the bottom of the tube, away from the balance.

The fumes generated from the pyrolysis reactions were collected by a funnel arrangement which was supported by the bottom furnace end cap. The fumes were directed to a water cooled condenser where the condensable fractions were removed. Non condensable gases were removed to exhaust from the output side of the condenser.

The vertical tube furnace was heated by kanthal electrical resistance elements. The heat was transmitted through the furnace tube and radiated to the crucible. A PID controller regulated the power to the furnace elements and hence controlled the temperature of the crucible.

The following procedure was used in the gram scale pyrolysis experiments.

- DBF pellets were dried at 100°C for at least 24 h prior to an experiment.
- the pellets were weighed into the crucible and the lid was placed into position. The crucible was suspended from the electronic balance, the thermocouples were put in position and the furnace sealed.
- the balance enclosure and furnace tube were flushed with nitrogen for at least 1 hour.
- the cooling water to the end caps and condenser was turned on and the data logger started.
- the furnace was turned on and a controlling program started. In general, the heating profile was: heat from room temperature to 150°C at 10°C/min, then heat to the experimental temperature at the planned heating rate, dwell at the planned temperature for a set time and finally turn off to allow the furnace to cool.

When the furnace was cool, the charcoal pellets and condensate were retrieved. The pellets were weighed and sent for analysis.

The volatile content and ash content of biomass and charcoal samples were determined by heating to 900°C and combustion at 815°C respectively. True density was determined by helium pycnometry using a Micrometrics multi volume pycnometer 1305. Apparent density was determined using mercury porosimetry using a Quantachrome porosimeter autoscan 60. Bulk density was determined by measuring the weight of one litre of the charcoal sample.

3 RESULTS

Table 2 shows the experimental conditions and the resulting charcoal proximate analysis, charcoal yield and density, of the gram scale experiments using DBF pellets. Table 3 shows the experimental conditions, yield and bulk density of charcoal made from DBF pellets using the kilogram scale pyrolysis equipment. Table 4 shows the experimental conditions, and the proximate analysis, yield and density of charcoal made from Blackbutt wood chips using the kg scale pyrolysis equipment. Charcoal yield is the amount of charcoal produced by the pyrolysis of dry biomass expressed as a percentage of the biomass weight.

Table 2: The experimental conditions, proximate analysis, charcoal yield, and density of charcoal produced in the gram scale pyrolysis experiments, (db = dry basis, GS = gram scale)

Test No.	Temp (°C)	Heating rate (°C/min)	Dwell time (min)	Ash content (% db)	Volatile matter (% db)	Fixed carbon (% db)	Charcoal yield (%)	Apparent density (g/cm^3)	True density (g/cm^3)
GS-1	650	1	15	1.8	5.5	92.7	30.0	1.053	1.619
GS-2	650	5	15	2.1	5.2	92.7	26.4	0.978	1.598
GS-3	650	10	15	2.1	6	91.9	24.9	0.919	1.584
GS-4	650	15	15	2.4	5.7	91.9	24.9	0.995	1.598
GS-5	650	0.3	15	1.7	4.7	93.5	31.9	1.044	1.644
GS-6	350	5	15	1.3	35.4	63.5	37.7	0.946	1.319
GS-7	450	5	15	1.6	22.9	75.5	30.9	0.975	1.382
GS-8	550	5	15	1.9	11.3	86.8	28.0	0.972	1.399
GS-9	350	5	60	1.5	32.5	66	36.4	0.988	1.303
GS-10	750	5	15	2	2.8	95.2	25.4	1.036	1.828

Table 3: Experimental conditions yield and bulk density of charcoal made from DBF pellets using kilogram scale pyrolysis equipment, (KS = kilogram scale)

Test No.	Temperature (°C)	Heating rate (°C/min)	Charcoal yield (%)	Charcoal bulk density (g/cm^3)
KS-1	350	1	42	0.43
KS-2	615	1	26	0.44
KS-3	615	2	24	0.46

Table 4: Experimental conditions, ultimate analysis and density of charcoal made from Blackbutt wood chips using kilogram scale pyrolysis equipment (db = dry basis, KS = kilogram scale)

Run No.	Temperature (°C)	Ash content (% db)	Volatile matter (% db)	Fixed Carbon (% db)	Charcoal yield (%)	Apparent density (g/cm^3)	True density (g/cm^3)	Bulk density (g/cm^3)
KS-4	300	0.33	64.9	34.8	65.3	0.69	1.376	0.226
KS-5	400	0.44	31.7	67.9	42.5	0.58	1.383	0.177
KS-6	500	0.24	20.6	79.1	37.1	0.55	1.407	0.193
KS-7	600	0.18	10.3	89.6	32.7	0.44	1.428	0.178
KS-8	700	0.28	3.9	95.9	30.2	0.49	1.541	0.198
KS-9	850	0.92	<0.5	99.1	29.6	0.50	1.806	0.215

4 DISCUSSION

4.1 Charcoal Yield and Volatile Content

Figure 3 shows that, in the pyrolysis of DBF pellets in the gram-scale apparatus, the yield of charcoal increased with decreasing heating rate. This observation agrees with the work of Antal and Gronli[1]. In a summary of pyrolysis work stretching back more than 150 years they concluded that as pyrolysis heating rate is decreased, an asymptote in the char yield is reached. Very low heating rates are not generally feasible due to the large time requirements. The lower heating rate provides more time for secondary char-making reactions to take place and hence results in higher charcoal yields. Figure 3 also shows that the volatile matter of charcoal made from the DBF pellets increased slightly with increasing heating rate, despite some scatter in the results.

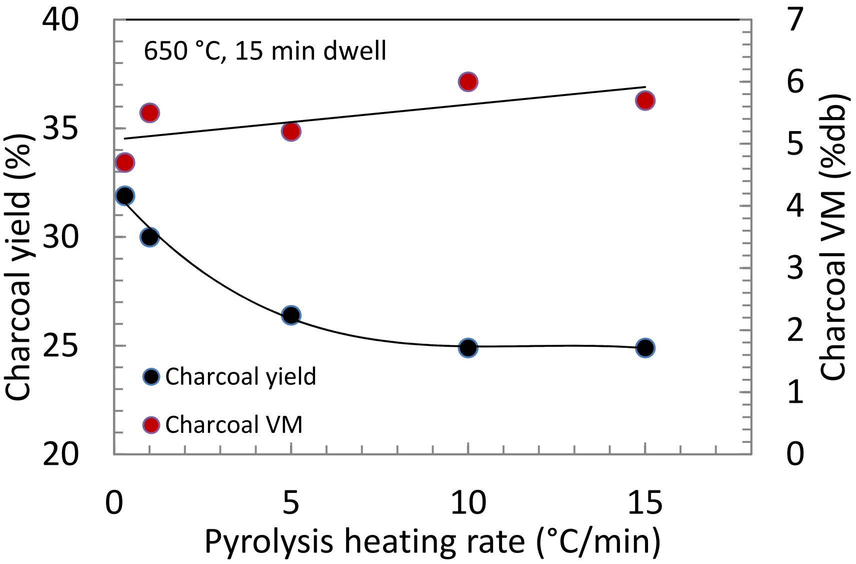

Figure 3: Charcoal yield and volatile content plotted against pyrolysis heating rate for charcoal made from DBF pellets using the 30 gram pyrolysis apparatus.

Figure 4 shows the effect of pyrolysis temperature on charcoal yield during pyrolysis for results of the present work and some literature data. As the pyrolysis temperature is increased more of the volatile components of the wood are lost to the system and hence the yield of charcoal decreases. The DBF pellets and Blackbutt chips were pyrolysed at different heating rates (5°C/min and 1°C/min) respectively. The difference in the charcoal yield curves for DBF pellets and Blackbutt wood chips is likely to be due to the different heating rates. The observed high yield of charcoal from Blackbutt wood chips at all temperatures is likely to be due to the relatively slow heating rate adopted. The data from Demirbus[2], from the pyrolysis of hazelnut shells also shows relatively high charcoal yield, especially at higher temperatures. Although the heating rate in these experiments was not noted, the reported yields are fairly close to the DBF and Blackbutt data charcoal yields. The data from Purdy et al.[3] was for mixed hardwoods. Their results show a relatively low charcoal yield, but within the range of the present results. Purdy et al also did not specify the heating rate of their experiments. Kumar, Gupta and Sharma[4] showed that for the pyrolysis of Acacia and Eucalypt wood, charcoal yield decreases quickly with increasing pyrolysis temperature up to about 800°C and decreases slowly at higher temperatures. This agrees with the results of the present work.

The fixed carbon (FC) content of charcoal increases, while the charcoal yield during pyrolysis decreases with increasing pyrolysis temperature. Charcoal prepared at high temperatures will contain a lower volatile content and will contain a higher purity carbon structure. Hence the recovery of FC during pyrolysis is likely to be relatively independent of pyrolysis temperature. The amount of carbon from the original biomass which could be available for high temperature reaction can be calculated by multiplying the charcoal fixed carbon (FC) with the charcoal yield. This product is termed the FC recovery. Figure 5 shows the FC recovery plotted against pyrolysis temperature for the charcoal made from DBF pellets and from Blackbutt woodchips.

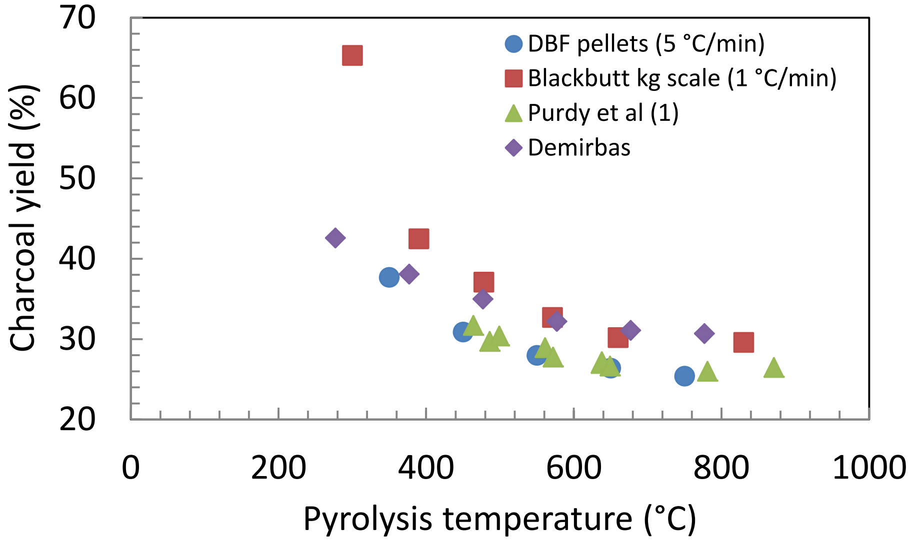

Figure 4: Charcoal yield plotted against pyrolysis temperature for charcoal made from DBF pellets, Blackbutt wood chips and some selected literature data.

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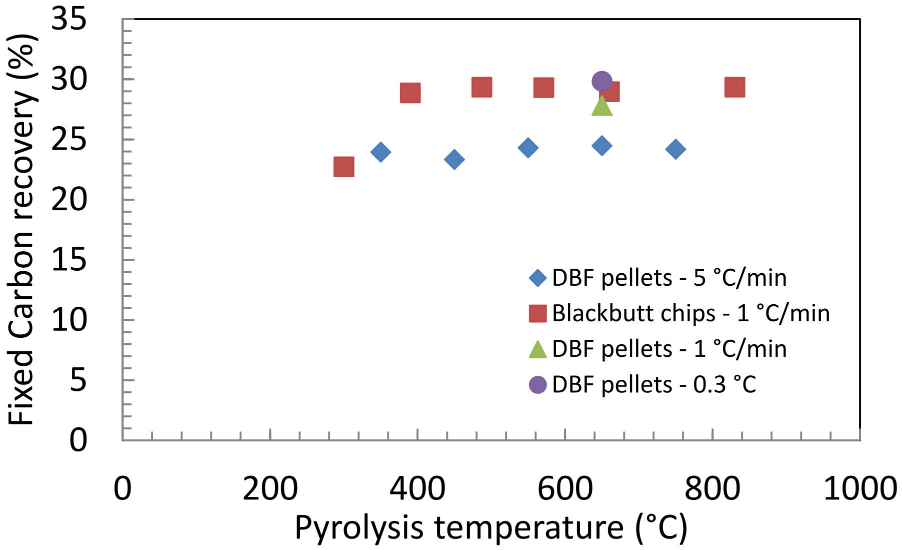

Figure 5: Fixed carbon recovery plotted against pyrolysis temperature.

Figure 5 shows that the recovery of FC is largely independent of pyrolysis temperature, especially above 400°C. For the charcoal made from DBF pellets at 650°C, the FC recovery increased with decreasing pyrolysis heating rate. The higher FC recovery for Blackbutt wood chips is likely to be due to the lower pyrolysis heating rate compared to the pyrolysis of DBF pellets. At a heating rate of 1°C/min the charcoal made from DBF pellets and Blackbutt wood chips showed very similar FC recovery.

4.2 Charcoal Density

Charcoal density can be expressed in a number of ways: true density concerns the solid carbon walls of the charcoal particles with no porosity considered, whilst apparent density concerns charcoal particles considering both solid walls and the porosity of the particles. Finally the bulk density is the macro property of a large assemblage of particles, which is related to the packing density of the particles. The internal porosity (ε_p) of the charcoal particles is related to the apparent (ρ_{app}) and true density (ρ_{true}) through the function shown in equation 1.

$$\varepsilon_p = 1 - \frac{\rho_{app}}{\rho_{true}} \qquad [1]$$

Figure 6 shows that the density and porosity of charcoal made from DBF pellets is largely independent of pyrolysis heating rate at a temperature of 650°C. Figure 7 shows that the true density of charcoal particles is about 1.4 g/cm^3 and is independent of pyrolysis temperature up to about 600°C. At higher temperatures the true density increases with increasing temperature. Kumar, Gupta and Sharma[5] showed that as pyrolysis temperature increases, the carbon microstructure becomes increasingly ordered, due to the growth of graphite microcrystallites. This increasing ‘graphitisation’ of the charcoal structure increases its true density.

At temperatures below 600°C, the true density of charcoal made from DBF pellets and Blackbutt chips is very similar. However, at higher temperatures the true density of charcoal made from the Blackbutt chips increases at a slightly slower rate. Kumar and Gupta[6] showed that the true density of Eucalypt and Acacia charcoal increased linearly with pyrolysis temperature. At a heating rate of 4°C/min charcoal true density increased from about 1.4 g/cm^3 at 400°C to about 1.6 at 1,000°C. These results are less than the true densities obtained in the present work.

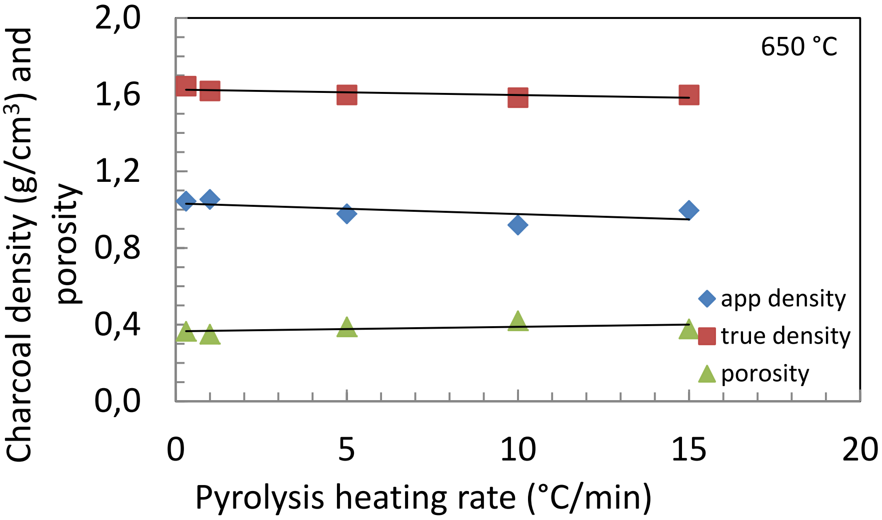

Figure 6: Density and porosity of charcoal made from DBF pellets plotted against pyrolysis heating rate.

Figure 8 shows that the apparent density of charcoal made from DBF pellets increases linearly from 0.95 to 1.04 g/cm^3 while pyrolysis temperature increases from 350 to 750°C. In comparison, the apparent density of charcoal made from Blackbutt wood chips decreases from 0.69 g/cm^3 at 300°C to a minimum at about 0.44 g/cm^3 at 600°C before increasing slightly at higher temperatures. This observed minimum in charcoal apparent density agrees with observations and data of Kumar and Gupta[6]. They showed that for conventional wood chips, charcoal porosity increases with increasing pyrolysis temperature due to loss of volatile components and crack formation. Charcoal shrinkage tends to decrease porosity. The net result is a minimum in charcoal apparent density at about 600°C.

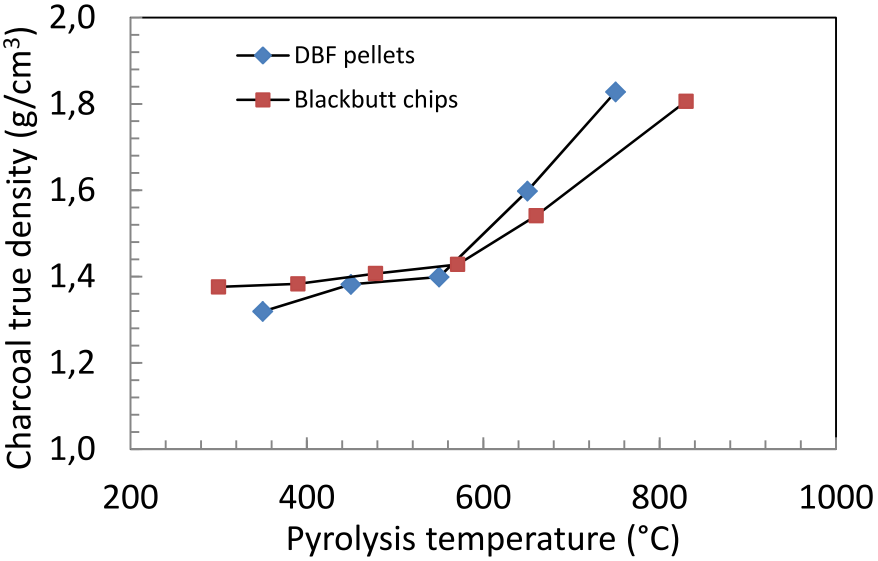

Figure 7: True density of charcoal made from DBF pellets and Blackbutt wood chips plotted against pyrolysis temperature.

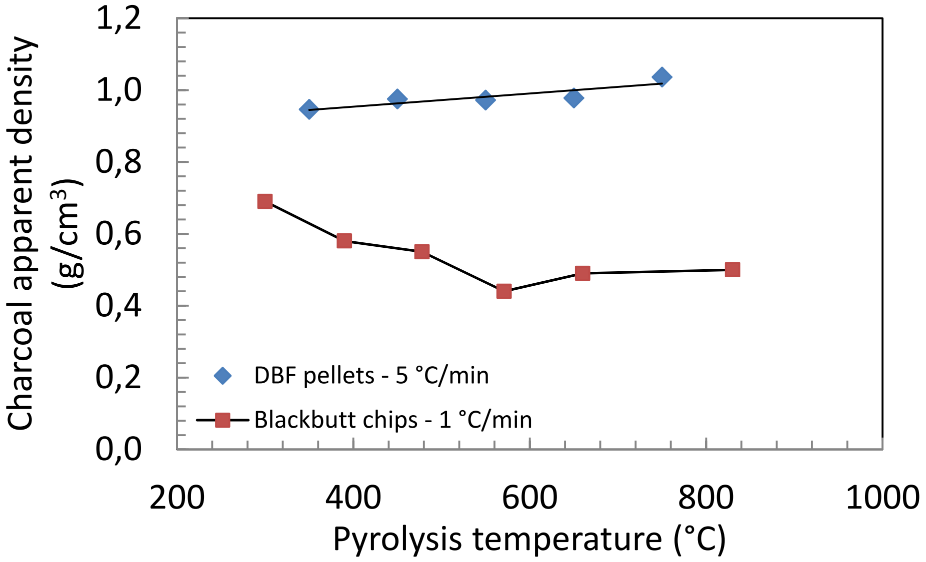

Figure 8: Apparent density of charcoal made from DBF pellets and Blackbutt wood chips plotted against pyrolysis temperature.

Figure 9 shows that the porosity of charcoal made from both DBF pellets and Blackbutt wood chips increases linearly with pyrolysis temperature. The porosity of Blackbutt charcoal increases from about 0.5 to 0.7 while the porosity of charcoal made from DBF pellets increases from about 0.25 to 0.45 when the temperature increases from 300 to 850°C. The lower porosity of DBF charcoal is due to the higher apparent density, illustrated in Figure 8.

Bulk density is an important property in the industrial processing of charcoal. Higher bulk density will decrease specific transport and handling costs as well as assisting to overcome problems of low rates of pneumatic transport for injection processes. Figure 10 shows a comparison of the bulk density of charcoal made from Blackbutt chips and DBF wood pellets. The bulk density of the chip charcoal is about 0.20 g/cm^3 and is almost independent of pyrolysis temperature at temperatures greater than 400°C. In comparison the bulk density of charcoal made from DBF pellets is 120% higher at about 0.45 g/cm^3. Figure 10 also shows that the bulk density of charcoal made from DBF pellets is independent of pyrolysis heating rate.

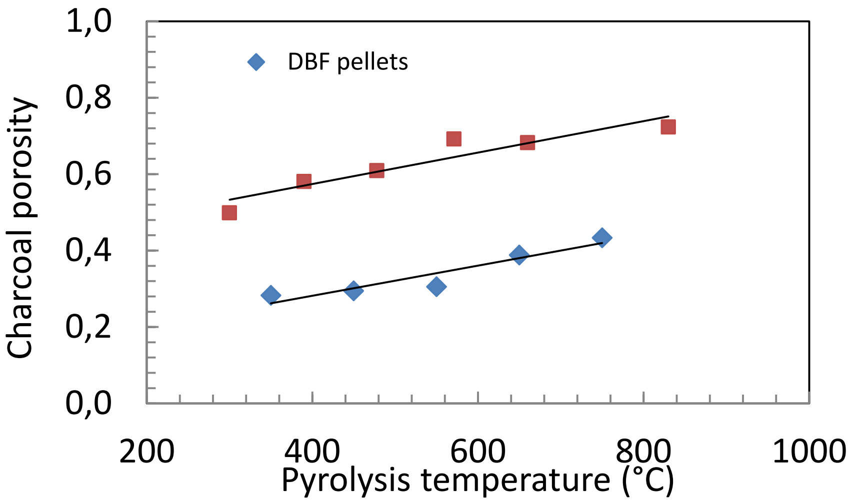

Figure 9: Porosity of charcoal made from DBF pellets and Blackbutt wood chips plotted against pyrolysis temperature.

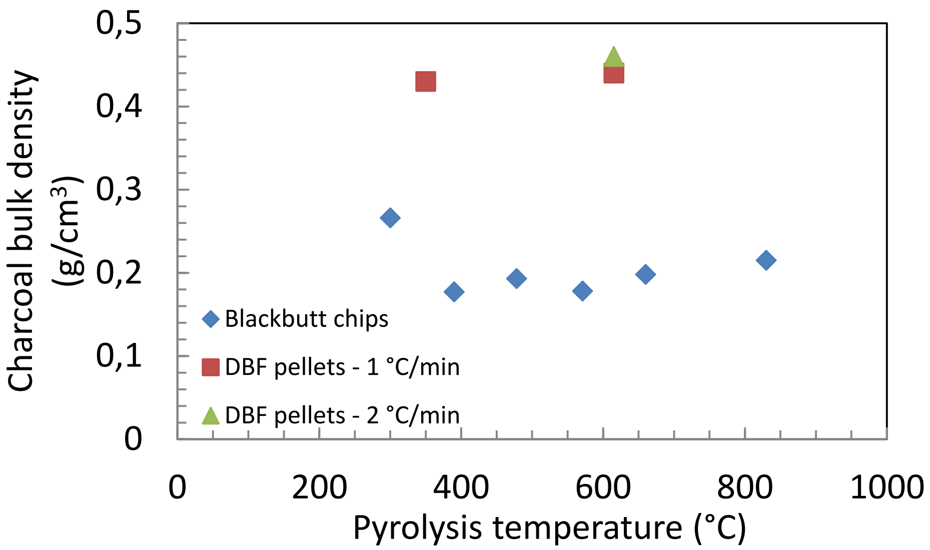

Figure 10: Bulk density of charcoal made from DBF pellets and Blackbutt wood chips plotted against pyrolysis temperature.

5 CONCLUSIONS

The yield of charcoal made from DBF pellets was found to be inversely related to the pyrolysis heating rate while the volatile content of charcoal has a slight positive dependence on the pyrolysis heating rate. The yield of charcoal was also found to decrease with increasing pyrolysis temperature. The differences between the yield of charcoal made from DBF charcoal and Blackbutt wood chips was due to variations in heating rates, rather than the intrinsic properties of the original biomass.

The density and porosity of charcoal made from DBF pellets was independent of pyrolysis heating rate. A comparison between the densities of charcoal made from DBF pellets and Blackbutt wood chips showed that the true densities were similar and both increased at temperatures greater than 600°C. The apparent density of DBF pellet charcoal had a slight positive dependence on pyrolysis temperature while the apparent density of charcoal made from wood chips had a minimum at 600°C and increased slowly at higher temperatures. The apparent density of the dense pellet charcoal particles was about 80% higher than that of conventional charcoal made from wood chips. The bulk density of charcoal made from conventional wood chips was about 0.2 g/cm^3 and independent of pyrolysis temperatures greater than 400°C. In comparison the bulk density of charcoal made from DBF pellets was about 120% higher at 0.45 g/cm^3 and was independent of pyrolysis heating rate.

The porosity of both charcoal types increased with increasing pyrolysis temperature. The porosity of DBF charcoal increased from 0.25 to 0.45 over the temperature range 350 to 750°C. In comparison the porosity of the wood chip charcoal increased from 0.5 t 0.7 over the temperature range 300 to 830°C.

The use of dense charcoal in steelmaking is expected to provide advantages in the applications renewable carbon to iron ore sintering, coke making and recarburisation. These applications are part of the on-going biomass experimental program being conducted at CSIRO.

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REFERENCES

1 ANATAL M. J AND GRONLI M., The art, science and technology of charcoal production, *Ind Eng Chem Res*, v. 42, p. 1619-1640, 2003.

2 DEMIRBAS A., Relationship between carbonization temperature and pyrolysis products from biomass, *Energy exploration and exploitation*, v. 22, No. 6, p. 411-420, 2004.

3 PURDY K.R., MARTIN C.E., CAMPBELL S.J., GARR J. D., GRAHAM G. M., KERR C. P. AND WYATT M. L., Empirical model of slow pyrolysis of hardwood chips, *App Biochem and Biotech*., v. 25, p. 49-65, 1990.

4 KUMAR M., GUPTA R.C. AND SHARMA T., Effects of carbonization conditions on the yield and chemical composition of Acacia and eucalypt wood chars, *Biomass and Bioenergy*, v. 3, No. 6, p. 411-417, 1992.

5 KUMAR M., GUPTA R.C. AND SHARMA T., X-ray diffraction studies of Acacia and Eucalypt wood chars, *J. Mat. Sci*. v. 28, p. 805-810, 1993.

6 KUMAR M. AND GUPTA R. C., Influence of carbonization conditions on physical properties of acacia and Eucalypt wood chars, *Trans Indian Inst Met*, v. 46, No. 6, p. 345-353, 1993.