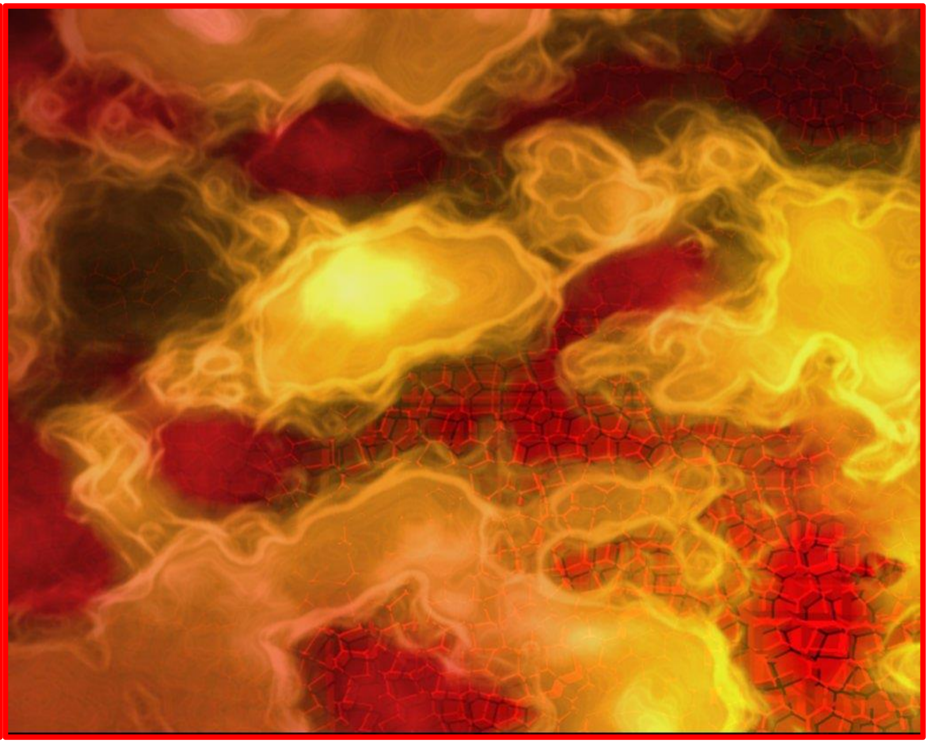
Low Reactivity Coke-like Char

from Victorian Brown Coal



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MONASH University

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BROWN COAL INNOVATION AUSTRALIA

INTRODUCTION

Metallurgical Coke

- Macroporous carbon material
- Produced from coking coal through **liquid phase carbonization**
- **Fused carbon, strong, chemically stable**
- **High strength;** has a measured compressive strength of 15-20MPa
- Has a **measured reactivity** (Coke Reactivity Index ,CRI 25-35)

Coke is used in a blast furnace to produce iron from iron ore

Acts as a

- **Fuel;** provides heat
- **Chemical reducing agent;** for smelting iron ore
- **Permeable support;** supports the iron ore bearing burden

Coke

There is no other material available yet to replace the coke in a blast furnace

*Díez MA, et al., Coal for metallurgical coke production: predictions of coke quality and future requirements for coke making, International Journal of Coal Geology, 50 (2002) 389-412.

INTRODUCTION

Coking Coal

- Some bituminous coals
- Higher rank coal
- **Melts** on carbonization
- **Resolidifies** at higher temperature to form **Coke**

BUT, Limited reserves and increasing demand

- Becoming more expensive

Victorian Brown Coal (VBC)

- **Low rank** coal
- Large reserves
- Very accessible, **very cheap**
- Very low concentrations of mineral **impurities**
- Therefore a very **attractive feedstock** for iron and steel industry

BUT

- Does not have coking properties; does not melt on heating
- Therefore, does not produce coke
- Only produces a char on carbonization
- **The char is too reactive to be used in a blast furnace**

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BUT

- Does not have coking properties; does not melt on heating
- Therefore, does not produce 'traditional coke'
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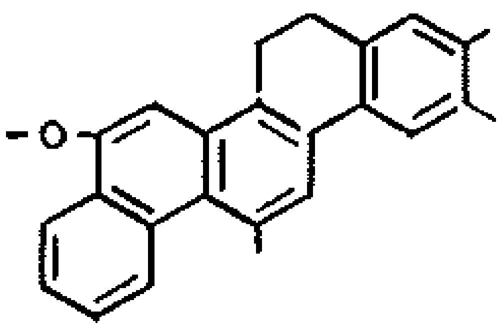
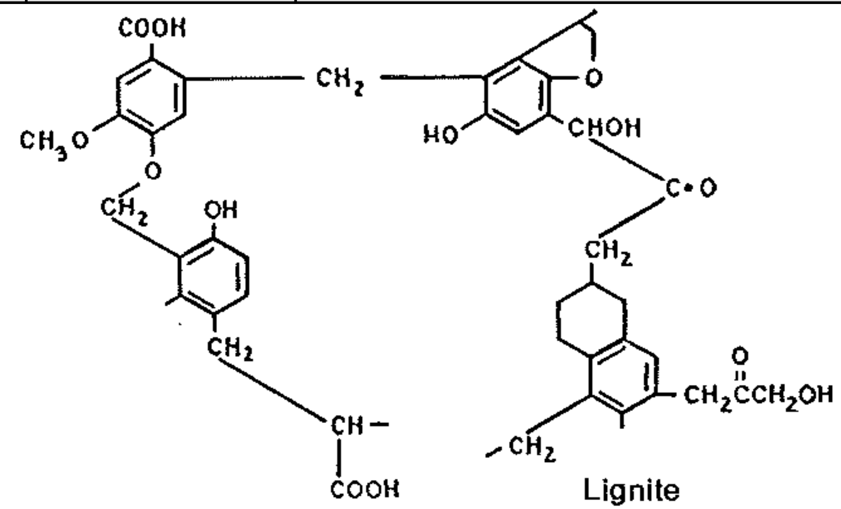
INTRODUCTION

	Coking Coal	Coke	Char	Victorian Brown Coal
Chemical Structure	**Mostly PAH**	Ordered graphitic	Disordered graphitic	**More aliphatic than aromatic**
Volatile matter (wt%)	**26-29**			**45-55**
Net Calorific Value (kcal/kg)	6000	6500	6000	4000 (air dry)
Ultimate Analysis (wt%daf)	C = 77-87 **O = 5-10** H = 4-7			C = 60-70 **O = 16-25** H = 4-7



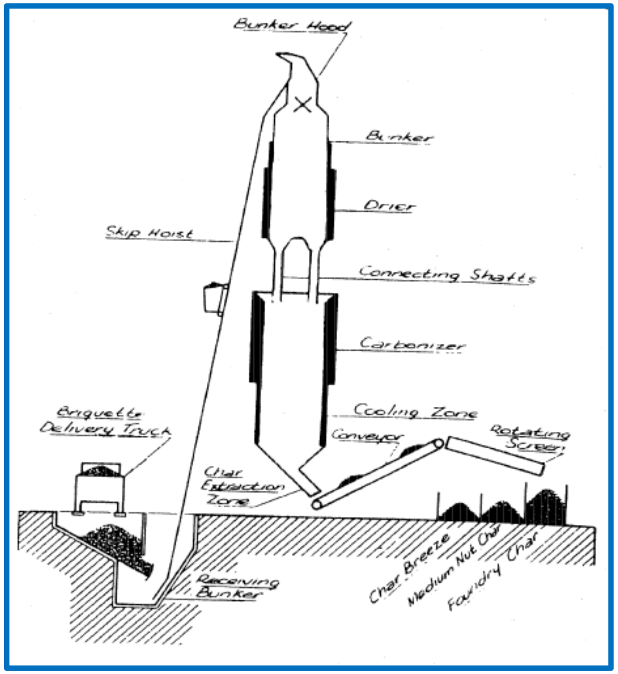
A characteristic structure of a coking coal



A characteristic structure of lignite

Note: daf = dry ash free, PAH= polyaromatic hydrocarbons

INTRODUCTION: Previous Studies



Auschar plant, Latrobe Valley, Victoria (1958 - 2014)

2.3 t briquettes

1 t hard char

Very strong product
Too reactive for blast furnace

Research by Higgins, Kennedy et al
Gas and Fuel Corporation of Victoria

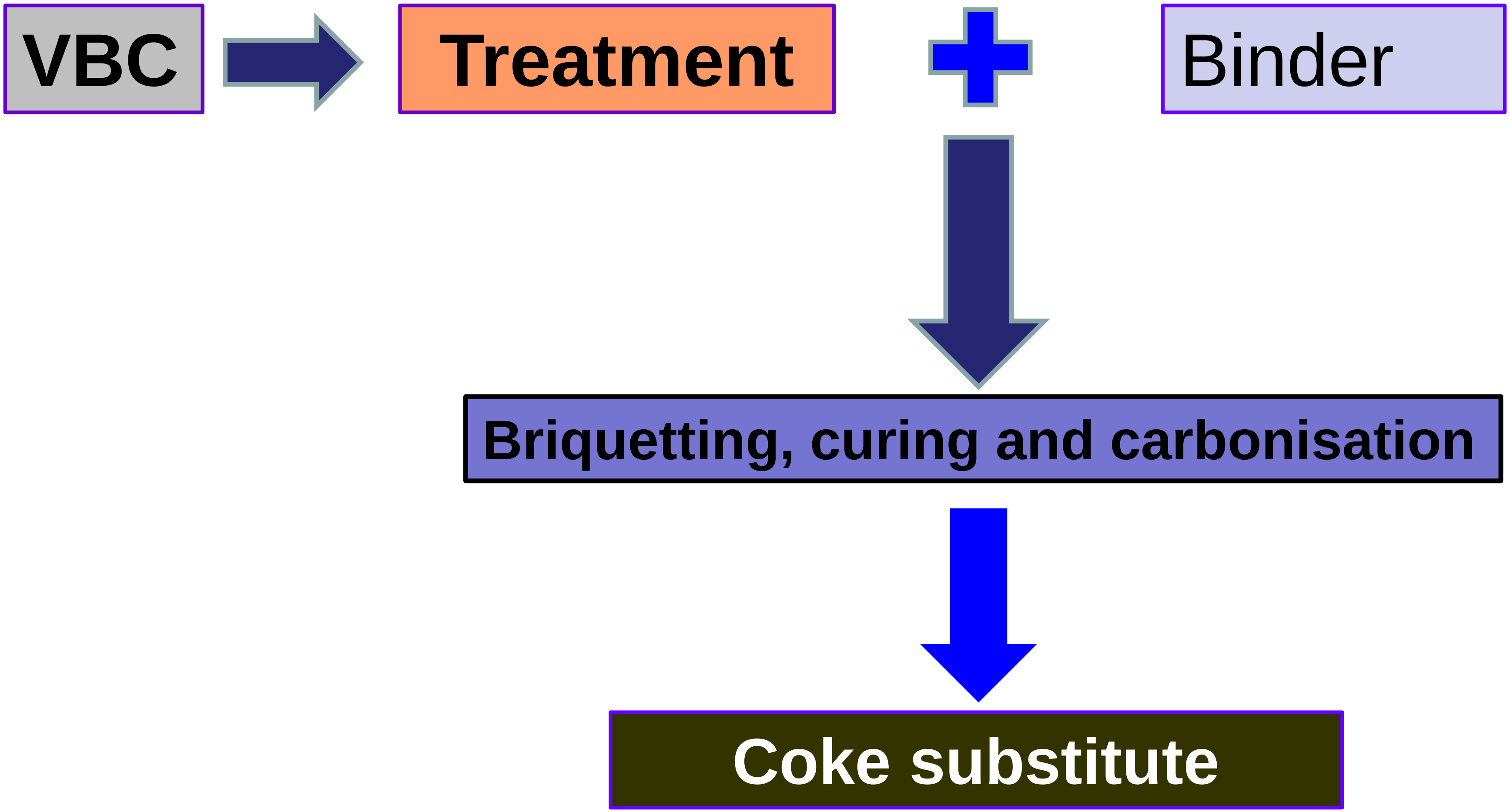
AIMS

To produce a blast furnace coke substitute from VBC:

To produce low reactive char

- **Investigation of cementing agents to strengthen the product**
- **Investigation of methods to reduce the reactivity of the product**
- **Comparison with conventional coke**

APPROACH


VBC
Treatment
Binder
Briquetting, curing and carbonisation
Coke substitute

EXPERIMENTAL

Loy Yang Low Ash (LYLA) coal

- 60 wt% moisture; 3.5 wt%db ash; 49.4 wt%db volatile matter
- Surface Area (CO_2) 230 m^2/g
- Treated with mild acid to give **AWC**

Hydrothermal Dewatering

- Coal (db):Water = 1:3 (w/w), N_2
- 320 ^oC held for 35 min
- The solid product was filtered out
- Washed with deionised water
- Dried at 105 ^oC in a flow of N_2

4 L autoclave

Alkali treatment

- Coal, KOH (7 M, aq), N_2
- 185 °C held for 10 h
- Neutralized with H_2SO_4
- Washed with deionized water
- Filtered and dried at 105 °C in a flow of N_2

EXPERIMENTAL Briquetting

Mixing the coal and binder

- Binder in THF
- Stirred for 1 h at 80 °C
- Dried and ground to <0.15 mm

Briquetting

- Coal or coal-binder
- About 1.2 g feedstock
- 200-230 °C: 20 kN (or 350 °C: 2.3kN) for 30 min
- Recover pellet when cool

INSTRON

Heated Die set

Pellet

EXPERIMENTAL

Curing:

- Industrial Air
- **200 ^{o}C – 2 h**
- Cool in the continuing air flow

Carbonisation:

- 1100-1200 ^{o}C for 2-8 h under N_2
- Slow heating rate to **prevent pellet cracking**
- Heating rate:
  - ❖ **2 ^{o}C/min** to 500 ^{o}C
  - ❖ **4 ^{o}C/min** to temperature
- Cooled in continuing N_2 flow

MEASUREMENTS

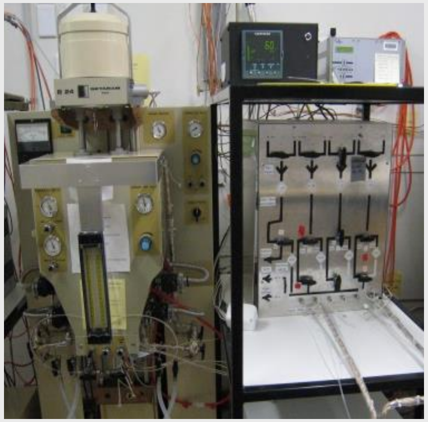
Compressive Strength (CS)

- Displacement rate of **0.05 mm/sec**
- Axial load applied **across the plane ends** until failure occurred
- Compressive Strength, $\sigma_c = (4F/\pi D^2)\ (H/D)^{0.5}$ (F= force, H= height, D= dia)

Reactivity Test - TGA

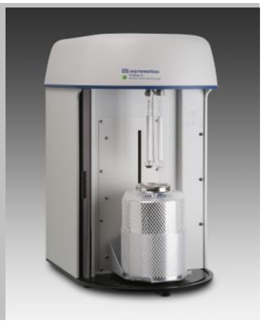
- Modified **ASTM D-5341**
- About 25 mg sample dried at 110 **^{o}C**
- Temperature **1000 ^{o}C**
- 35mL/min with 50% **CO_2** for **1h**
- **R60CO2** = [(A-B)/A] x100

(A = sample wt before reaction and B= sample wt after reaction



Surface Area (SA)

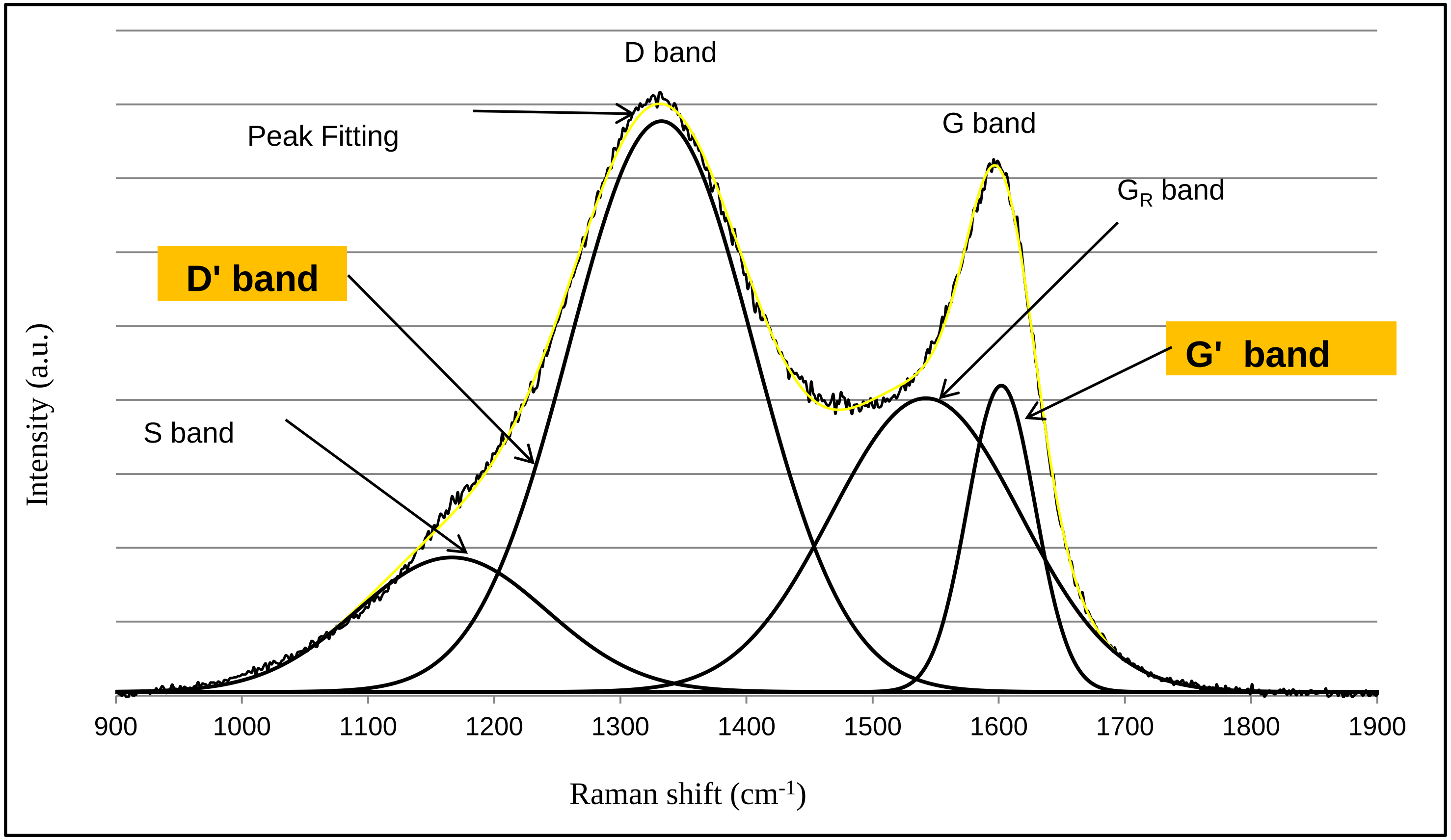
- Sample **dried under vacuum** at 160^{o}C for at least 8 hours
- **CO_2** adsorption at **273.15K**
- SA calculation using the **Dubinin– Radushkevitch** equation



*CS- Ref. Johns, R. B., Chaffee, A. L., Harvey, K. F., Buchanan, A. S., Thiele, G. A., The conversion of brown coal to a dense, dry, hard material. *Fuel Processing Technology* **1989**, 21, 209-21.
SA- Hutson, N. D., Yang, R. T., Theoretical basis for the Dubinin-Radushkevitch (D-R) adsorption isotherm equation. *Adsorption* **1997, 3, 189-95.

MEASUREMENTS cont.

Deconvolution of a typical Raman spectrum



The ratio of D′ and G′ band intensities (areas) is inversely correlated with the amount of graphitic structure [Sheng C. Fuel 2007;86:2316-24.]

RESULTS

The **product characteristics** are given for the two least reactive samples for each of the **following treatments**

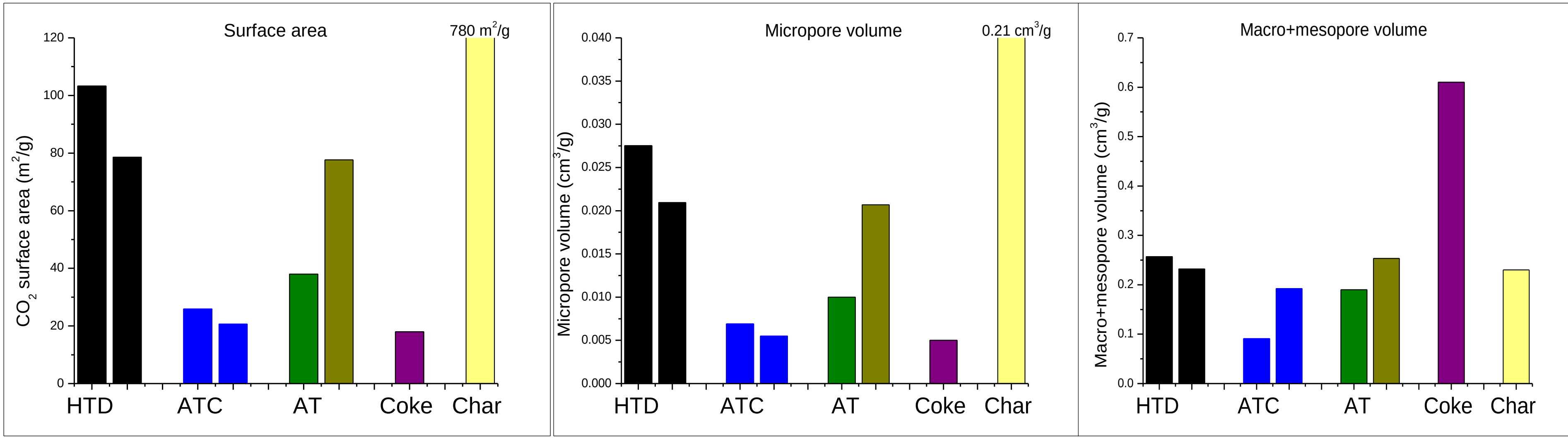
1. **Hydrothermally dewatered acid washed coal (HTD)**
   - Briquetting: 230 °C-20 kN-30 min
   - Curing: Cured/not cured
   - Carbonization: 1200 °C-2 h
2. **Alkali treated coal (ATC)**
   - Briquetting: 200 °C-20 kN-30 min
   - Curing: Cured/not cured
   - Carbonization: 1200 °C-8 h
3. **Alternative treatment (AT)**
   - Briquetting: 350 °C-2.3 kN-30 min/ 230 °C-20 kN-1 h
   - Curing: Not cured/cured
   - Carbonization: 1150 °C-30 min/ 1200 °C-2 h

RESULTS Carbonization Yield (wt%)

- The overall yield was about 50 wt% (db) for all treatments, compared to about 75 wt% for coke from a typical coking coal.
- The low yield is a consequence of the high volatile matter content (~50 wt%) of brown coals.

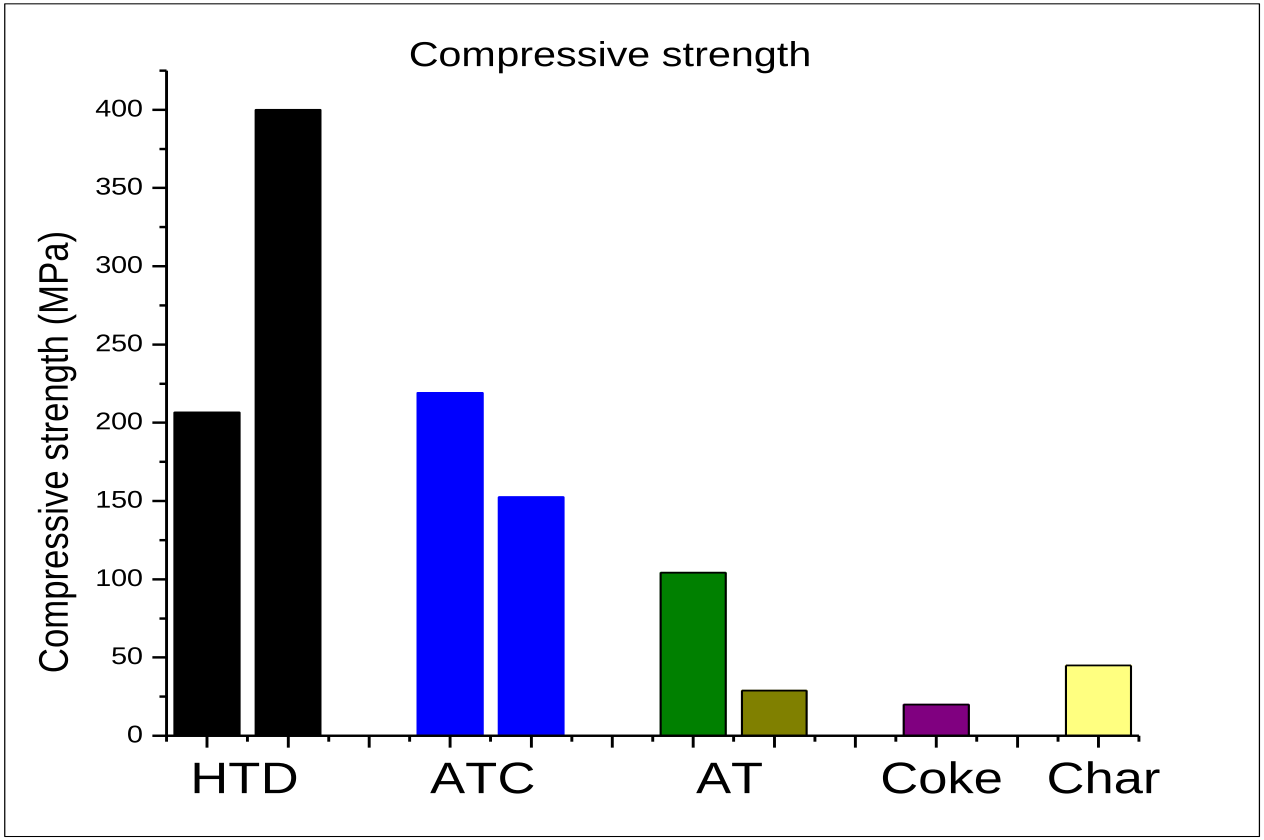
RESULTS

Surface Area (SA)



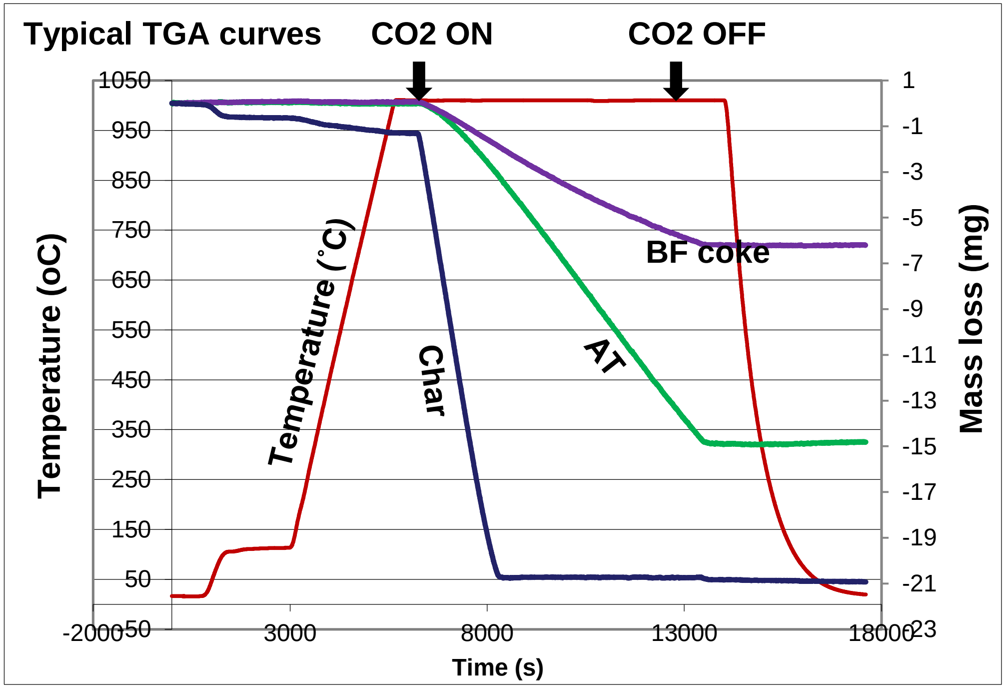
- Uncertainty about ± 5–15% of surface area (SA) or micropore volume value and 0.01 cm^3/g for meso+macropore volume
- ATC had very low SA like BF coke. HTD and AT had higher SA, but much less than brown coal char
- AT and HTD treatment had little effect on meso+macropore vol, but ATC had much lower values. BF coke had much higher meso + macropore volume than any product.

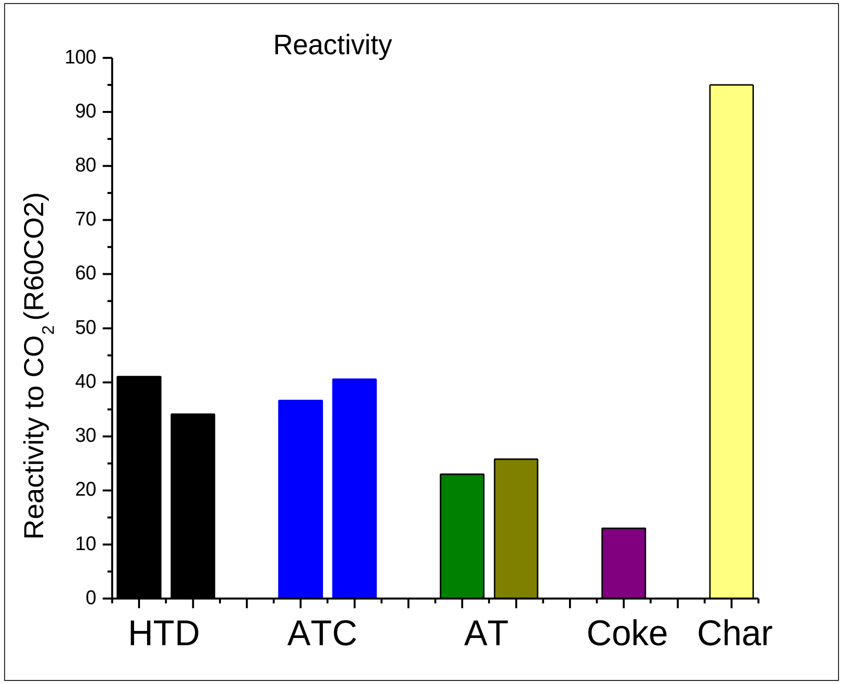
RESULTS Compressive Strength (CS)



- Uncertainty ± 20% of the average value.
- All the products including char were stronger than BF coke
- AT products were weaker than HTD and ATC products

RESULTS Reactivity Test (Thermogravimetric analysis)





Aim is to reduce the reactivity to the coke level (R60CO2 13)

- Uncertainty in R60CO2 +/-2%
- Least reactive samples approached the reactivity of BF coke
- For SA <100 m^2/g, no correlation between SA and reactivity

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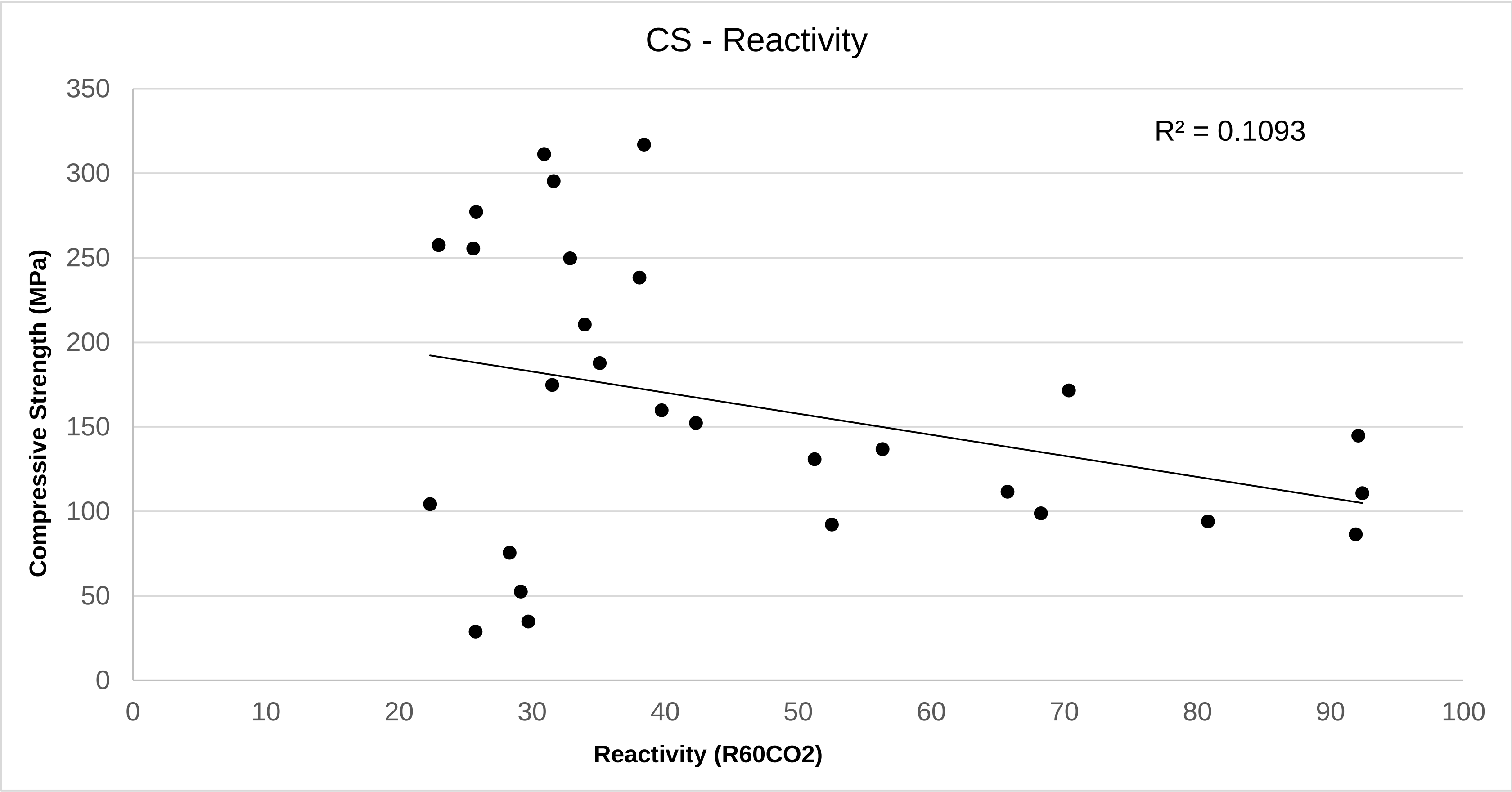
RESULTS

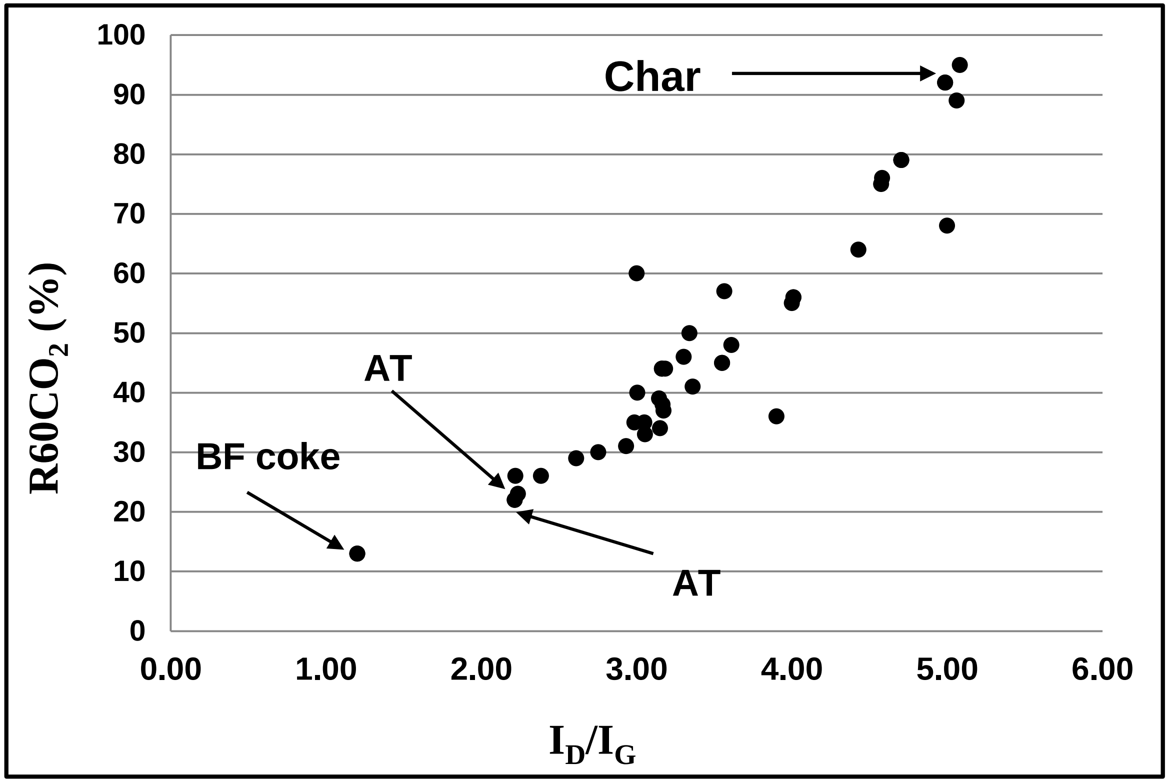
Relation between CS and reactivity



No significant correlation between CS and reactivity

RESULTS

Raman spectroscopy

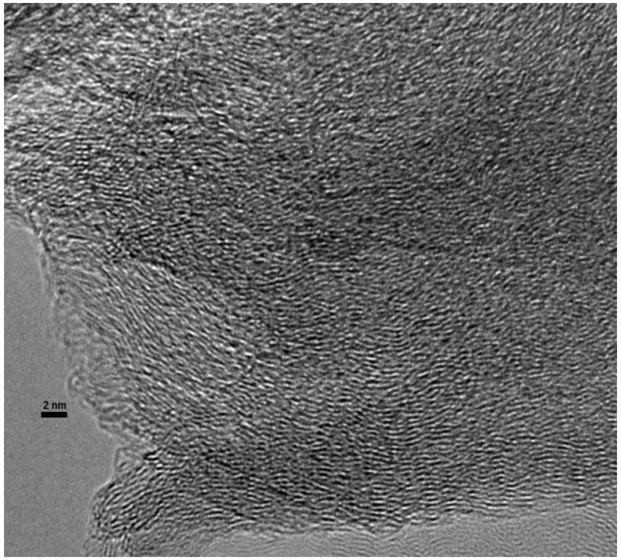


I_D/I_G is inversely correlated with amount of graphitic structure

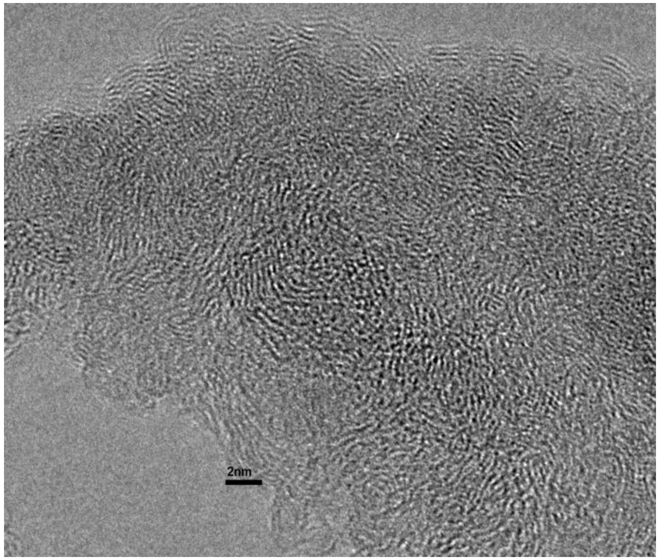
Reactivity **inversely correlated** with the proportion of graphitic structure

RESULTS

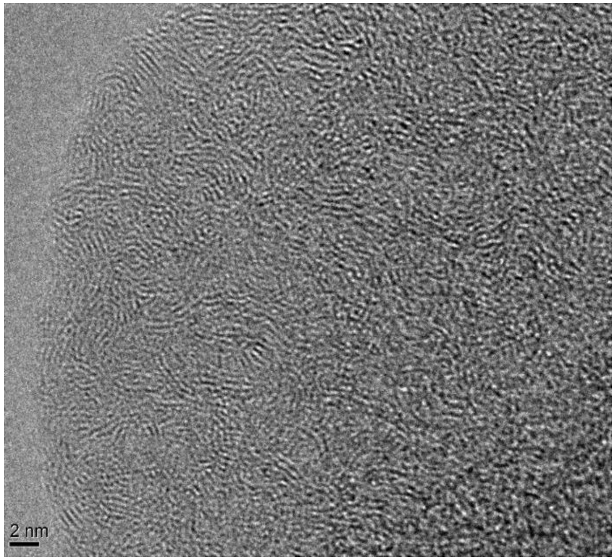
HRTEM Images



BF coke



AT product



Char

- **BF coke:** More and larger ordered regions
- **Products:** Fewer and smaller ordered regions
- **Char:** Almost entirely amorphous

CONCLUSIONS

Clean, cheap Victorian brown coal was successfully converted into a coke-like substitute:

- Very **hard products** are obtained
- A product was developed with **reactivity approaching** that of a BF coke
- There was **no relationship between strength and reactivity** in these products
- A strong **inverse correlation between reactivity and graphitic structure** was observed

Monash University is seeking partners to further develop this VBC product as a blast furnace coke substitute or blendstock.

ACKNOWLEDGEMENTS

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Thank you

Questions/Feedback