Biomass Gasification Research:
Applications and synergies from Coal R&D

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Biomass Gasification Symposium
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CSIRO ENERGY TECHNOLOGY
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Outline

Introduction to CSIRO

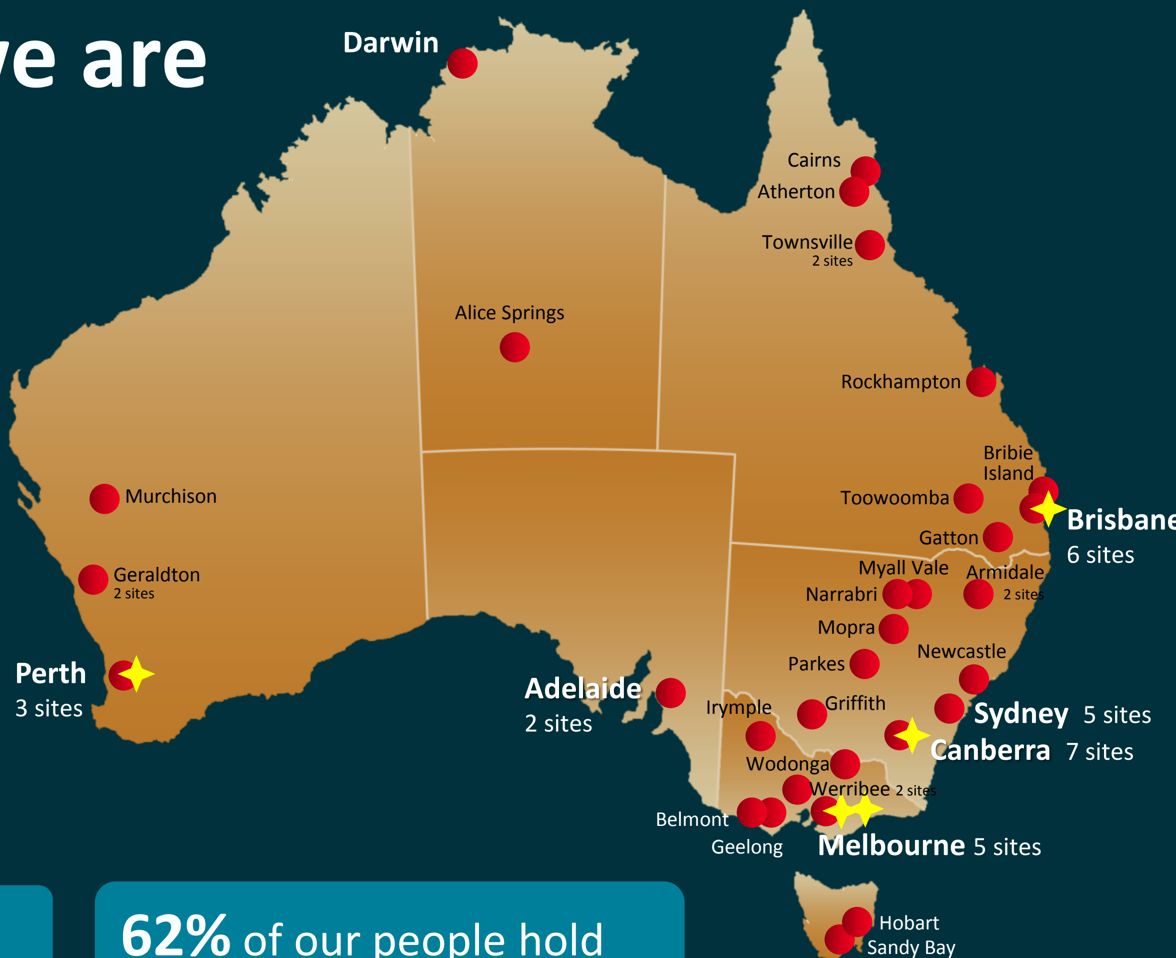
Australia's Gasification Research Program

- Coal gasification fundamentals
- Fuel property impacts on gasification performance
  - Gasification Conversion reactions
  - Mineral matter behaviour
- Application of research data through reaction and process models

Relevance to biomass gasification applications

- Lessons learned and special issues
- Torrefaction of biomass
  - An enabling technology for efficiency and scale?

CSIRO - Who we are



People	**6500**
Divisions	**12**
Locations	**58**
Flagships	**11**
Budget	**$1B+**

Top 1% of global research institutions in 14 of 22 research fields

Top 0.1% in 4 research fields

62% of our people hold university degrees

2000 doctorates

500 masters

With our university partners, we develop **650** postgraduate research students

Our business units

FOOD, HEALTH & LIFE SCIENCE INDUSTRIES

ENERGY

ENVIRONMENT

INFORMATION & COMMUNICATIONS

MANUFACTURING, MATERIALS & MINERALS

11 National Research Flagships

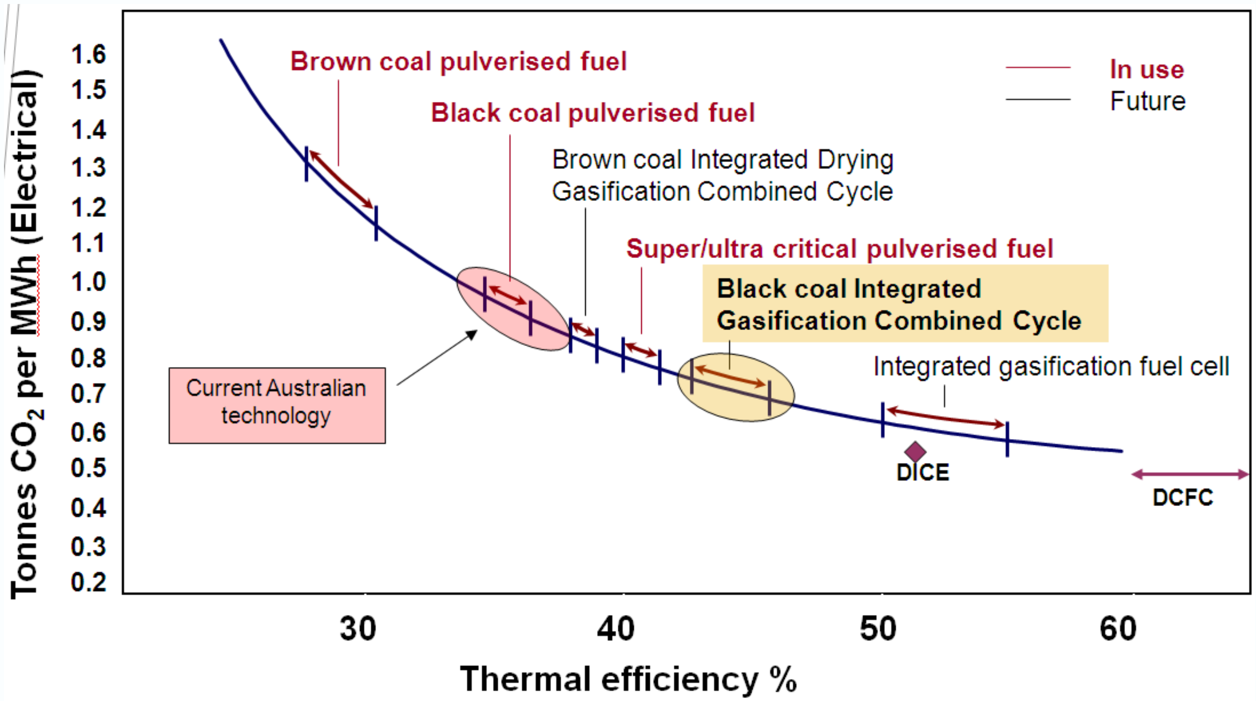
+ National Research Facilities and Collections

12 Research Divisions

+ Transformational Capability Platforms

Coal Gasification R&D

Technology efficiency impact on CO_2 emissions



Gasification and IGCC systems – several fuel dependent issues to be addressed

- Increase availability – slag management, fouling, corrosion, refractory degradation
- Improved cold gas efficiency
- Coal preparation & feeding (dry and slurry systems)
- High temperature syngas cleaning

For pf systems, most future improvements are NOT coal related issues

- Advanced materials – higher steam T, P
- Coal issues affecting efficiency - slagging, fouling, drying, milling…

Coal Gasification & IGCC Research

To improve the understanding of coal performance in gasification technologies, supporting:

- Coal selection and use in new technologies
- Implementation of advanced coal technologies
- Development of high efficiency IGCC-CCS systems

High pressure, high temperature coal conversion measurements

- Effects of reaction conditions and coal type
- Development of coal test procedures

Fundamental investigations of coal gasification reactions

- mechanisms, kinetics, models

Slag formation and flow

Syngas cleaning & processing

Gas separation (H_2/CO_2)

Technology performance models

CSIRO

CSIRO Gasification Research

Gasification Research

Fuel Reactivity

- Reaction Fundamentals
- Gasification Behaviour
- Pyrolysis and Char Formation
- Alternative Fuels

Mineral Matter

- Slag formation and flow
- Trace element behaviour

Modelling

- Mechanistic Gasification Models
- Gasifier Models
- Process model Integration

Pilot scale performance studies

Coal Conversion in Gasification

Gasification is a multi-stage process

Coal pyrolysis

- Rapid volatile release
- Determines char yield and morphology

Combustion

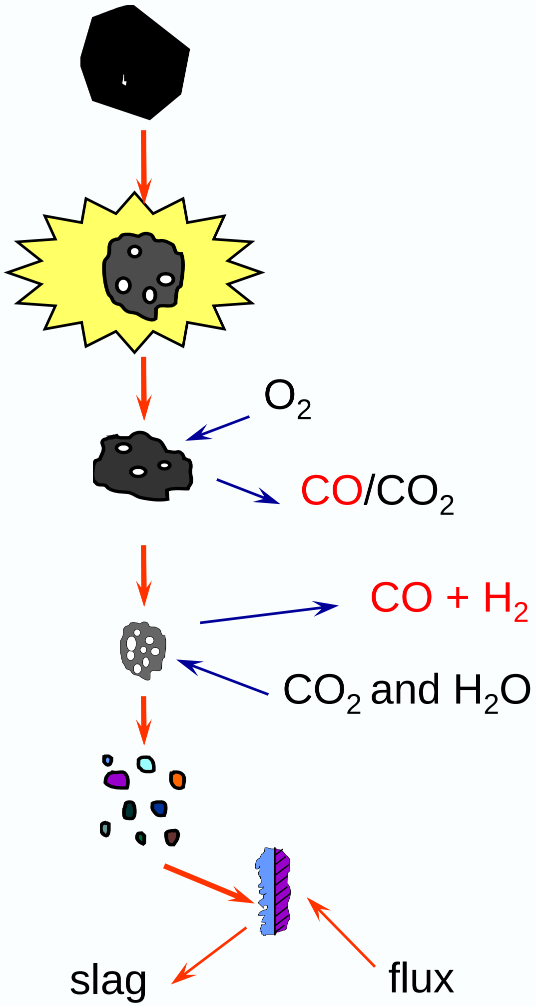
- Limited, fast. O_2 consumed early in process
- Exothermic, provides heat for endothermic gasification reactions

Char Gasification

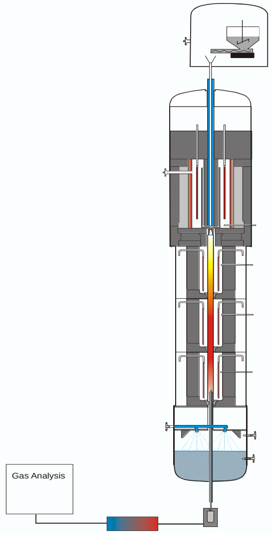
- Slow, rate determining. Endothermic
- CO_2 and H_2O converted to CO and H_2.

Slag formation and flow

- Flux may be required to achieve adequate viscosity



Interrogating the Gasification Process



Laboratory investigations to understand the important processes that combine to gasify coal under practical conditions.

Larger-scale testing to ‘recombine’ process steps under process conditions

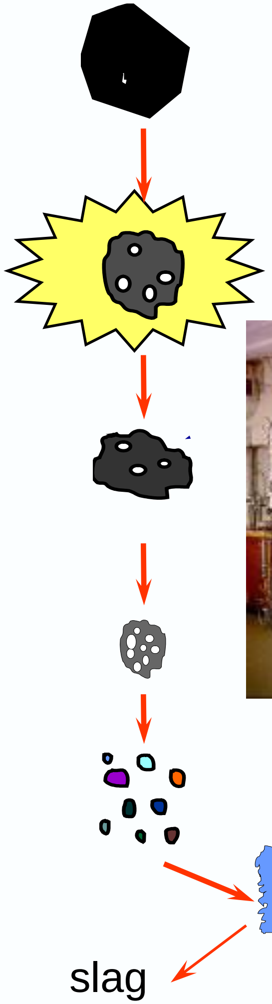
Predictive capability of gasification behaviour

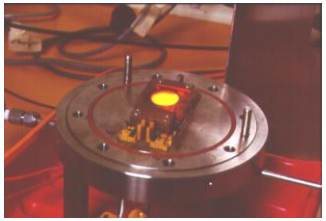
Assess coals for specific gasification technologies

Develop operating strategies

Troubleshooting gasification processes

Support technology development

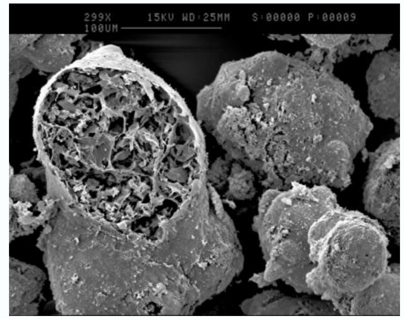


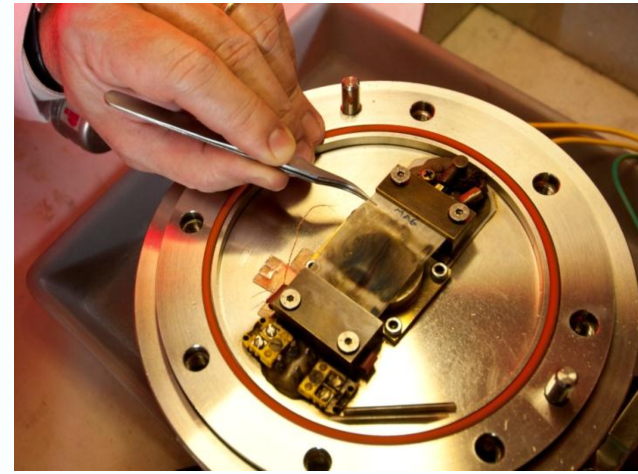


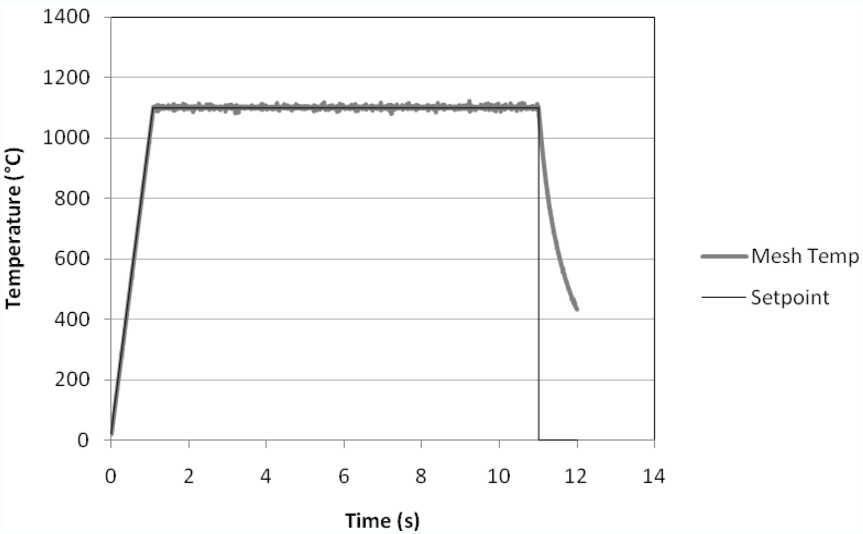
Its not all about simulating the industrial process!

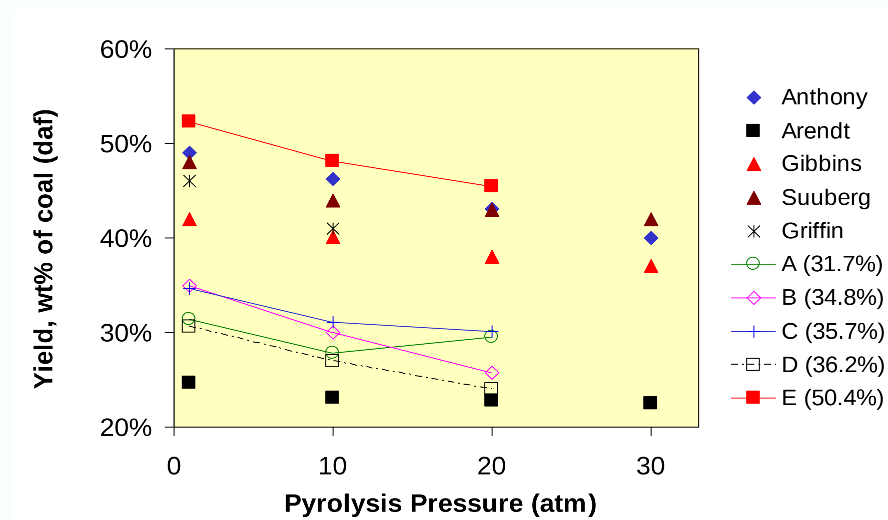
Devolatilisation and Char Formation

- **High pressures**
  - Up to 30 bar
- **High temperatures and heating rates**
  - Up to 1100°C
  - Over 1000°C/s









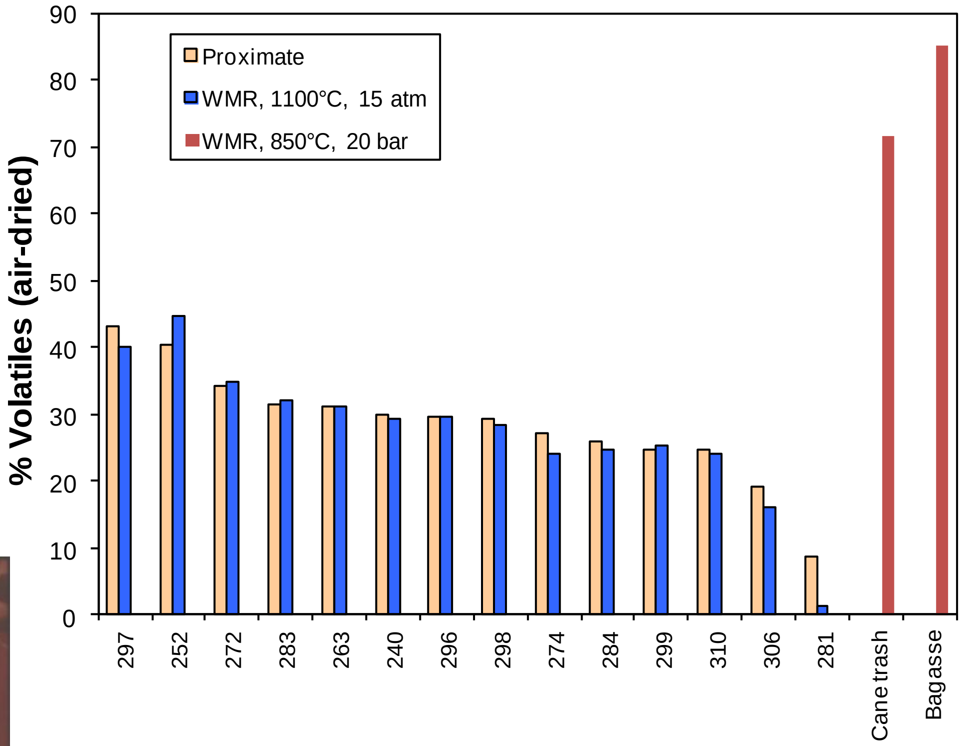
Volatile yield of coals and biomass

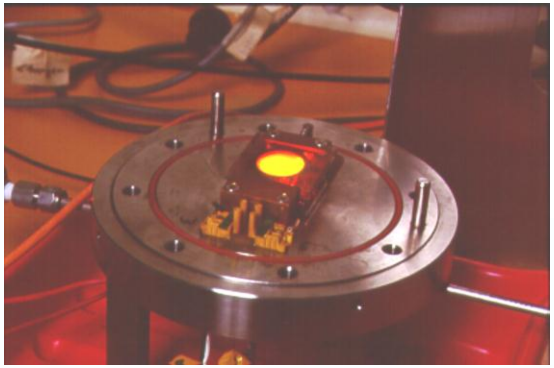
Rapid devolatilisation measurements

- High heating rate (~1000°C/s)
- Pressure 15-20bar

Cane trash and bagasse have extremely high volatile yields

- 70-85% (ad basis)
- char yield is low



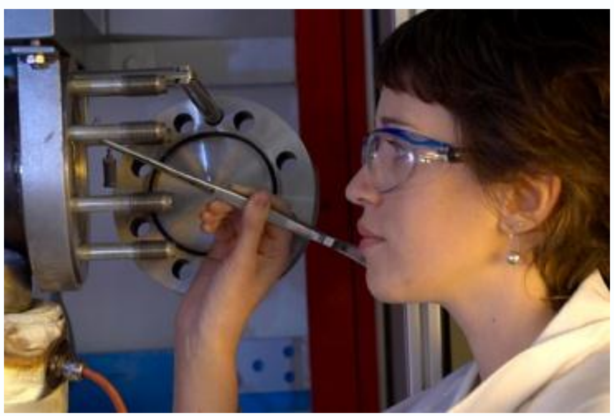


Pyrolysis profiles of sawdust

Simple non-isothermal TGA experiment

Drying, pyrolysis

- Inert atmosphere
- Devolatilisation complete by ~400°C
- Total volatile yield ~85%
  - char yield low



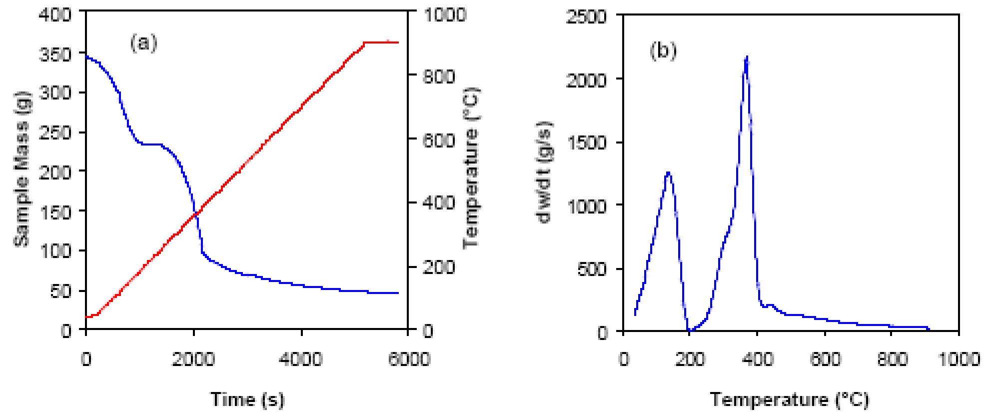


Figure 4: (a) Mass and temperature vs time and (b) rate of mass loss vs temperature for the as-received sawdust sample.

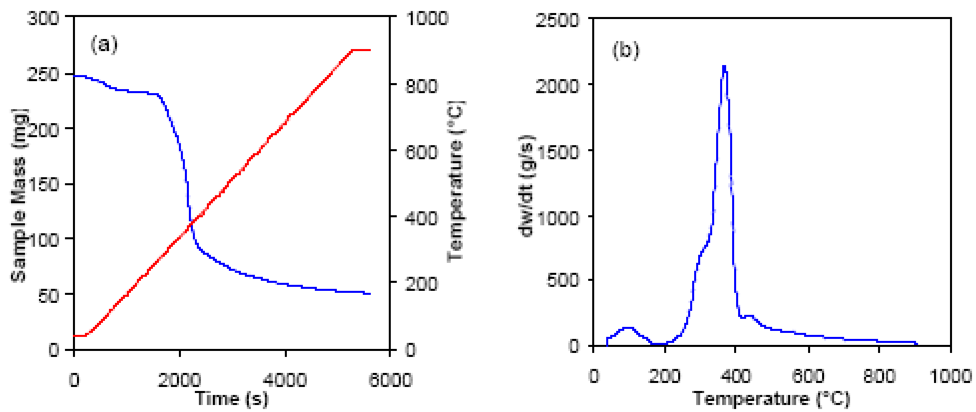


Figure 5: (a) Mass and temperature vs time and (b) rate of mass loss vs temperature for the air-dried sawdust sample.

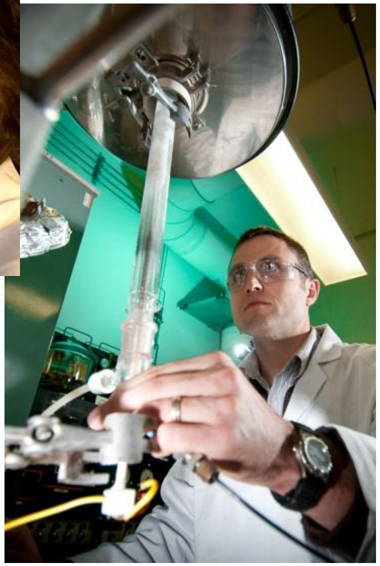
Char Reactivity

Fixed Bed Reactor

- **Intrinsic** reaction kinetics of chars with CO_2, H_2O, O_2
- Detailed information regarding reaction rates & mechanisms, and how these relate to char properties (surface area, porosity, petrography etc)

High Pressure TGA

- Reaction rates at high pressures of CO_2, H_2O, CO, H_2, and their mixtures
- Impacts of high pressures on gasification reaction processes
- Fundamental data for application of char reaction kinetics to relevant process conditions



Carbon-Gas Reactions

Char-CO_2:

$$C_f + CO_2 \rightleftharpoons C(O) + CO$$

$$C(O) \rightarrow CO + C_f'$$

Science issues:

- Competing reactions
- Role of char surface
- Complex kinetics

Application issues:

- Coal properties and pyrolysis conditions affect char reactivity
- Char structure changes during reaction

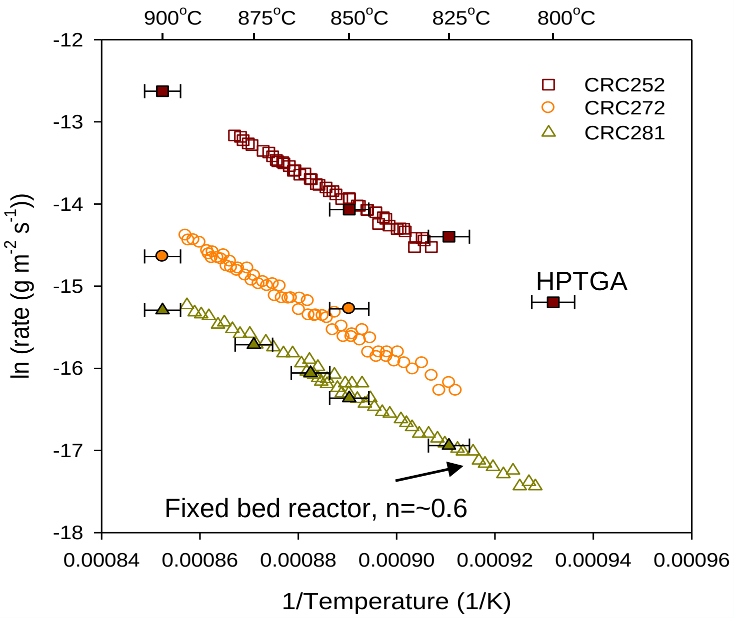
Char-H_2O:

$$C_f + H_2O \rightleftharpoons C(O) + H_2$$

$$C(O) \rightarrow CO + C_f'$$

Complicated by:

$$C_f + H_2 \rightarrow C(H_2)$$



Gasification reactivity of biomass char

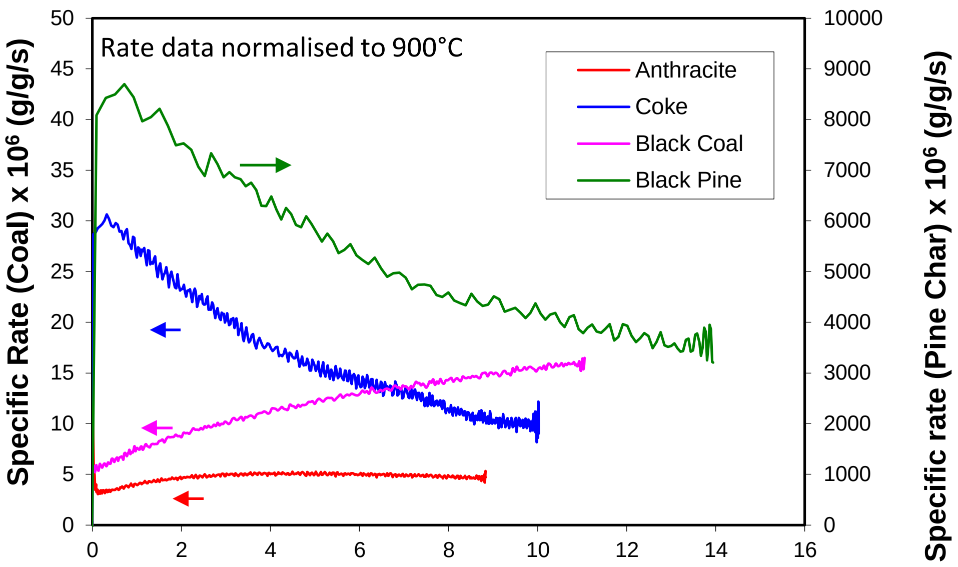
Gasification rate of wood char is approx 100x greater than coal char

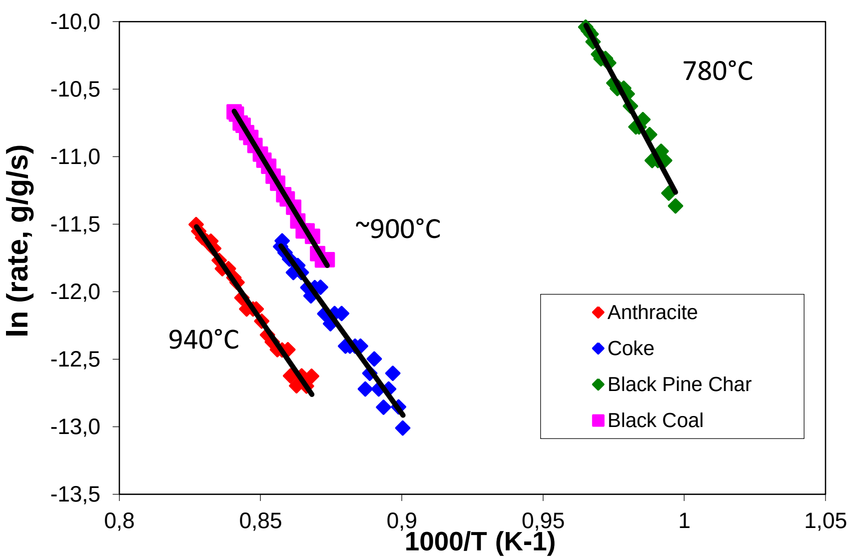
- wood char surface area usually greater than coal char
- 'intrinsic' reactivity of sawdust char still ~10x greater than coal char

Activation energy similar for coal and biomass chars (240-300kJ/mol)

Low char yield and high char reactivity indicate that this is less likely to be limiting factor in biomass gasification

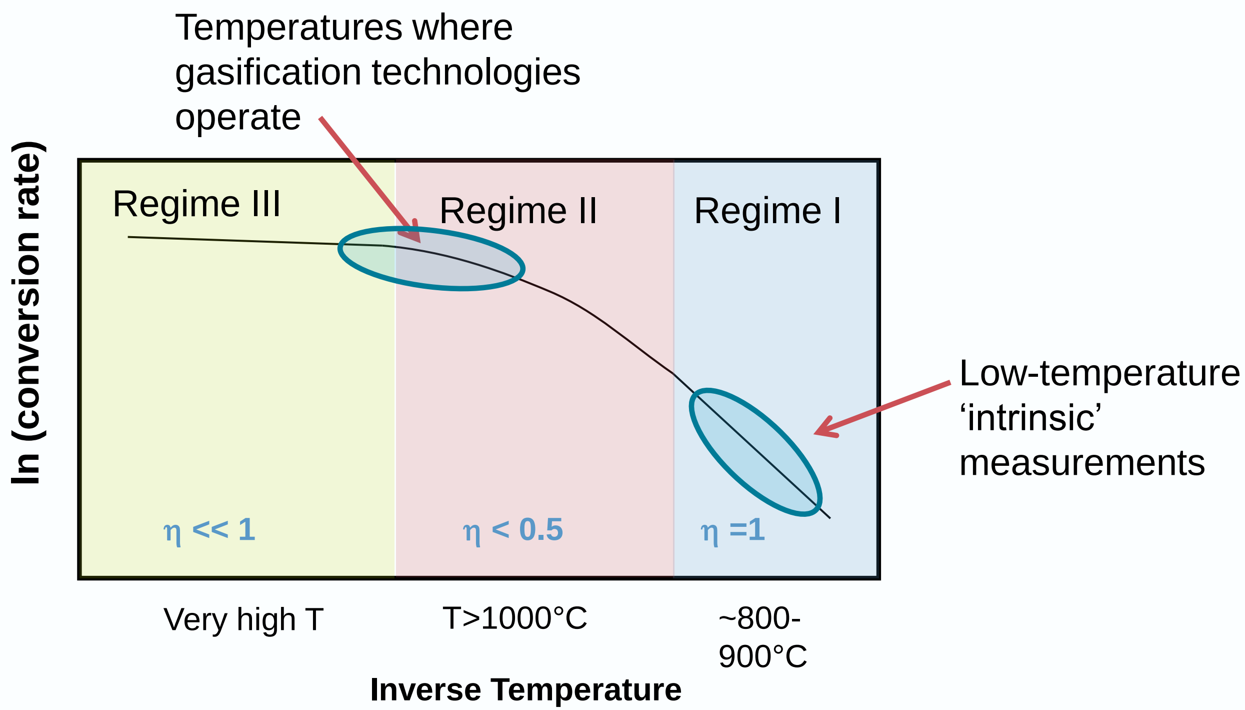
- Affects T, particle size etc





Moving up the Arrhenius Curve:

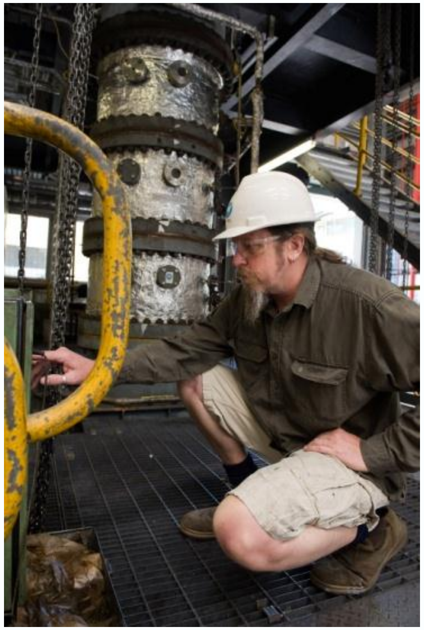
High Temperature Rates



External mass transfer control

Chemical + pore diffusion control

Chemical rate control



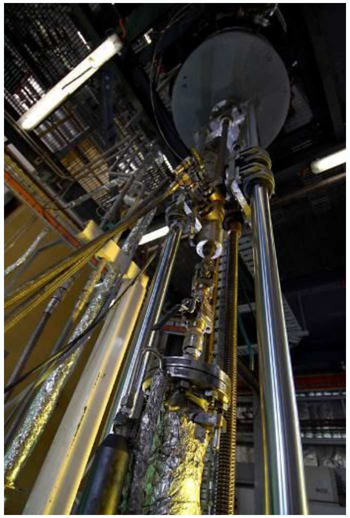
High Pressure Entrained Flow Reactor

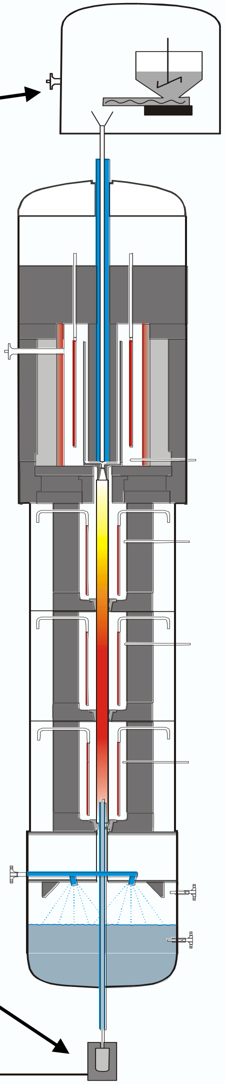
20 bar pressure, up to 1500°C

Coal feed rate of 1-5 kg/hr

Gas mixtures of O_2, CO_2, H_2O and N_2

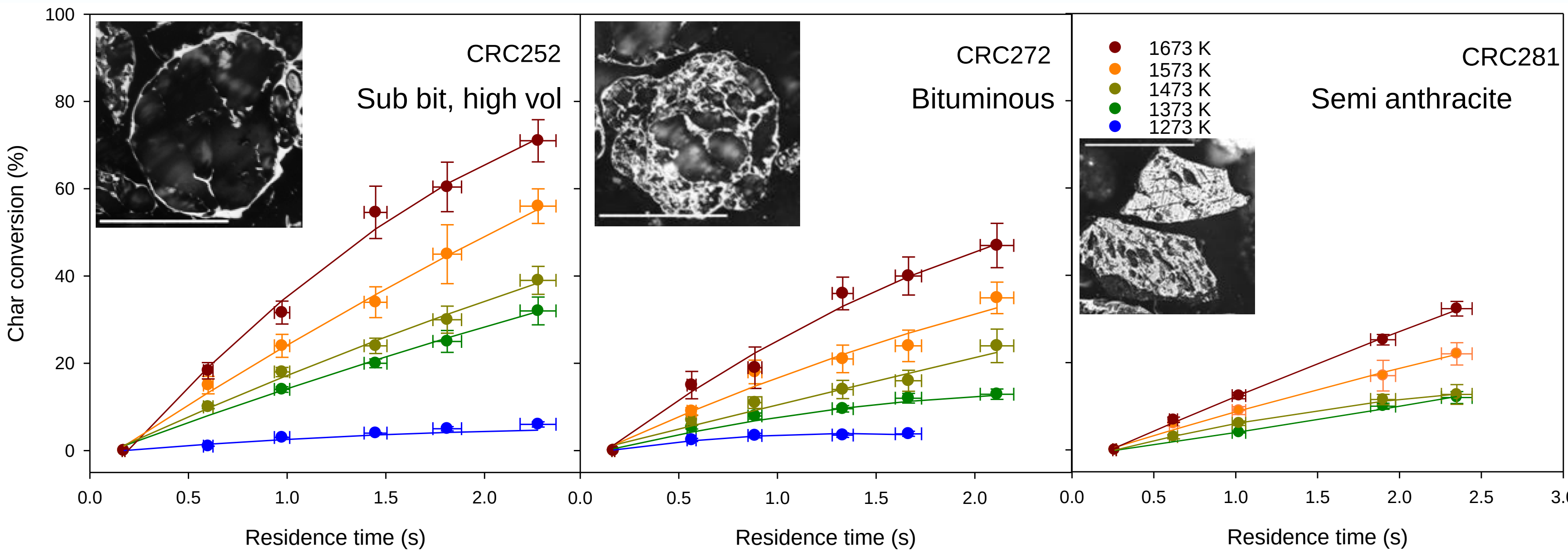
Adjustable sampling probe - char and gas samples collected at different residence times (0.5-3s)

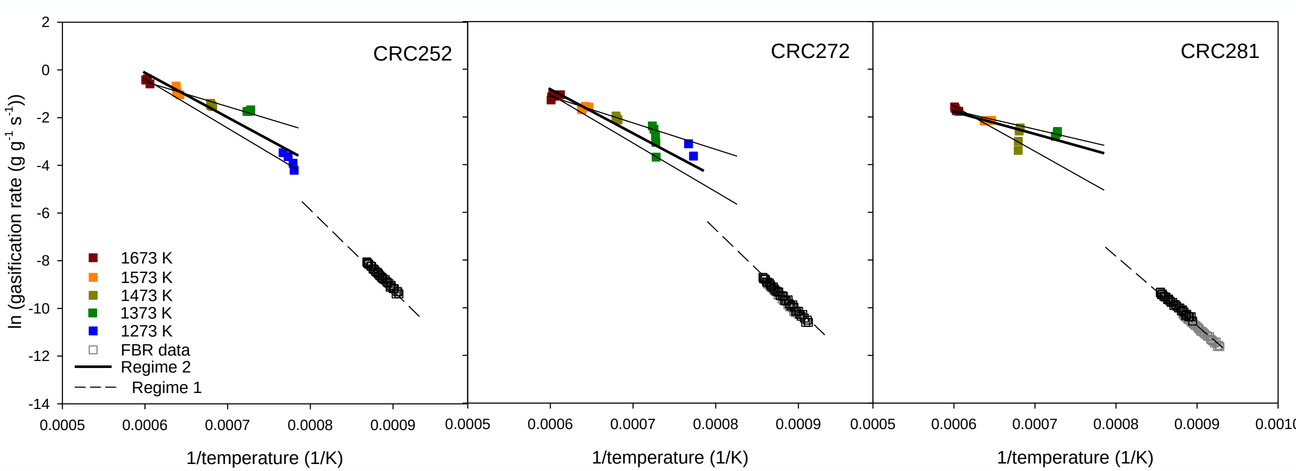




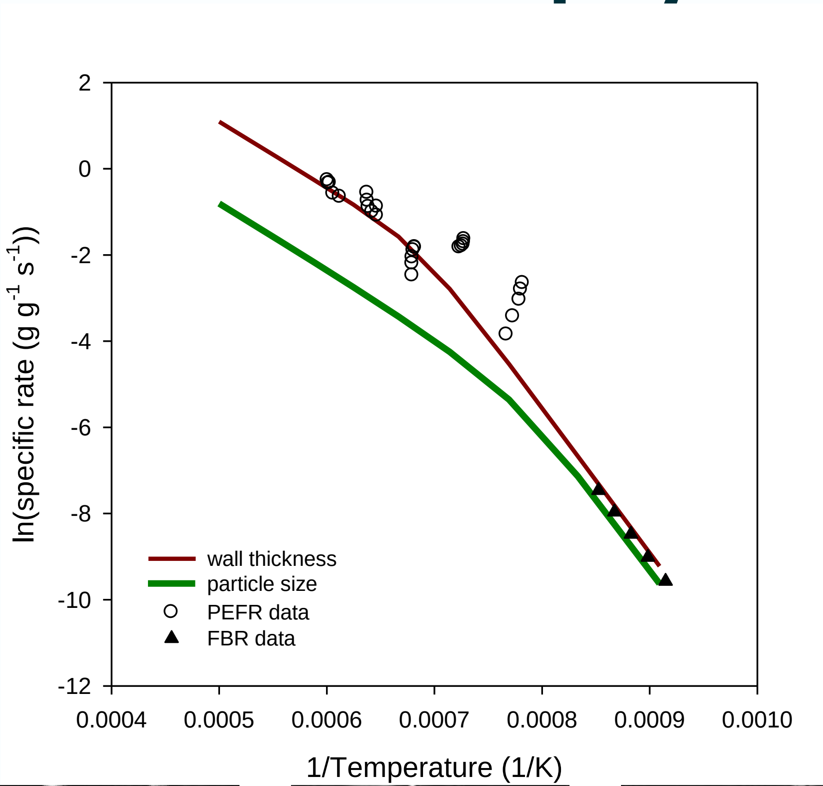
CO_2/char reaction rate at 'high' temperature

20 bar total pressure, 5 bar CO_2 partial pressure





Char/CO_2 reaction rates: understanding chemical and physical factors



First of a kind data for high pressure char/CO_2 and char/steam reactions (PEFR)

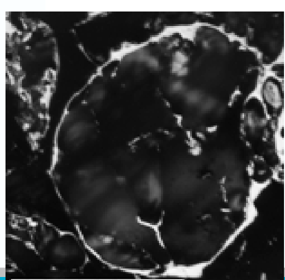
Thiele modulus and effectiveness factor based on observed particle morphology

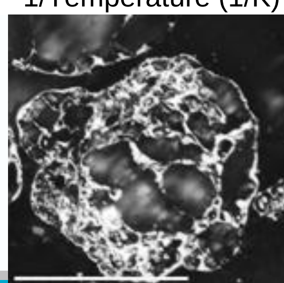
- ‘effective’ diffusion length

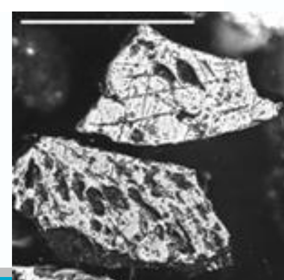
Low T ‘intrinsic’ and high T ‘practical’ rate data can be reconciled when a detailed understanding of char structure is available

Still difficult to resolve burnoff effects

Challenge to extend to multiple reactants

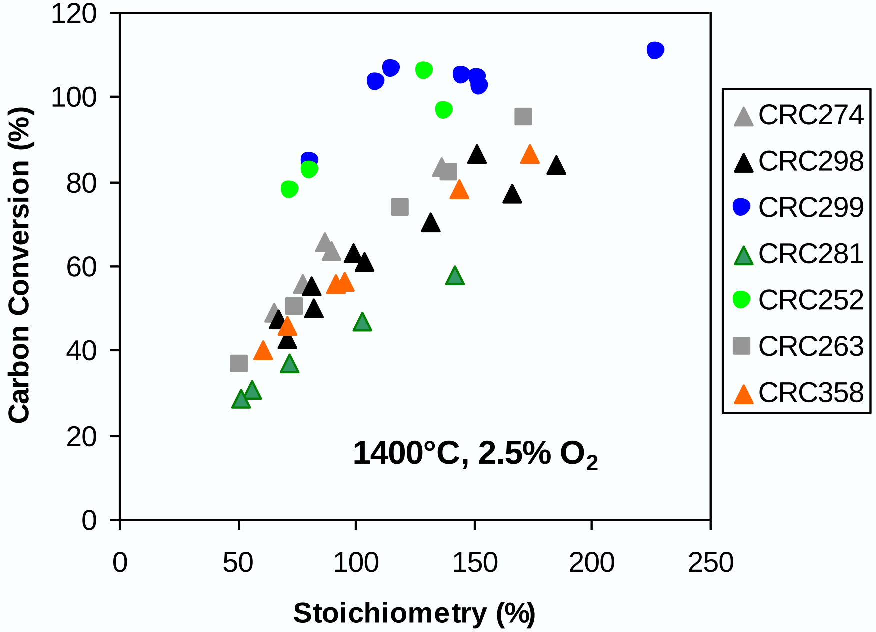


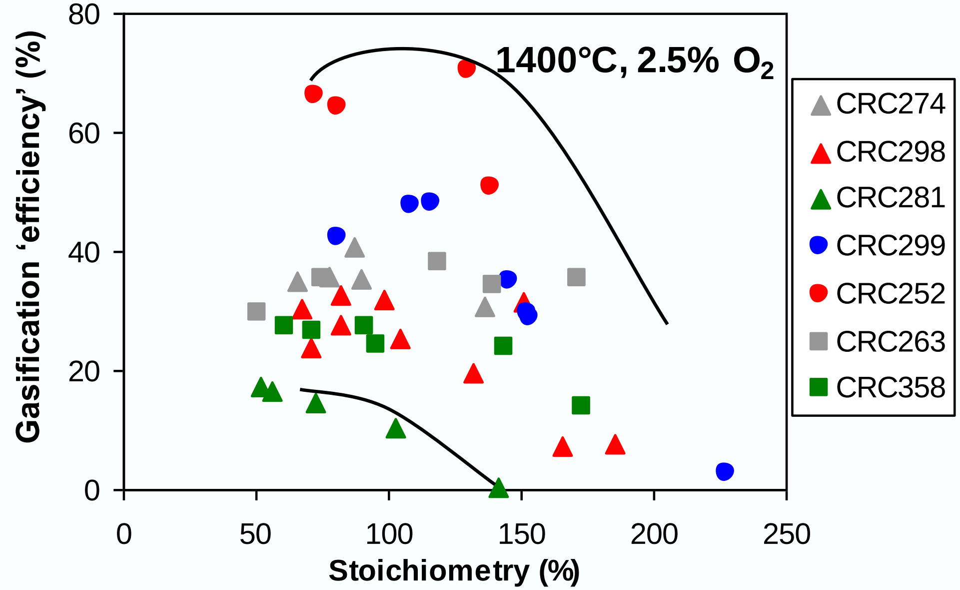




E M Hodge, D G Roberts, D J Harris and J F Stubington. *The Significance of Char Morphology to the Analysis of High Temperature Char-CO_2 Reaction Rates,* Energy and Fuels (2009).

Evaluation of Coal Gasification Behaviour





Optimum range of stoichiometries for 'gasification efficiency'. Trade-off to achieve maximum conversion.

Higher volatile coals (generally) achieve greater conversion than lower volatile coals

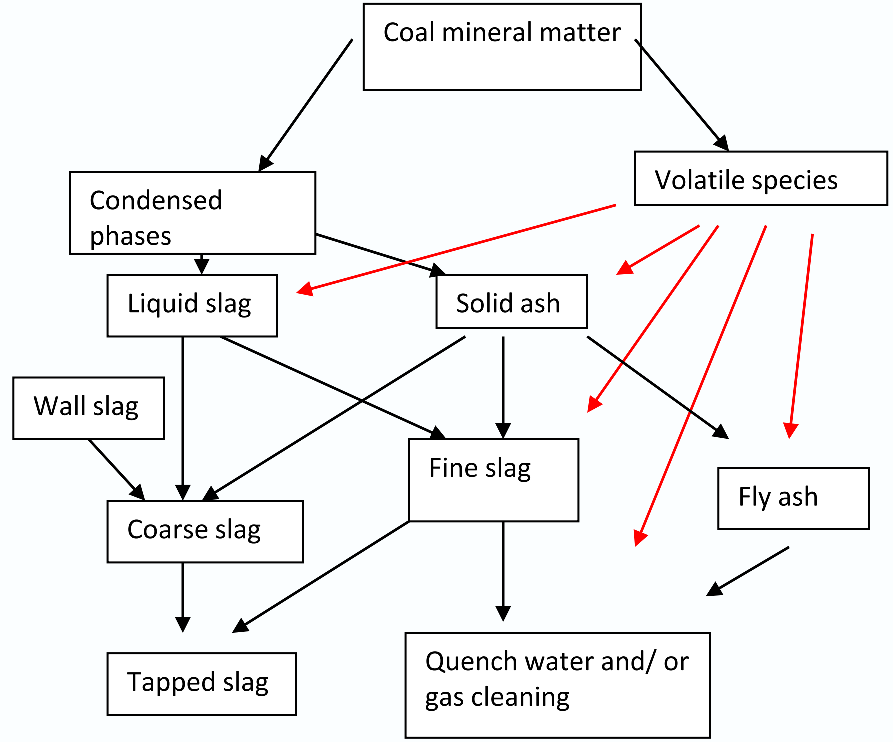
- Exception is CRC299 – indicates that char reactivity is also significant (agrees with TGA testing of coal suite)

Higher temperature differentiates coals on the basis of different char reactivities

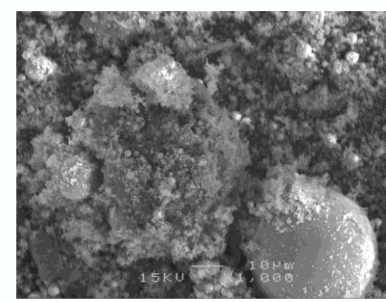
Effect of coal type also reflects extent of conversion

Conversion drives syngas composition (via gas phase equilibria)

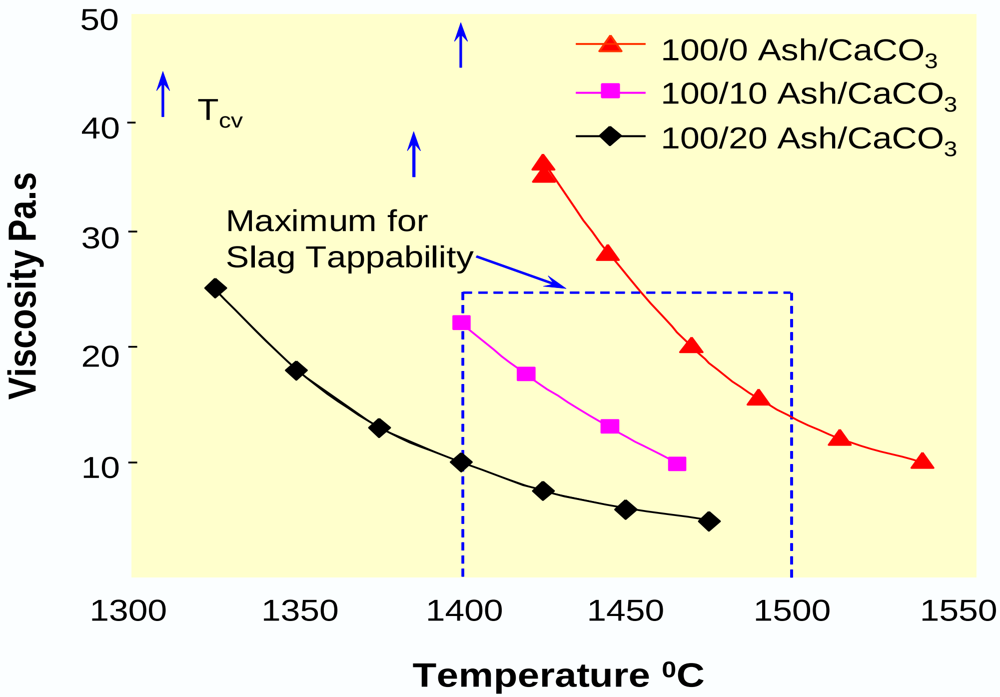
Mineral matter in gasification



- **Volatile species (in syngas):**
  - requirements for syngas cleaning
- **Condensed phases (slag, fly ash):**
  - Syngas cleaning
  - Operational: slag viscosity
  - Utilisation/handling of waste
  - Physical & chemical properties: trace elements, leaching



Slag Viscosity Testing



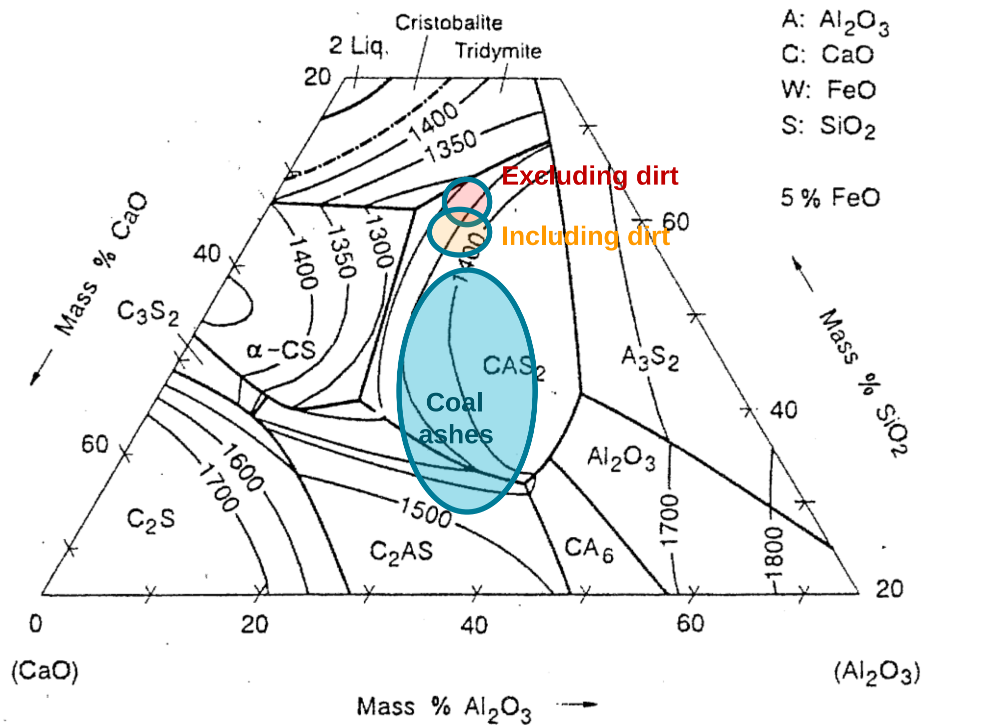
- Slag Viscosity
  - 25 Pa s is the accepted maximum viscosity at the slag tap for successful operation
  - Flux addition required if viscosity is too high
- Temperature of Critical Viscosity
  - Slag becomes heterogeneous
  - Trouble-free tapping of slag is not possible

Bagasse ash composition

Component	Wt.%
Ash content	0.62-3.2*
SiO_2	**78.3 - 85.5**
Al_2O_3	5.3 - 8.6
Fe_2O_3	1.3 - 5.2
CaO	2.1 - 3.3
Na_2O	0.1 - 0.3
K_2O	**1.5 - 3.5**
MgO	0.2 - 1.7
P_2O_5	0.5 - 1

Bagasse ash composition [1-3]

* Excluding dirt, and up to 7% with dirt



Bagasse and coal ash compositions in SiO_2-Al_2O_3-CaO phase diagram at 5wt.% FeO

Mineralogy:

- Mainly quartz, SiO_2,
- also phosphates: ($Ca_9MgK[PO_4]_7$ and $KAlP_2O_7$)

[1] Dordeiro, et al, in Used of Recycled Materials in Building and Structures (2004)
[2] Zanderson et al, Biomass&Bioen (1999)
[3] Souza et al, J. Environ. Manage. 92 (2011)

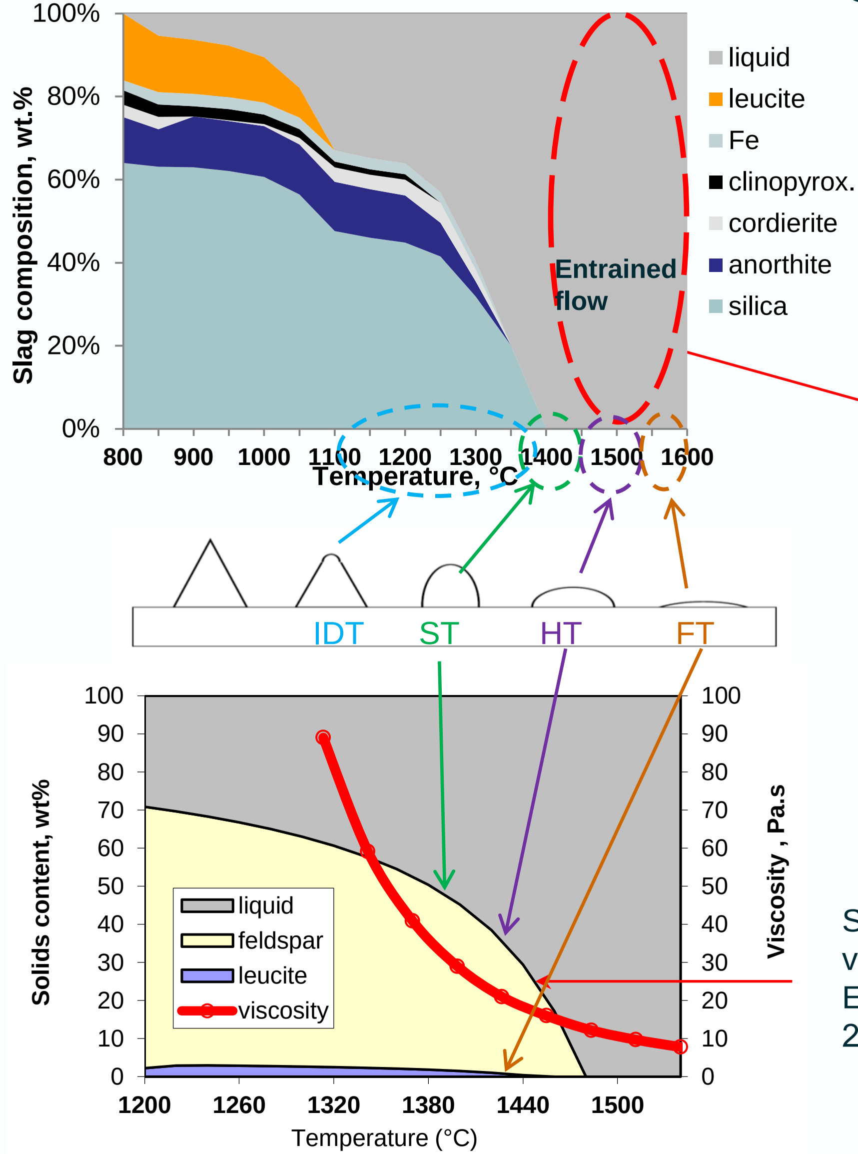
Melting & flow behaviour of bagasse ash

AFT is bulk characteristic of ash and depends:

- Kinetics of melting
- Melting temp. of minerals
- Viscosity of slag

AFT for bagasse ash:

- IDT (initial deformation temperature) depends on low melting point fraction (K-species) and different than eutectic T.
- ST (spherical temperature), and HT (Hemispherical temperature), are high due to slow melting and high viscosity of melt
- FT (Flow temperature) is (>100 °C) higher than liquidus temperature



No solids involved, slag flow only depends on viscosity of liquid, which is very high

CRC703f coal slag (example):

Slag flow depends on viscosity of liquid with solids. Even with some solids (up to 20%) viscosity < 25Pa·s.

Bagasse in entrained flow gasifier

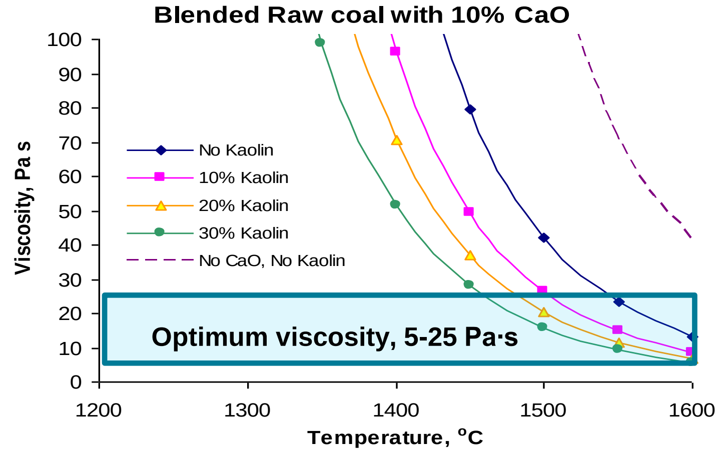
	Bagasse	Ref coal*	Coal for blending
Ash content	0.62-3.2	~10	~10
SiO_2	78.34-85.5	78.5	36
Al_2O_3	5.3- 8.55	10.8	30
Fe_2O_3	1.3-5.24	4.6	1.1
CaO	2.1-3.27	0.3	29
Na_2O	0.12-0.33	1.1	0.17
K_2O	1.51-3.5	0.72	0.07
MgO	0.15-1.1	0.6	0.26

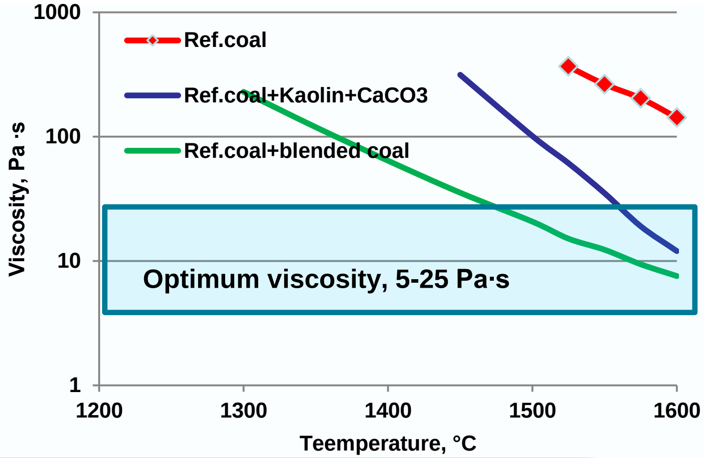
* Ref coal with similar ash composition

Estimated bagasse slag viscosity - too high!:
- SiO_2 - rich melt, high S/A,
- low CaO and FeO

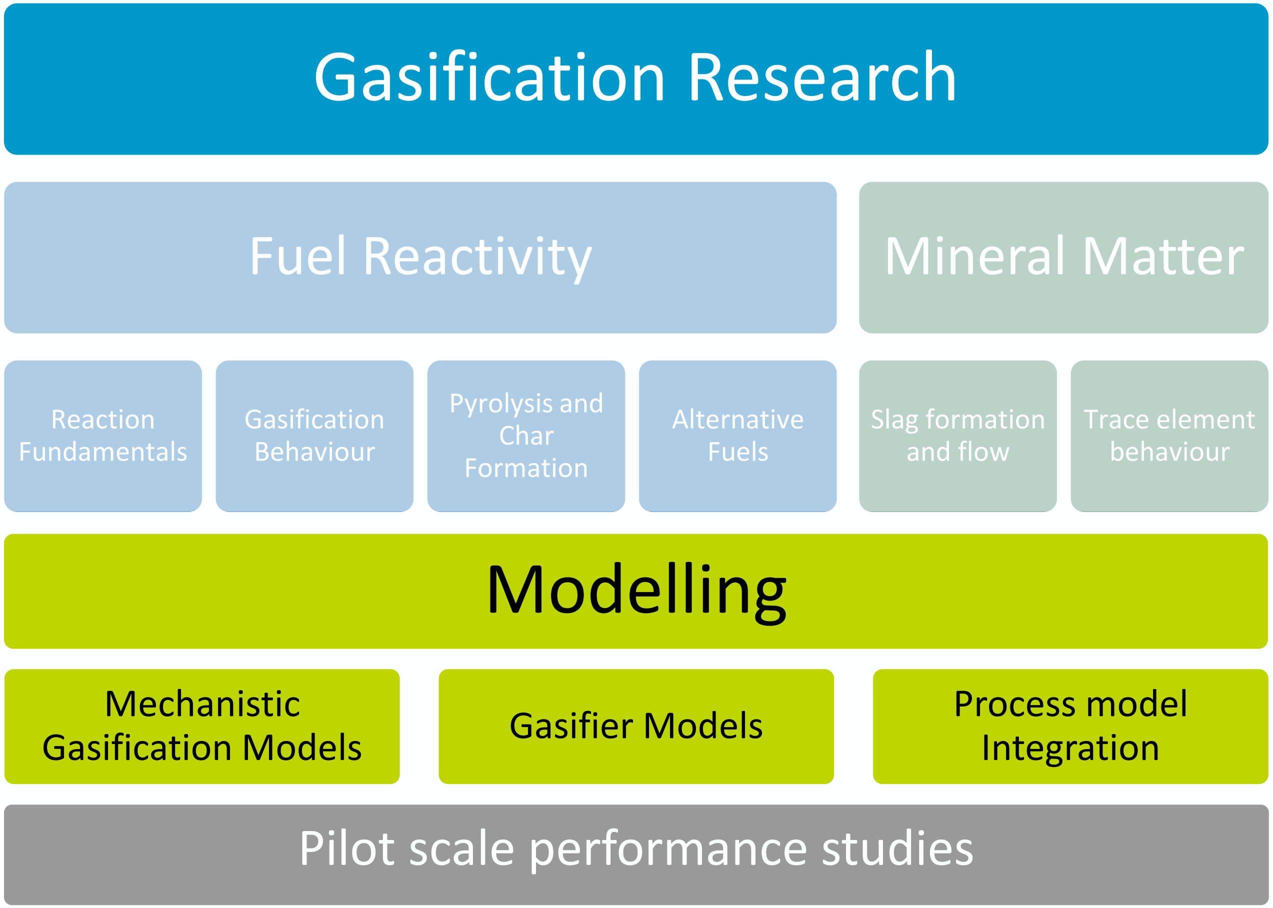
Possible approaches:

- Blending with kaolin** (70:30 ratio) to reduce S/A ratio and fluxing with $CaCO_3$ (~10%)





Blending with coal with low S/A and high CaO (~85:15 ratio)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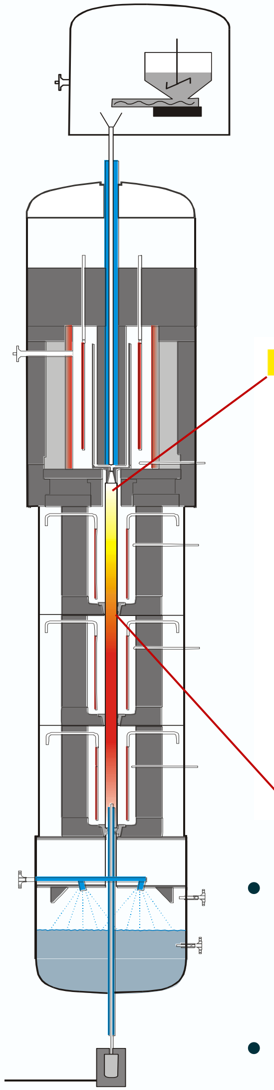
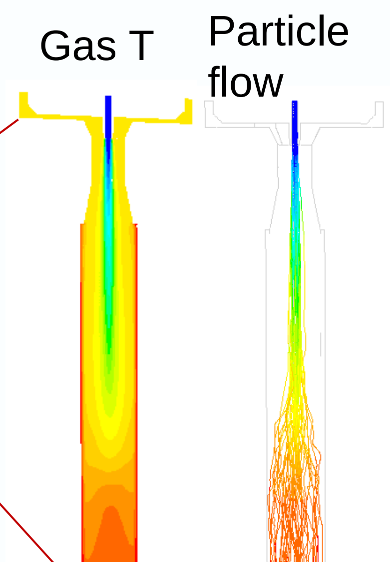
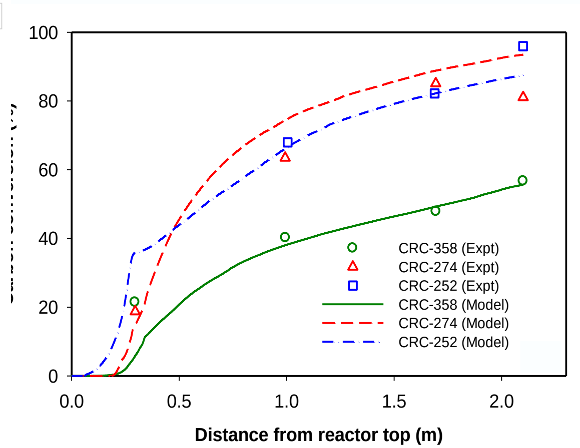
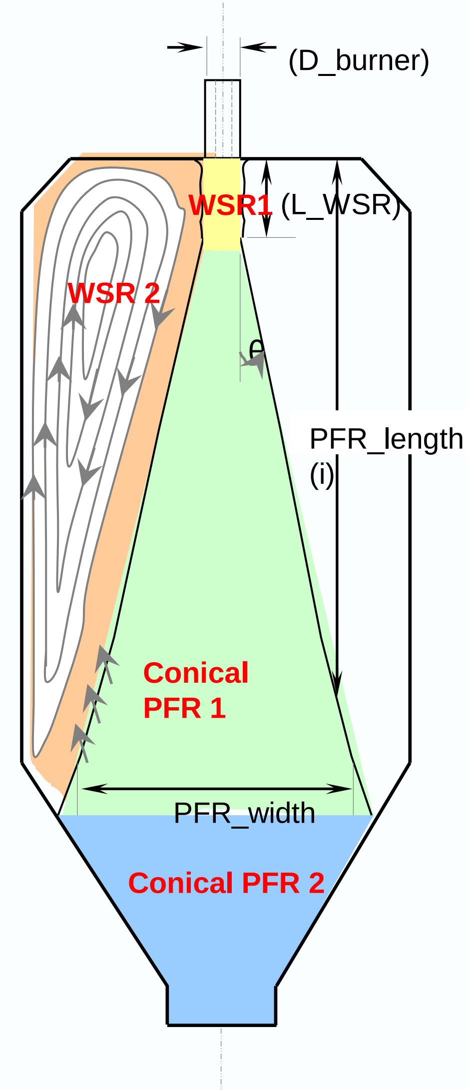
Coal gasification models









- Entrained-flow reactor
  - Application of transportable fundamental kinetics and structure data
- Pilot and full scale modelling
  - Integration of coal performance data into process flow sheets

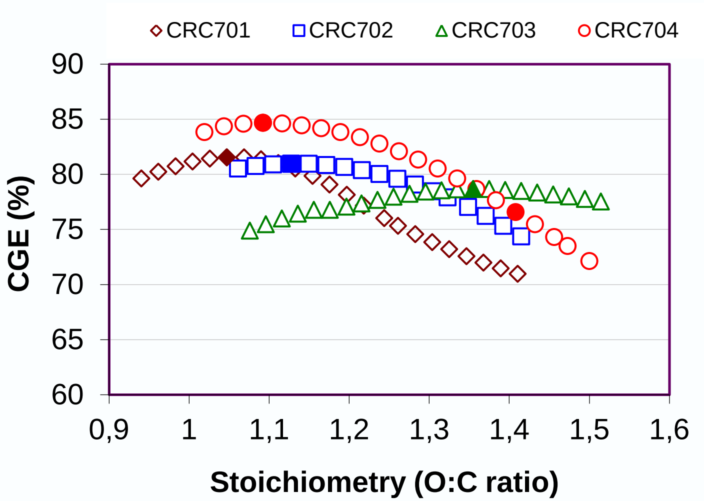
Model performance

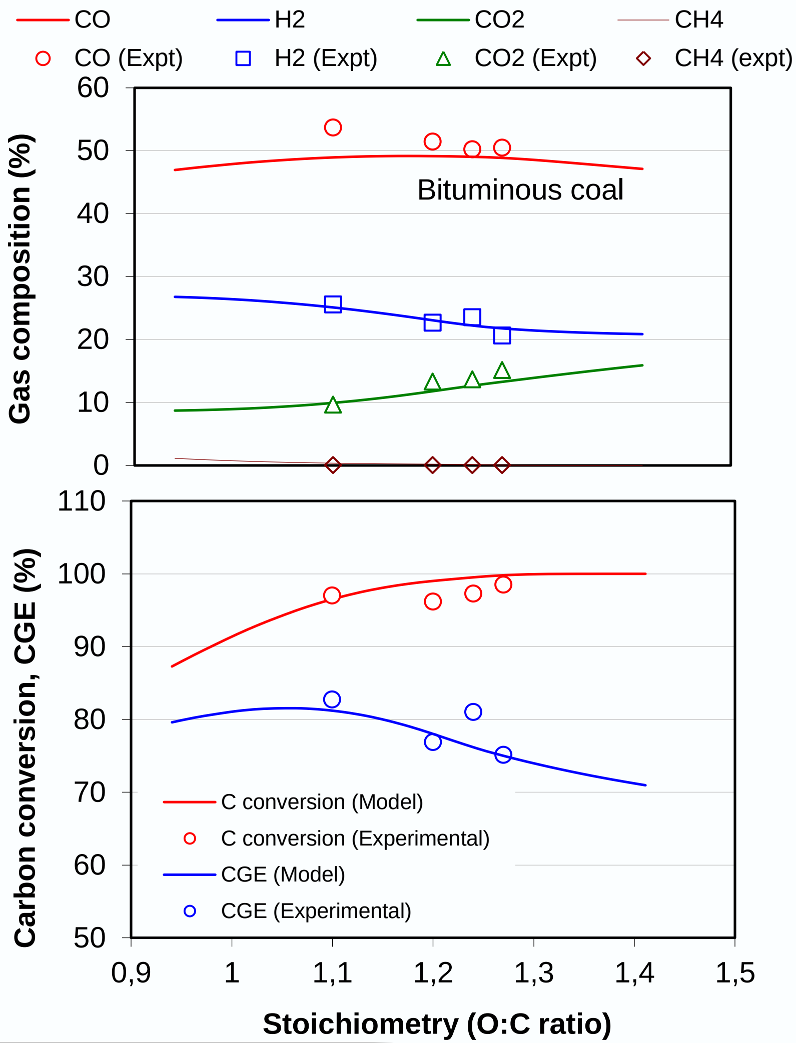
Reconciliation with pilot and lab scale data

Pilot scale test data consistent with laboratory based estimates for similar conditions

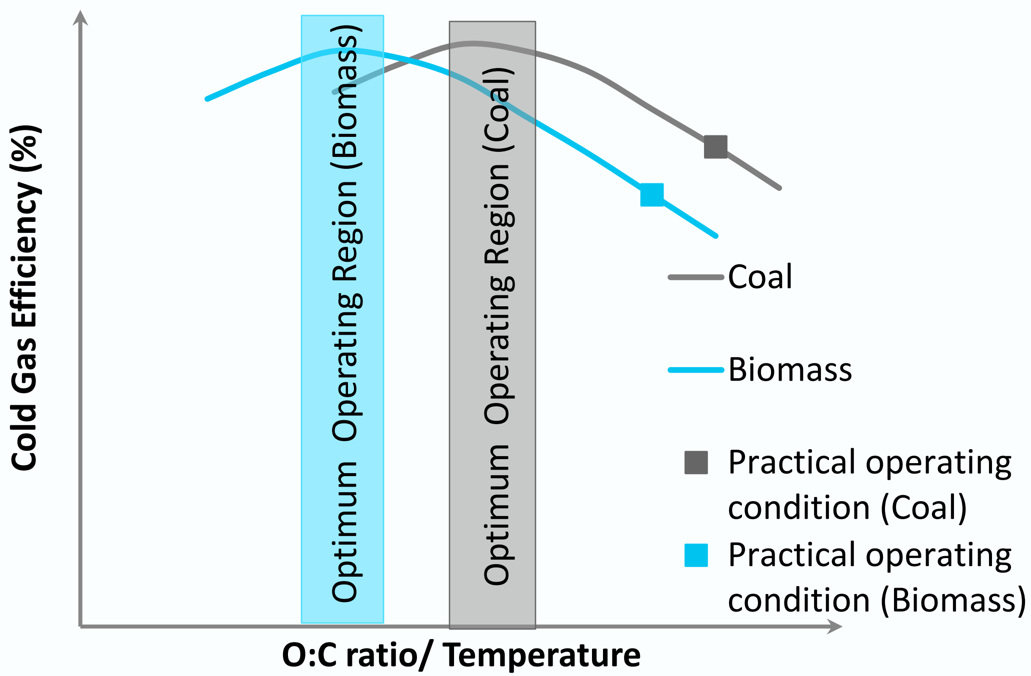
In practice many factors determine practical operating conditions

- Slag requirements may over-ride gasification reaction requirements
- eg CRC704 where O:C of ~1.4 was needed





Optimum Vs Practical operating conditions



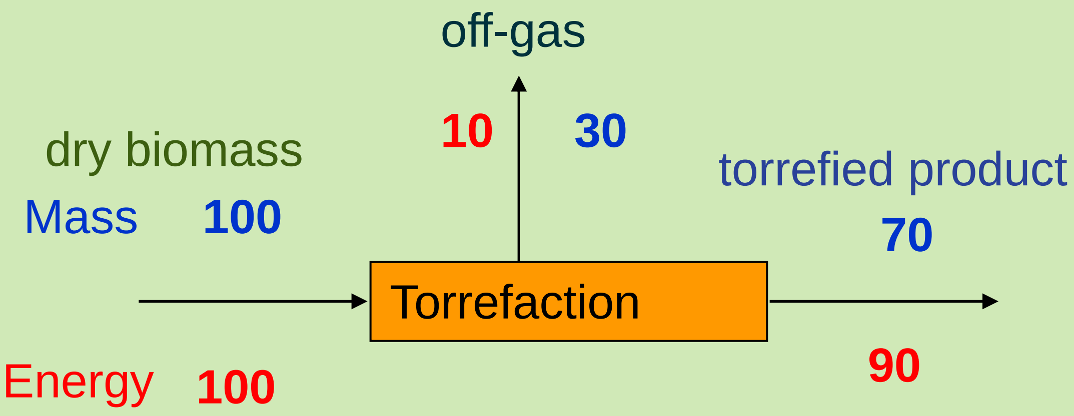
- **Our modelling results shows that some coals must be operated under higher O:C ratio than targeted optimum operating conditions due to their slagging behaviour.**
- **Similar behavior is expected for biomass in entrained flow gasifier.**

Torrefaction

Preprocessing bagasse for transport, feeding and efficiency benefits

The torrefaction process

Mass and energy balance



Energy densification = $1 \times \frac{90}{70} = 1.3$

Process Conditions:

- 200° - 300°C
- Near atmospheric pressure
- Absence of air
- Residence time of 10-30 min
- Volatilisation of hemicellulose component
- Heating rate <50°C/min

Torrefied bagasse

Physical properties

Typically ~24 MJ/kg (HHV)

Hydrophobic (maintains ~3% moisture)

Stable in long term storage

Friable

- 10% of the comminution energy required for untreated biomass
- Compatible with conventional coal milling equipment

Readily pelletised

- 50% of energy required to pelletise raw biomass
- High residual lignin (bonding agent)

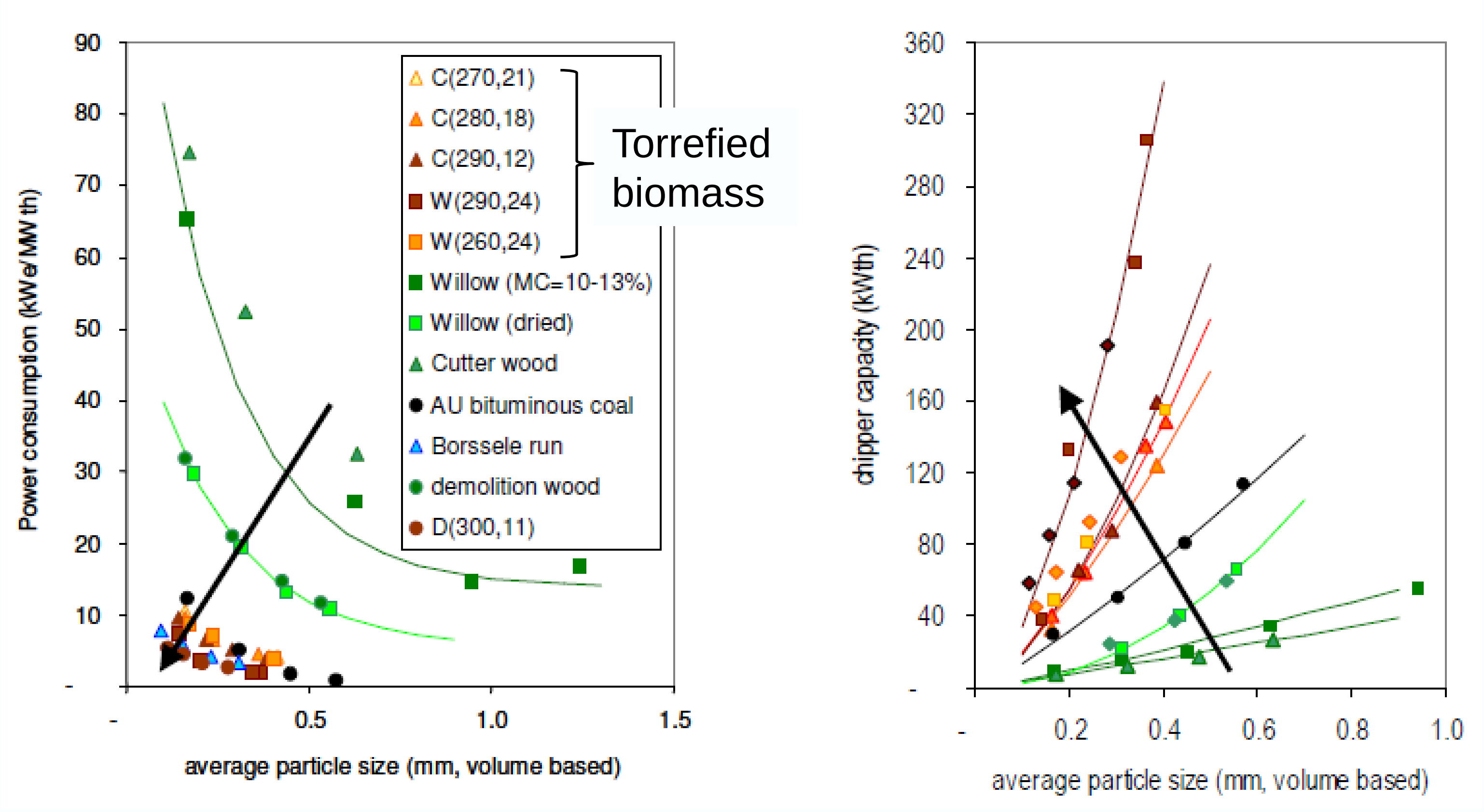
Volatiles retained

- 50% to 60% volatiles

Coal-like energy density and handling properties

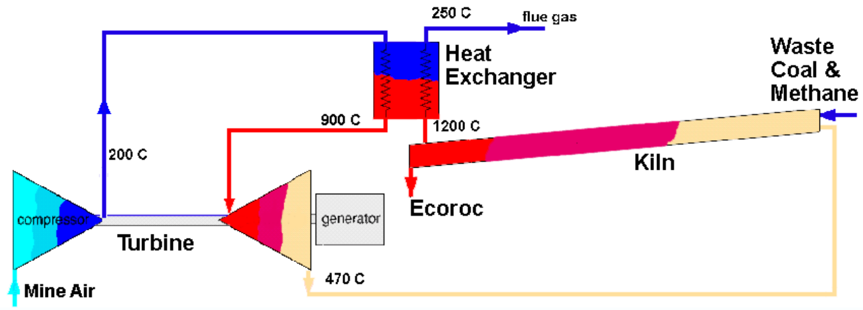
Grinding and milling

Torrefaction improves energy and performance



Rotating Kiln Facility:

Torrefaction, pyrolysis, combustion



- ~500kg/h capacity (low grade coal combustion)
- LPG pre-heater
- Kiln temperature ≤900°C
- Has been used with steam turbine and small gas turbine

CSIRO Advanced Syngas Technologies Research

Syngas Technologies

Gas Cleaning
- Particle removal
- High temperature sorbents

Syngas Processing
- Catalysts for liquid fuels production
- High temperature WGS catalysts

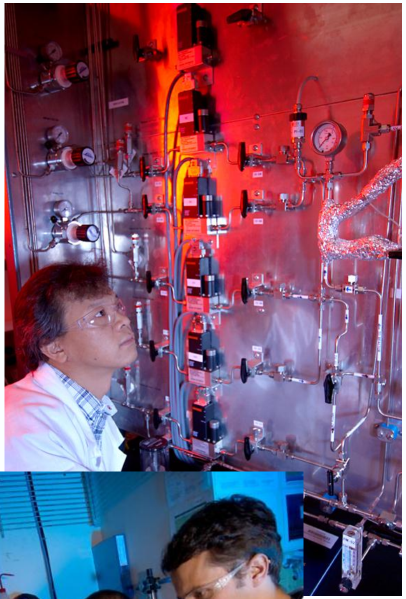
Gas Separation Membranes
- Amorphous membranes
- Crystalline membranes
- Fundamental studies of metal-H_2 interactions

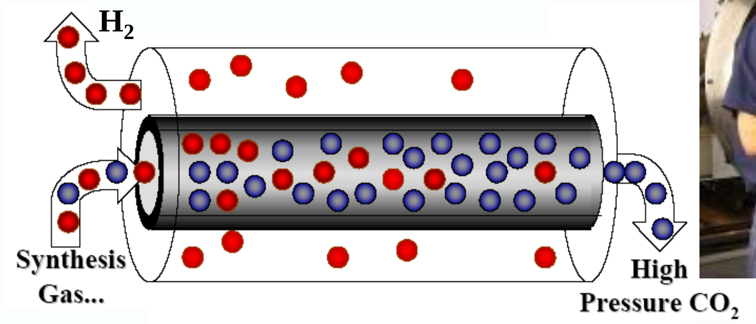
Catalytic Membrane Reactors
- Fabrication
- Demonstration
- Process optimisation

Slipstream testing in coal-derived syngas

Gas Cleaning, Processing and CO_2/H_2 Separation

- Key enabling technologies for next generation coal based H_2 energy systems
  - Large scale, low cost processes essential
  - High temperature gas cleaning systems
  - Catalytic shift reactions
  - Membrane separation systems
  - Membrane reactors
    - Shift and separation in a single unit





Bagasse gasification R&D drivers

No insurmountable technical barriers

- Coal Gasification science is applicable
  - Devolatilisation, reactivity, mineral matter & slag behaviour
- Relative importance of the fundamental processes varies
  - Drives technology & operating conditions

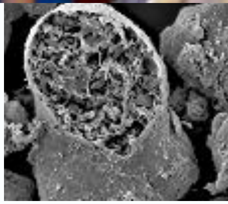
Most issues relate to the nature of biomass as a feedstock

- Torrefaction may be an important enabler
  - Dispersed and costly to transport
  - High moisture (30% to 60%)
  - Low volumetric energy density
  - Fibrous – not readily milled & fed into pressurised gasifier
- Mineral matter content and composition
  - Alkali and silica affect slagging & downstream syngas processes
  - engineering design & operating strategies

International partnerships are needed to facilitate research development, demonstration and deployment

- Coordination and ‘critical mass’ are essential





Thank You

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Operating window of main gasifiers types

	Moving beds		Fluidized beds		Entrained flow
	Downdraft	Updraft	Bubbling	Circulating	
T°C	700-1200	700-900	<900	<900	1200-1500
Tars	low	Very high	intermediate	intermediate	Absent
Control	easy	Very easy	intermediate	intermediate	very complex
Scale	<1-5 MWth	<20 Mth	10-100 Mth	20-100 Mth	> 100 MWth
feedstock	very critical	critical	less critical	less critical	fine particles