Thermo-chemical Conversion R&D Activities at CRL Energy - Including the Gasification of Coal and Biomass for Purified Hydrogen Production

Tana Levi

IEA Workshop - Bioenergy Task 33

14th April 2011

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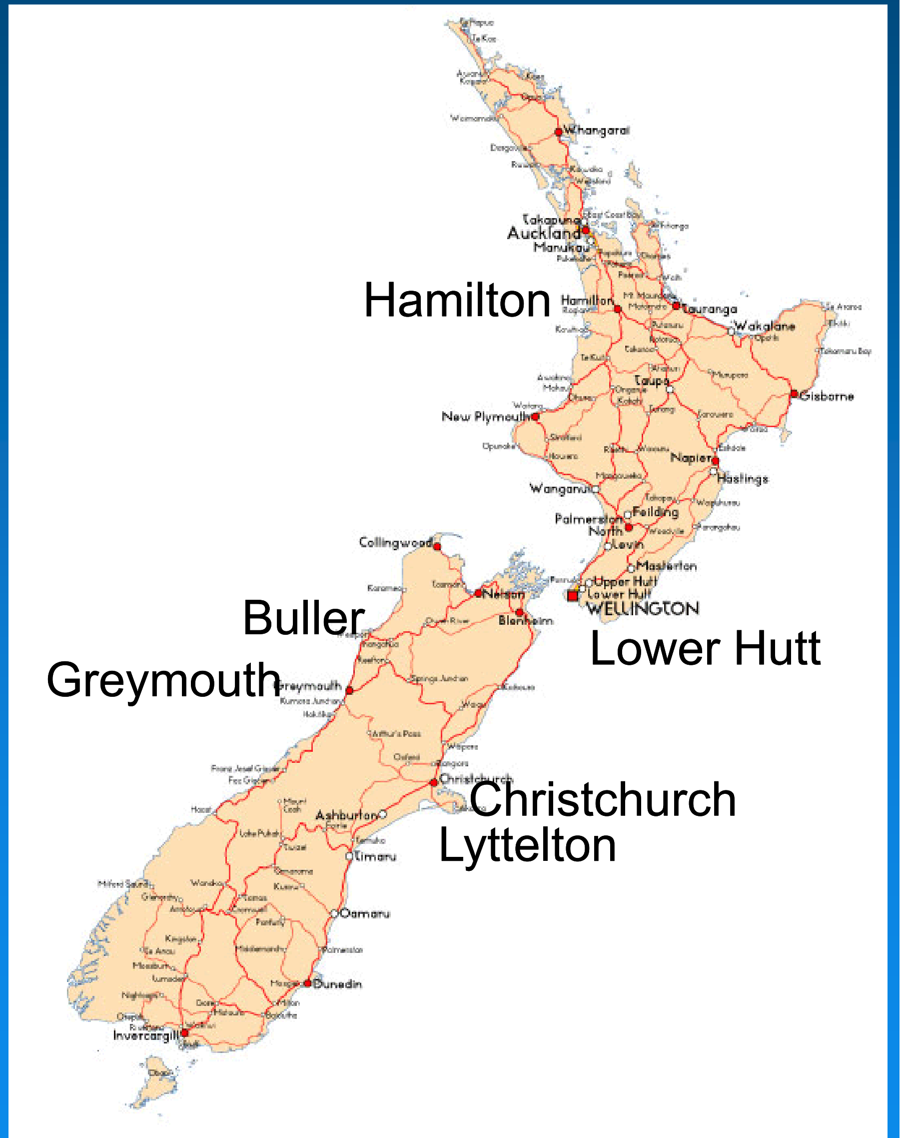
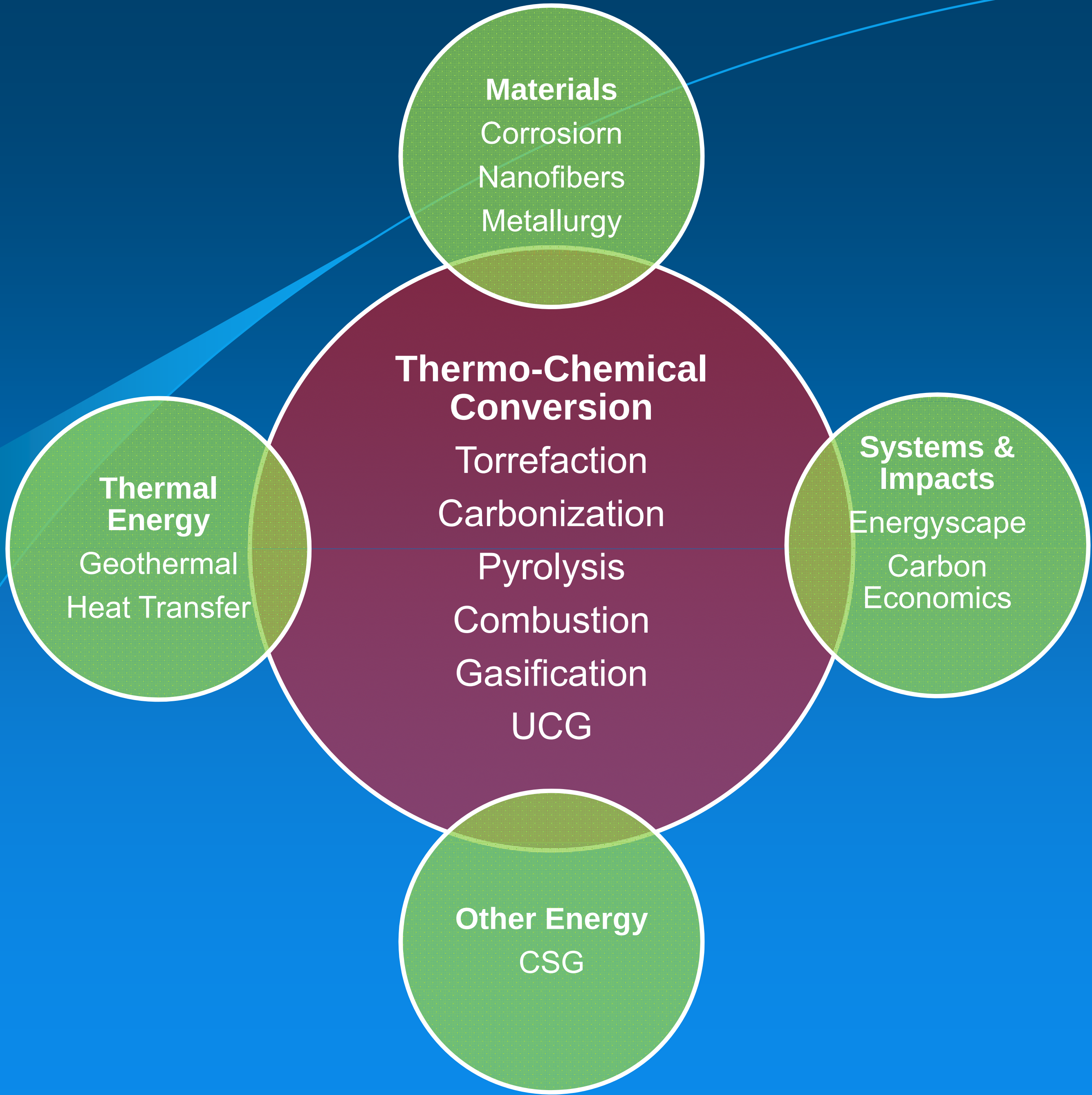
About CRL Energy Limited

- Coal Association of New Zealand
- Staff of 50
- Main facility at Lower Hutt,
  - offices in:
    - Christchurch and Hamilton
  - laboratories in:
    - Greymouth, Lyttelton and Buller
- Technology
- Geology
- Environment
- Analytical
- SpectraChem





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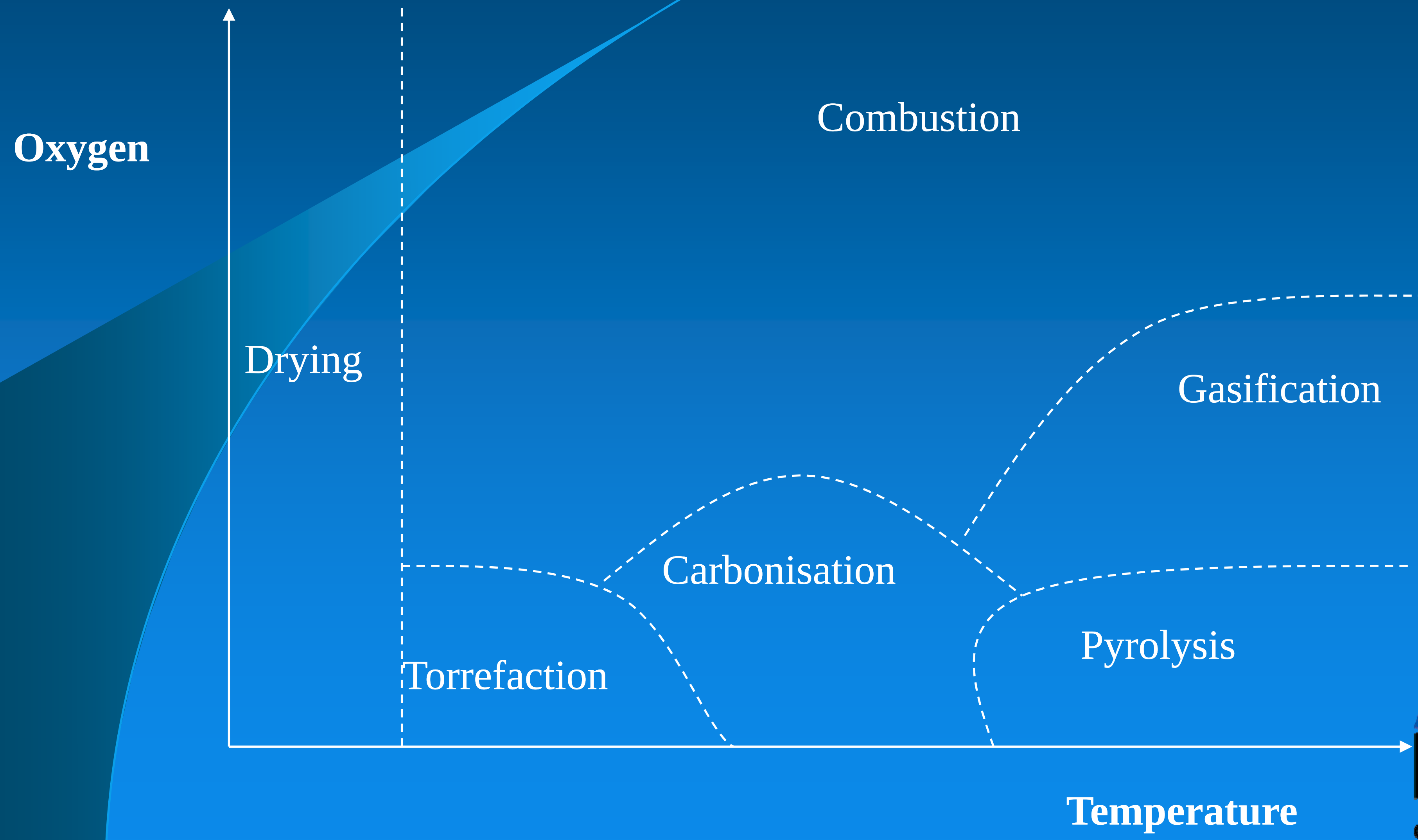
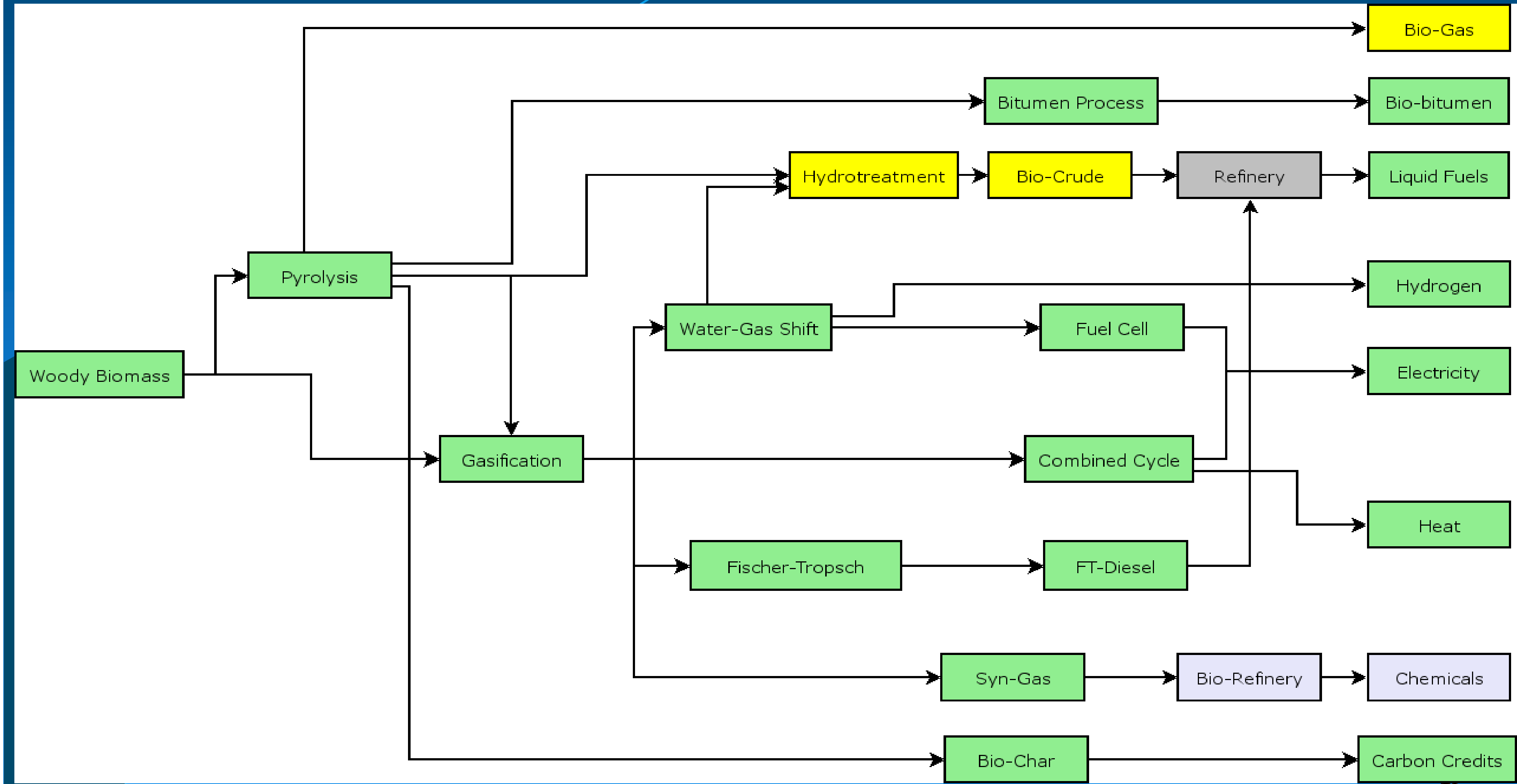
Thermo-chemical Conversion Methods



Thermo-chemical Conversion Pathways



Torrefaction

- Torrefaction of biomass for energy densification and improved storage
  - Pre-treatment step in pyrolysis and gasification
  - Temperature range 200-300°C
  - Constructing small scale test rig
  - Can also operate at carbonization temperatures

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Carbonisation

- Conversion mode that produces highest yields of biochar
- Processes increases energy density of biomass
- Improves storage and handling properties of solid products
- Applications for carbonisation include:
  - Production of slurry fuels
  - Biochar for soil enhancement
  - Extraction of complex chemicals

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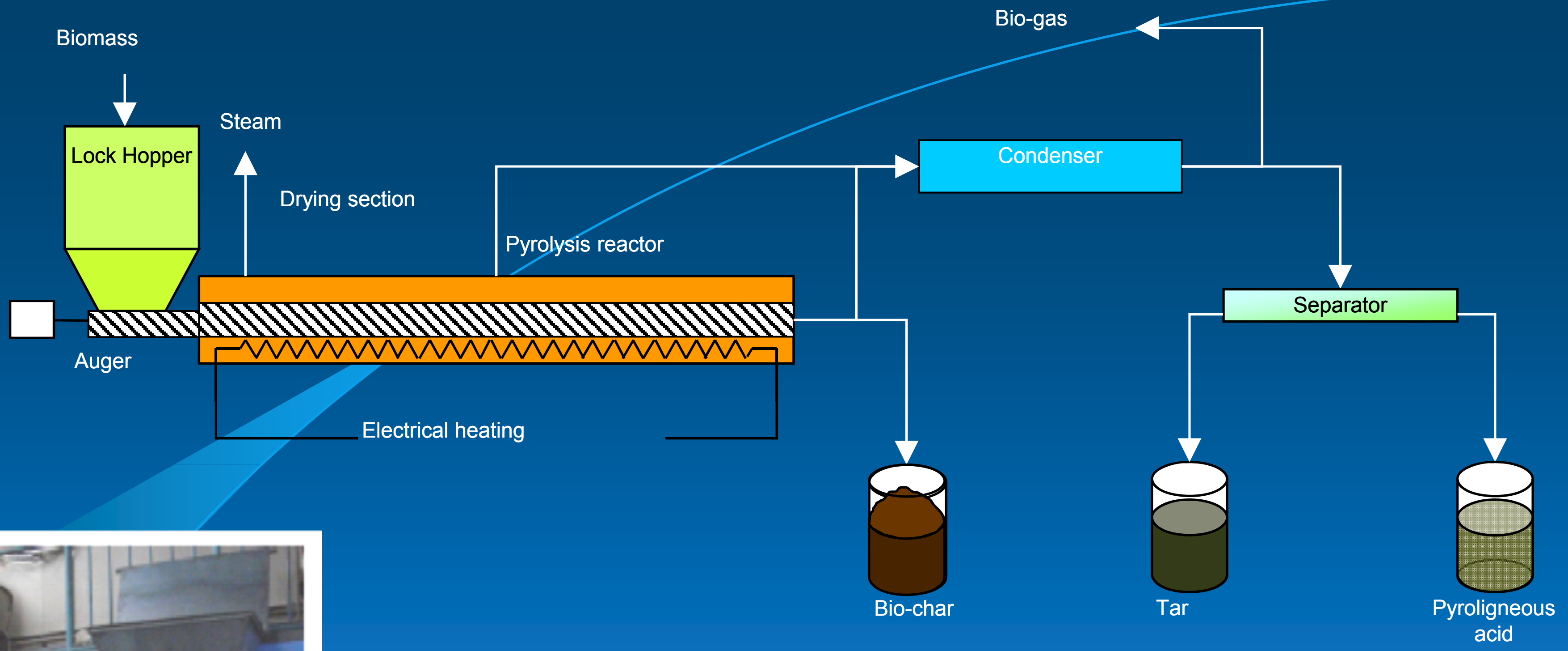

- Designed for use on:
  - Bagasse, Bio-solids, Seaweed, Wood
- Target specific product species

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Biomass Pyrolysis

- 6 year programme (2009 – 2015)
- Pyrolysis of biomass for production of bio-bitumens
  - Design and testing using bench scale pyrolyser
  - Up-scaling to proof of concept scale
  - Road testing
- Fluidized bed fast pyrolysis rig - convert sawdust into solid and liquid products

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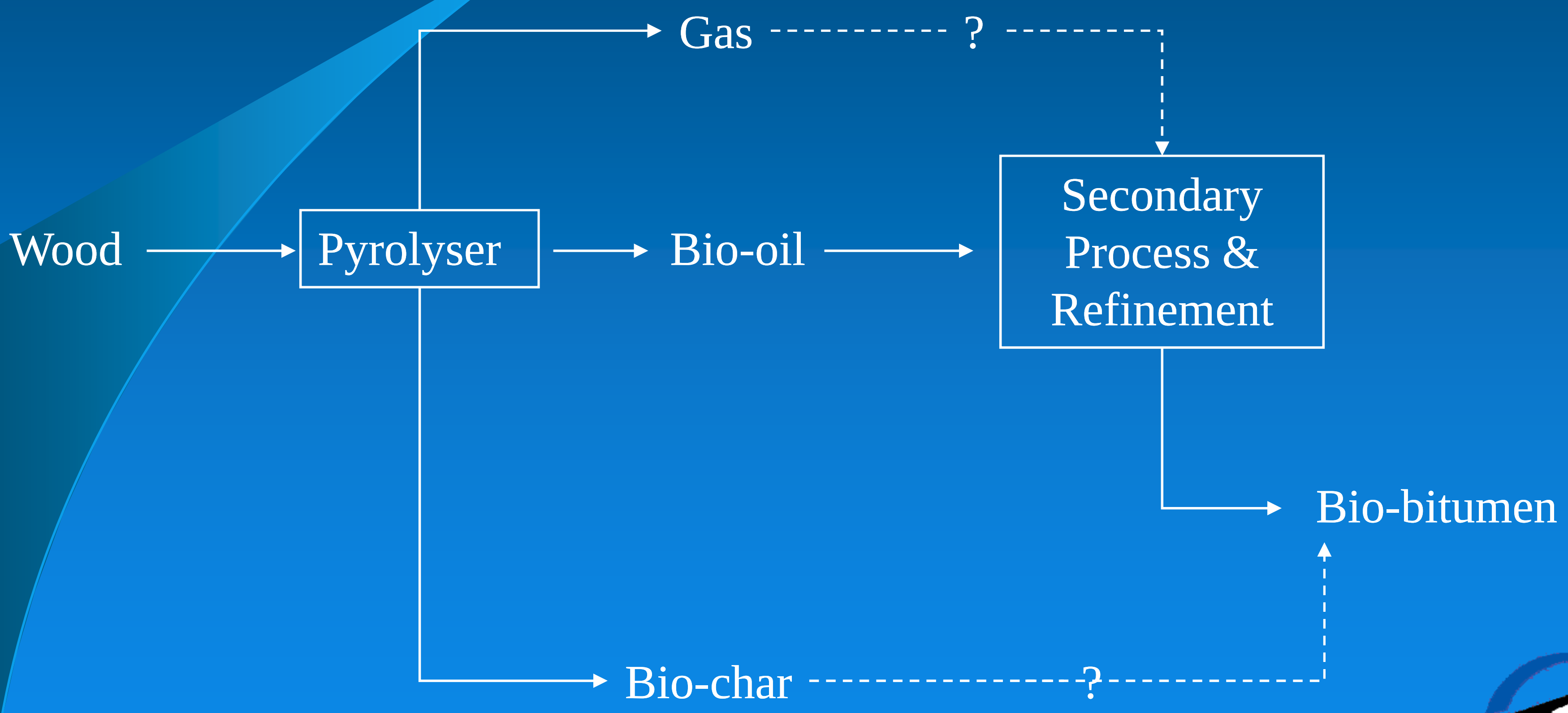
Bio-bitumen Pathway



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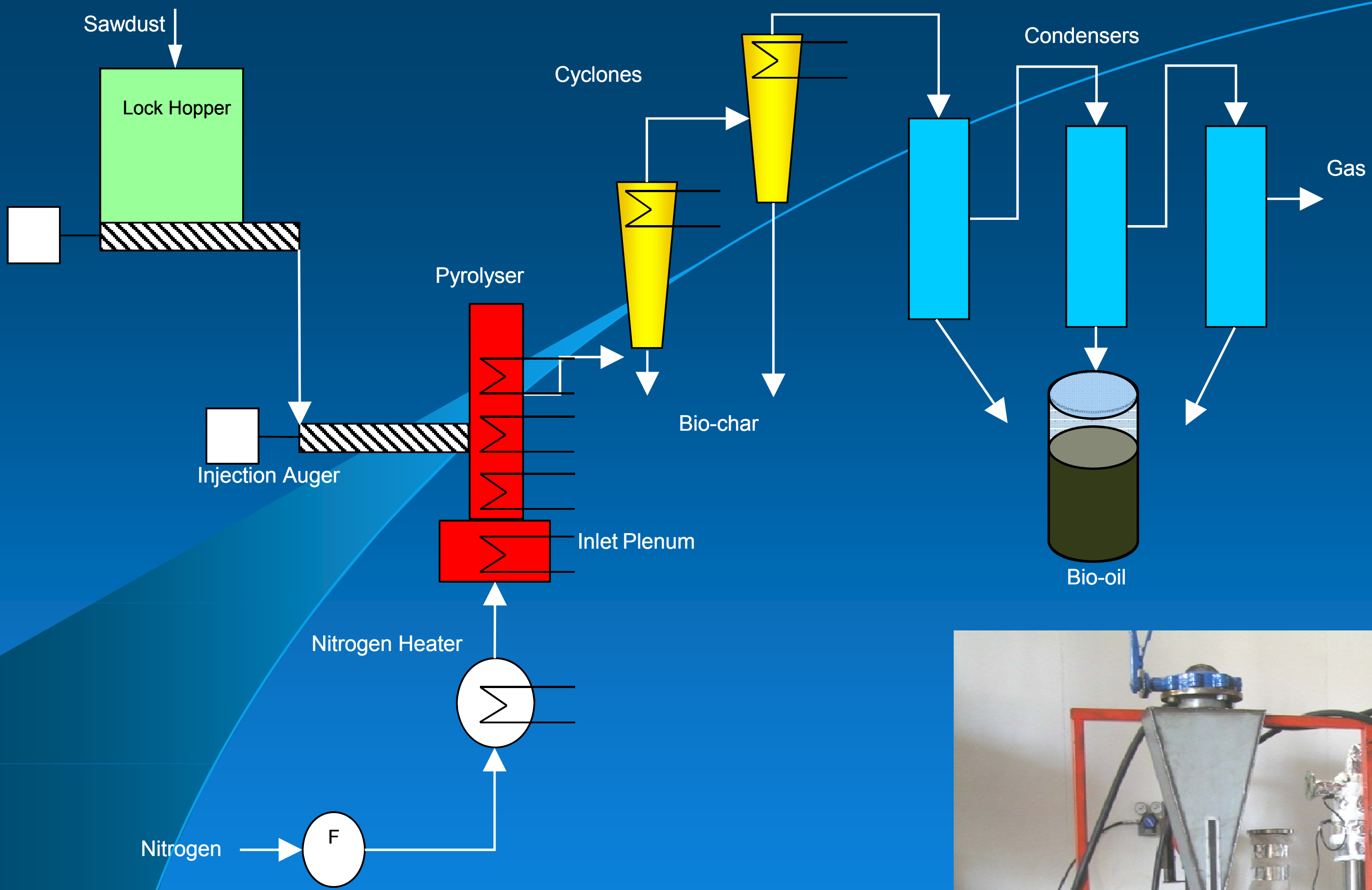
Sawdust
Lock Hopper
Cyclones
Condensers
Gas
Pyrolyser
Bio-char
Injection Auger
Inlet Plenum
Bio-oil
Nitrogen Heater
Nitrogen
F

Solid Fuel Combustion

- Fuel Performance Evaluation
- Emissions Testing
- On-Site Boiler Optimisation
- Plant Design

CRL Energy Hydrogen and Coal Gasification Research Programme

- The CRL Energy Research Programme
  - Stage 1: Understanding gasification of NZ coals (1996-2002)
  - Stage 2: Design, Construction and Commissioning a Coal to Hydrogen Technology Package (2002-2008)
  - Stage 3: Introducing Biomass and electrolysis into the Mix (2008-2012)

- Hydrogen in NZ's Energy Future

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Why Are We Looking at Biomass?

- NZ traditionally uses renewables

  2009 70% electricity and 35% primary energy

- By 2020 energy landscape must transform

  Low carbon and sustainable energy sources

- Hydrogen store excess renewable off peak electricity
- Transport sector undergo transformation

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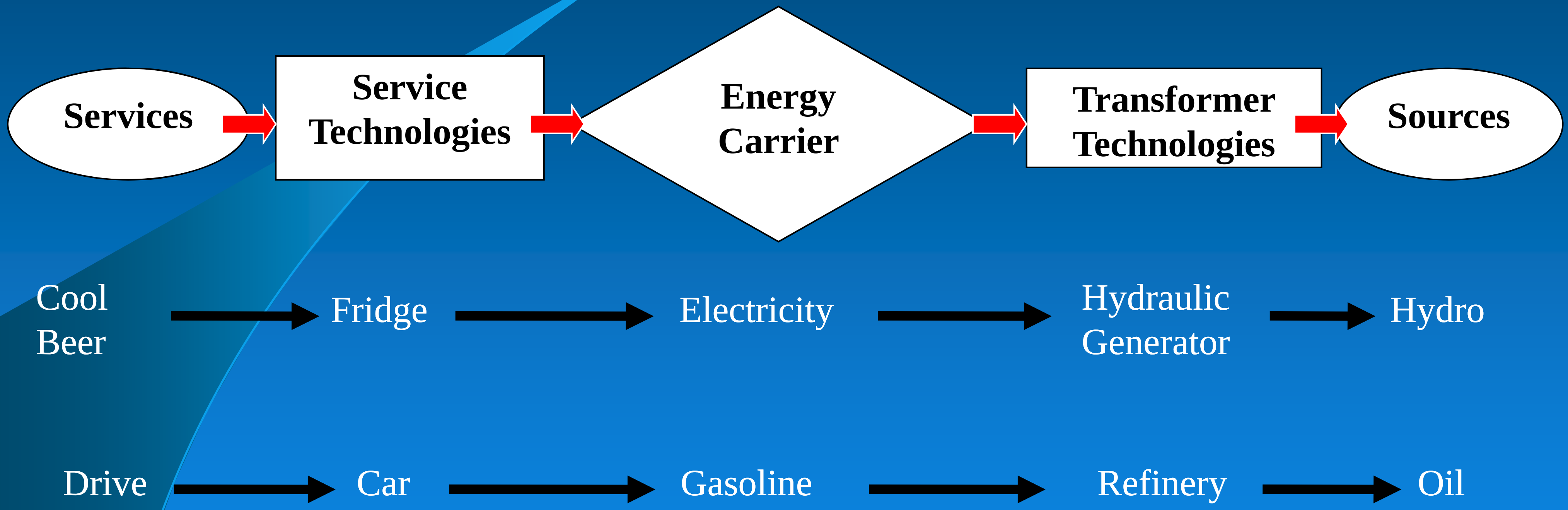
The Current Energy System



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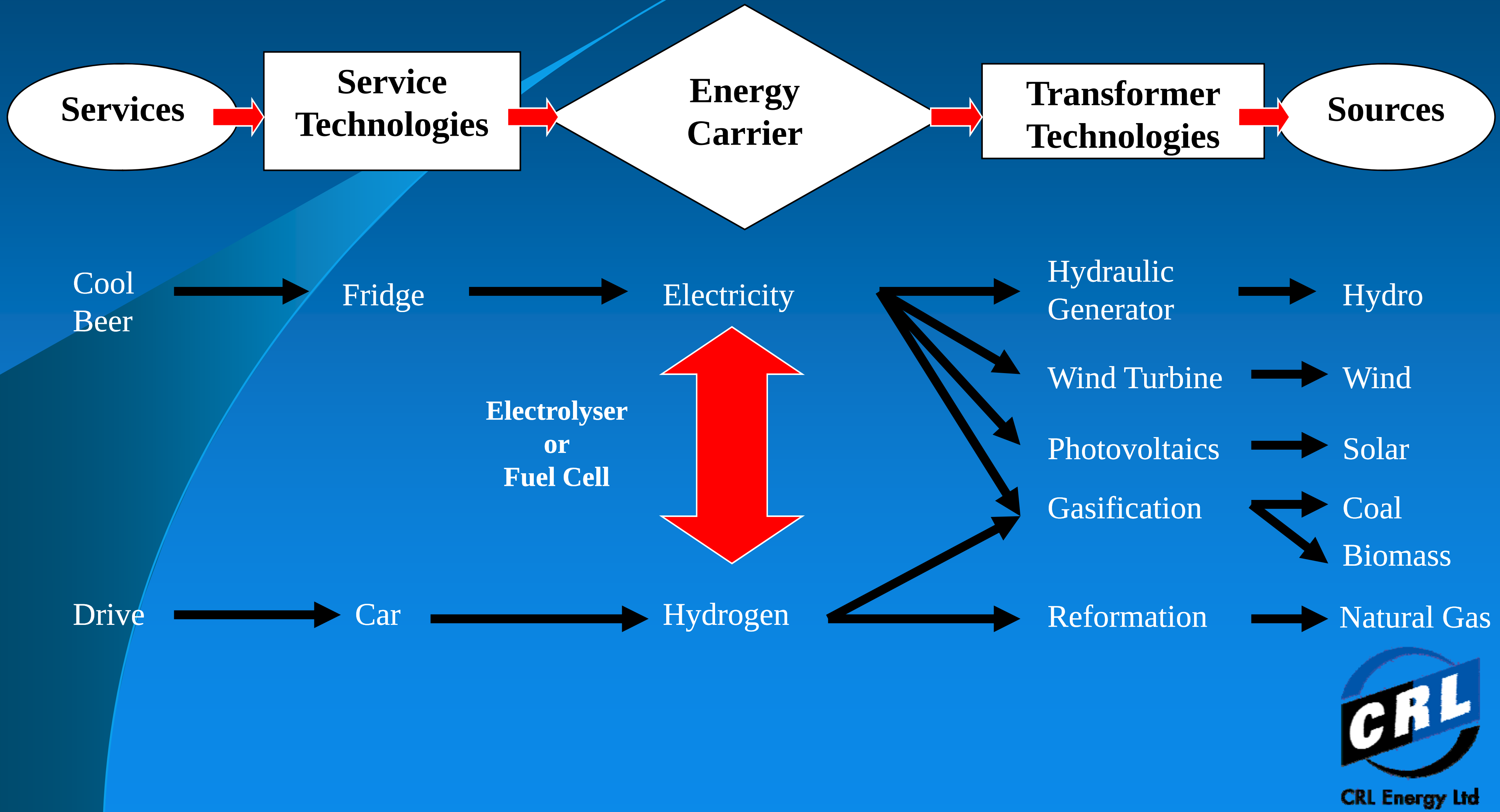
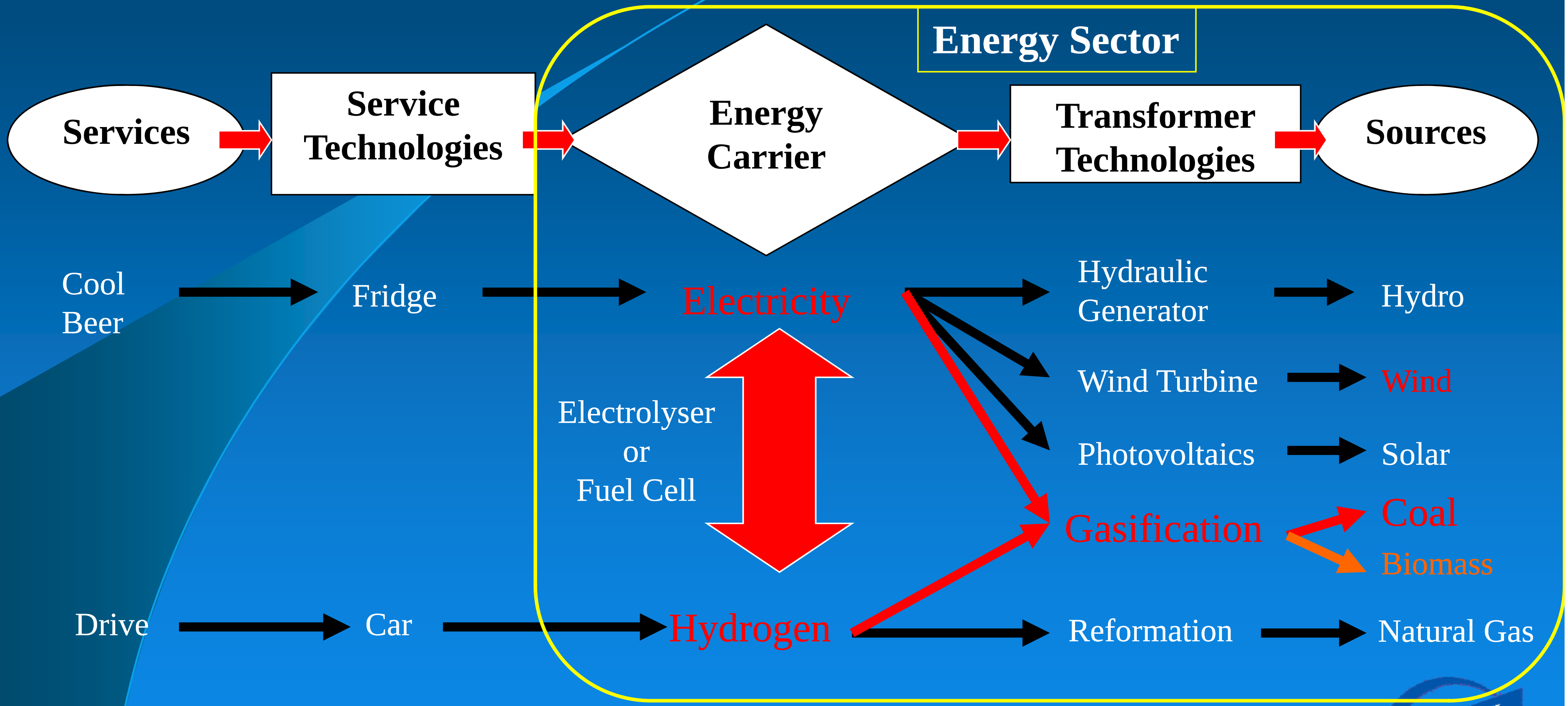
An Energy System With Hydrogen



Alignment of CRL Energy's Research Programmes



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Recoverable Energy Reserves

Assuming 350 PJ needed:

- Renewables 120 PJ pa
- Oil and condensate – 402 PJ
- Natural Gas - 2300 PJ
  - Future discoveries estimated at 80 PJ pa
- Coal – 150,000 PJ
  - Sufficient to meet energy demands for 100s of years

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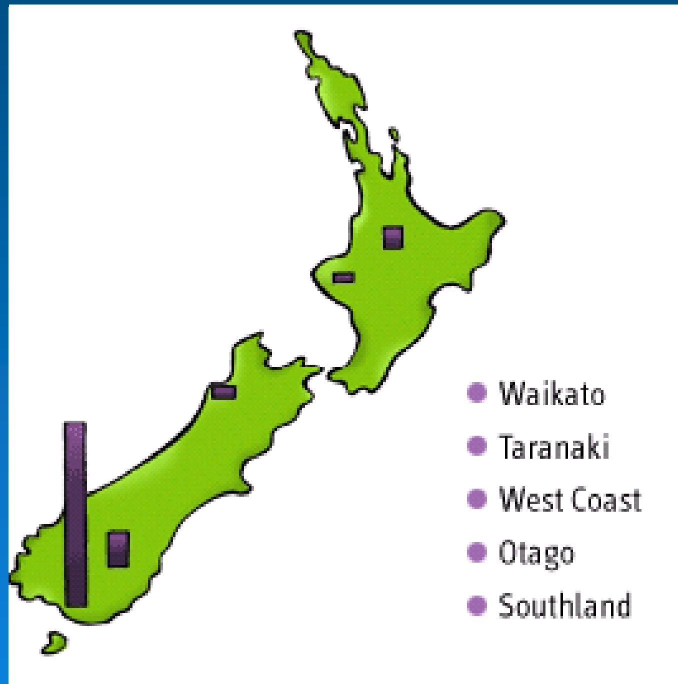
New Zealand Coal Resources

- NZ has 10 times more coal per capita than the average for the rest of the world
- 9 billion tonne reserve
- 5 million tonne production p.a.
- 75% lignite, 15% sub-bituminous, 10% bituminous



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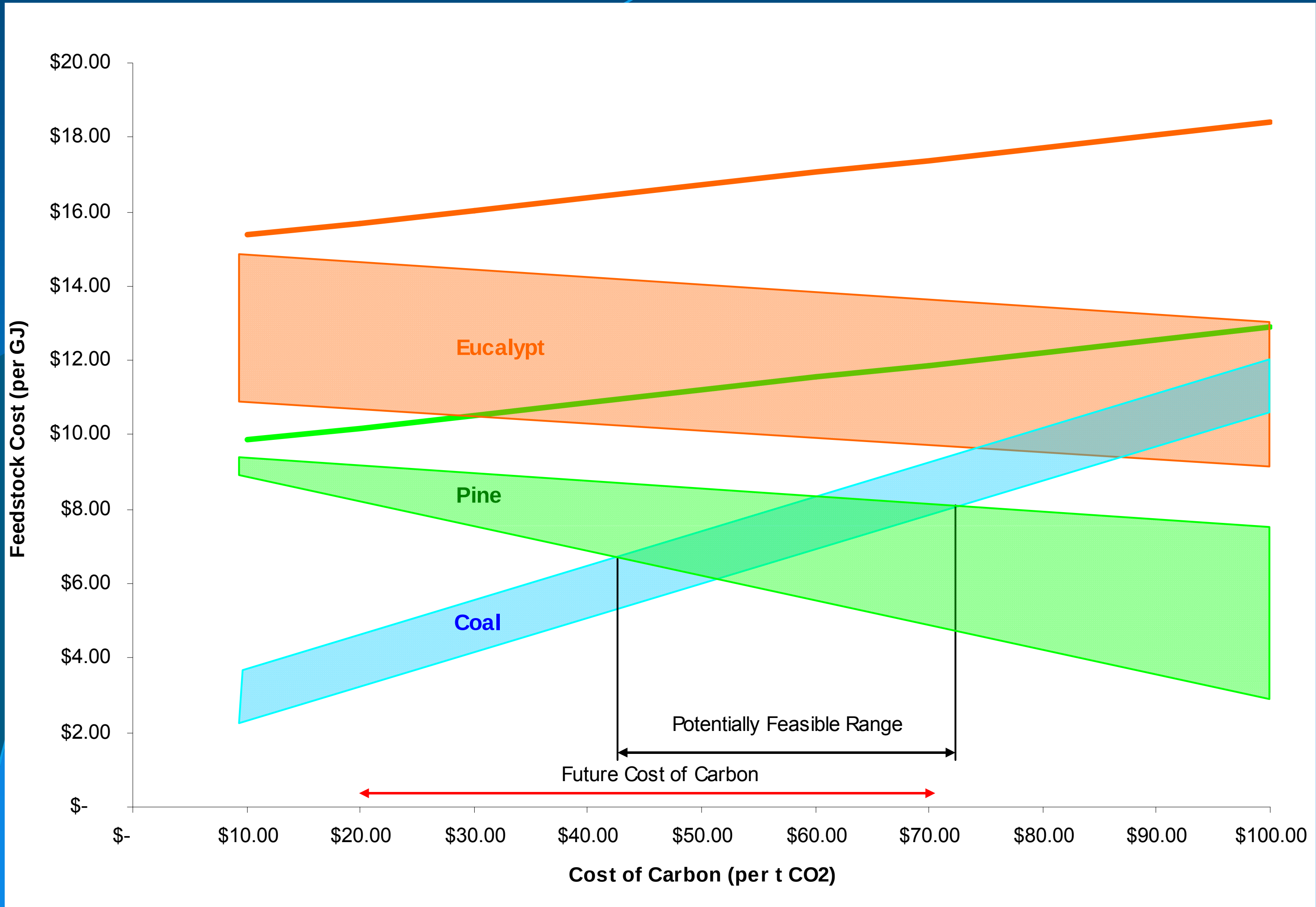
Feasibility of Biomass



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Hydrogen and Clean Energy Technology Package

Four year programme

10 milestones
8 relate to gasifier and modifications
2 relate to improving syngas clean up

Bench scale gasifier tests on coal/biomass blends

Modelling char reactivity and product streams

Proof of Concept O_2 blown coal/biomass gasifier + electrolyser

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Hydrogen and Syngas – Flexible, Valuable Products

Feedstocks

- Coal
- Biomass
- Petroleum Coke
- Heavy Oil Residues
- Asphaltenes
- Natural Gas

→ Advanced Co-Gasification Plant

Products

- Chemicals
  - Oxo-alcohols
  - Methanol
  - Ammonia
  - Urea
- Hydrogen
- Electricity
- Clean Fuels (FT)
- (WGS) (CO_2) (CCS)

Renewable electricity → Electrolyser

Electrolyser → O_2 → Advanced Co-Gasification Plant

Electrolyser → H_2 → Products

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Why Coal:Biomass Gasification ?

- Biomass gasification is a carbon neutral process
  - But a limited resource
- Coal gasification is not a carbon neutral process
  - But is a huge natural resource
    - Energy security
    - Inexpensive
    - Regular quality

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Why Coal:Biomass Gasification ?

- Enables a transition between fossil and plantation biomass technologies

- Use a product that may otherwise be disposed of as waste - e.g. timber milling plant waste, corn husks, municipal waste, chicken waste

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Synergies

- *U of C Contract: What happens to gasification behaviour when coal is added to biomass?*
  - Using an abundant fuel to augment a lower CV, less abundant one
- *CRL Energy Contract: What happens to gasification behaviour when biomass is added to coal?*
  - Using a carbon neutral fuel to reduce carbon footprint

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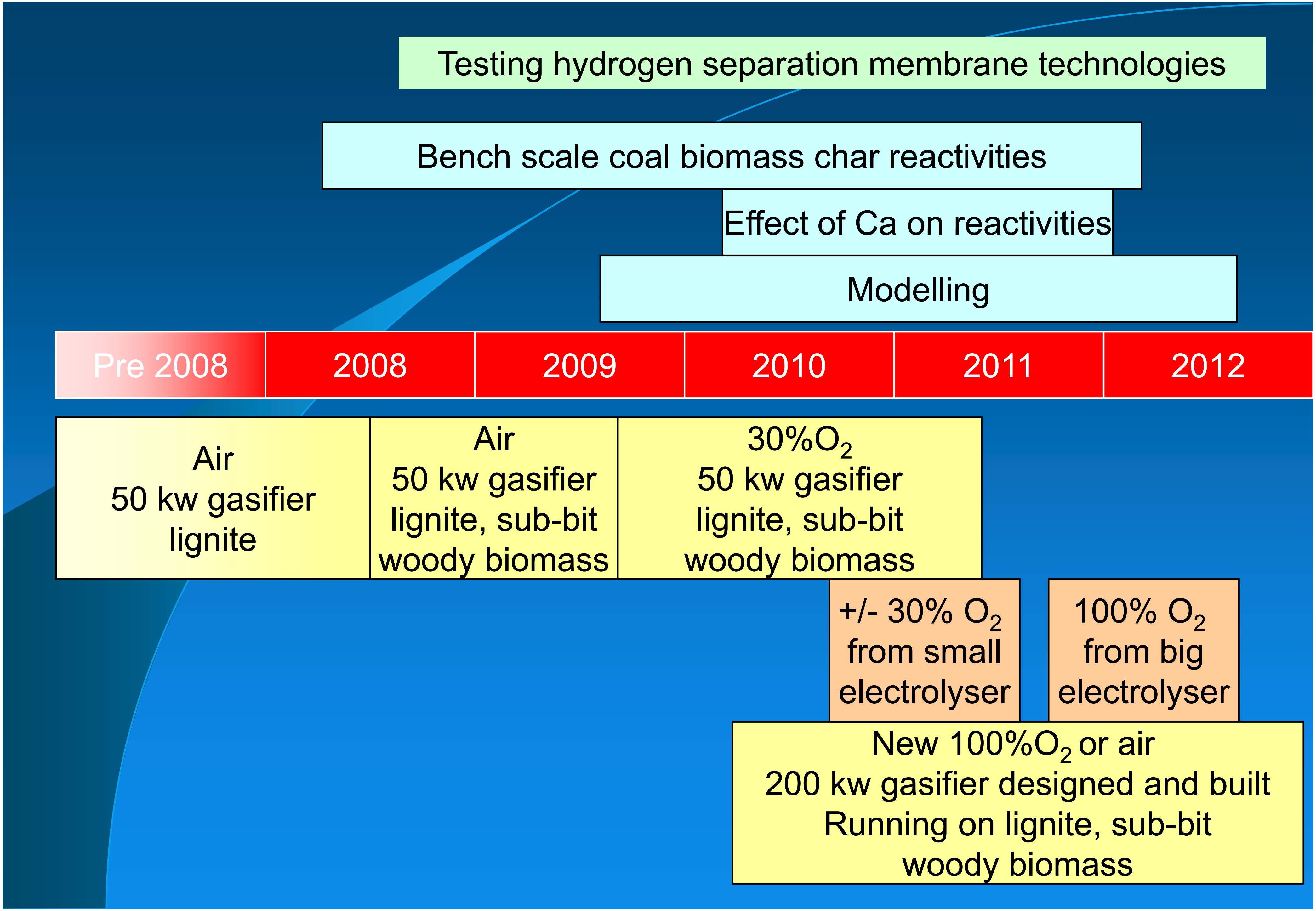
Testing hydrogen separation membrane technologies
Bench scale coal biomass char reactivities
Effect of Ca on reactivities
Modelling
Pre 2008
2008
2009
2010
2011
2012
Air 50 kw gasifier lignite
Air 50 kw gasifier lignite, sub-bit woody biomass
$30\%O_2$ 50 kw gasifier lignite, sub-bit woody biomass
+/- 30% O_2 from small electrolyser
100% O_2 from big electrolyser
New $100\%O_2$ or air 200 kw gasifier designed and built Running on lignite, sub-bit woody biomass

Questions around Co-gasification

Feedstock quality
vs
product quality

landscape

soil

Geographic implications

Carbon balance

climate

biodiversity

incentives

market

constraints

Scale

Economic implications

supply chain

margins

sustainability

Optimum % of
various blends

Coal:Biomass Co-gasification: Issues

size

compressibility

density

Dissimilar fuels

expansion

moisture %

strength

Variable reaction rates

plant feed requirements

transportation

Handling

feed preparation

storage

Variable syngas composition

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Biomass Selection

- *E. nitens*
  - Short rotation forestry
  - Efficient use of land
  - Difficult to prepare

- *P. radiata*
  - Longer rotation
  - Available
  - Easy to prepare

Making Coal:Biomass Pellets

- Enables regular feedstock quality
  - Reproducible results
- Small size
  - Easy for handling
  - Easy to transport and store
- Fluidise well
  - Avoids segregation
  - Steady gaseous out stream

Making Coal:Biomass Pellets

- Make up coal:biomass blends (0, 20%, 40%, 50%, 60%, 80% 100%) by weight.
- Fuels used: *E. nitens*, *P radiata*, Lignite, Sub-bituminous coal
- Test that pellets are strong enough to feed to gasifier

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Making Pellets - Methodology

- Air dry biomass to approximately 3% moisture
- Grind biomass and lignite/sub-bituminous < 1.0 mm
- Biomass and lignite/sub-bituminous ball milled with binder (water and 9% wt flour)
- Ideal moisture content level of blends is ~24%
- Feed mixture into hot roller press pelletizer (2 passes)
- Pellets 8-10 mm Ø, 10 – 30 mm long
- Pellets dropped x 10, 2 m onto concrete floor

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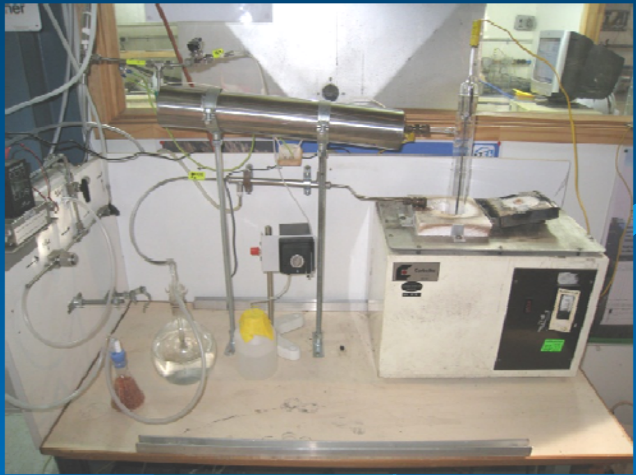
Things did not always go quite to plan !!!

Analysis of Feed Stocks

			Dry Basis						
CRL Ref	Description		Ash ASTM D1102	Vols ISO 562	Fixed Carbon by difference	Total Carbon SC144-DR	Total Carbon ISO/TS 12902	Total Hydrogen ISO/TS 12902	Total Nitrogen ISO/TS 12902
93/000	Pine	%	0.37	84.6	15.0		51.2	5.87	<0.03
93/001	e niten	%	0.40	86.2	13.4		50.2	5.89	<0.03
93/002	Lignite	%	6.1	51.8	42.2		62.6	4.50	0.68
93/003	Sub-bit	%	6.3	44.7	49.1		68.8	4.75	1.19
93/004	L-P 20/80 Char	%	4.9	3.2	91.8	90.4			
93/005	L-P 50/50 Char	%	8.3	4.3	87.4	86.2			
93/006	L-P 80/20 Char	%	10.7	7.0	82.3	83.9			
93/007	S-P 20/80 Char	%	5.2	4.8	90.1	88.8			
93/008	S-P 50/50 Char	%	8.7	9.7	81.6	83.7			
93/009	S-P 80/20 Char	%	10.1	3.3	86.6	86.1			
93/010	100% Pine Char	%	1.9	2.1	95.9	94.7			

Bench Scale Gasifier



- Determine reactivities of mixed chars
- Calculate rate at which char is converted to carbon containing gases
- Identify time to 50% conversion
- Identify syngas composition at that time

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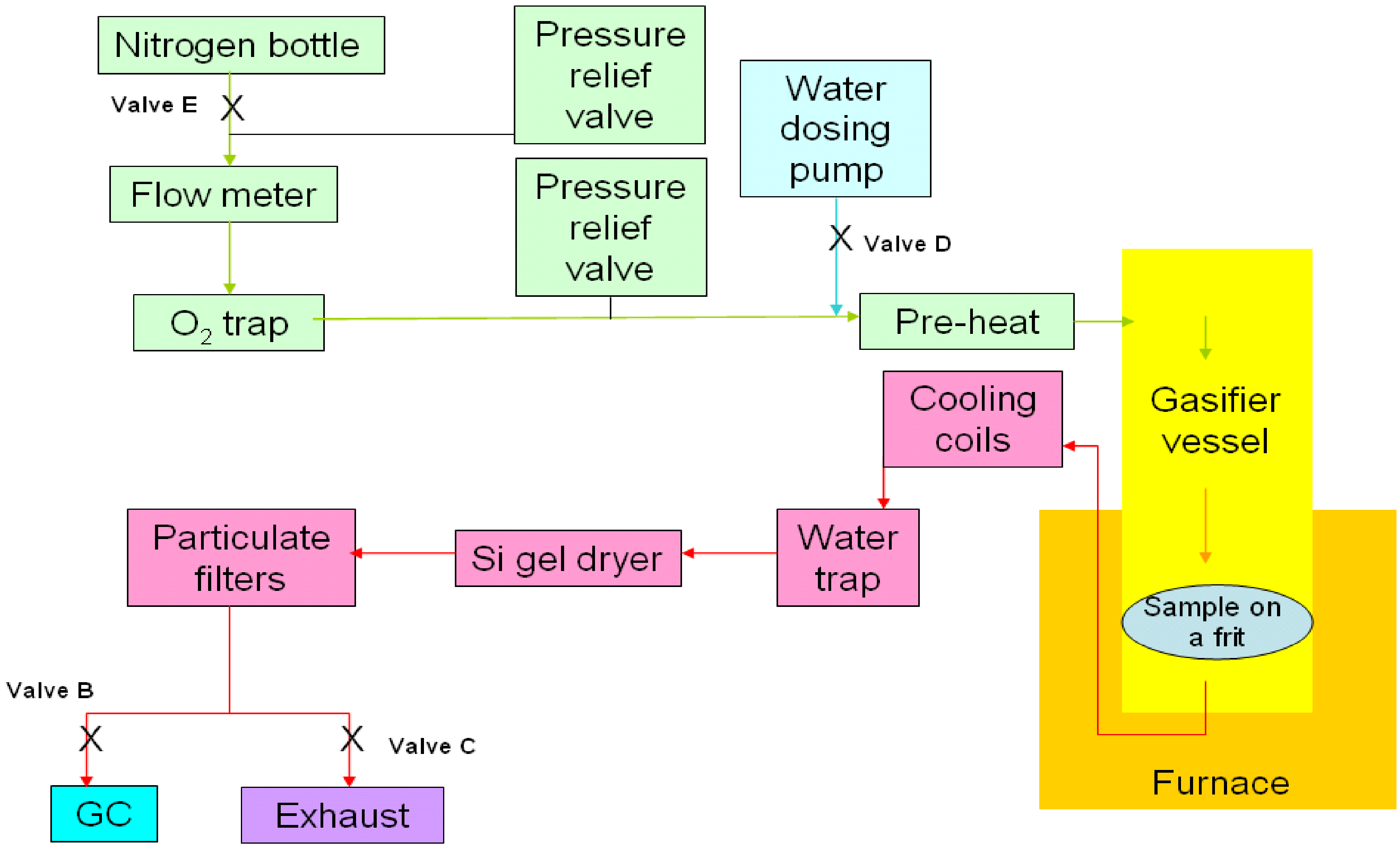
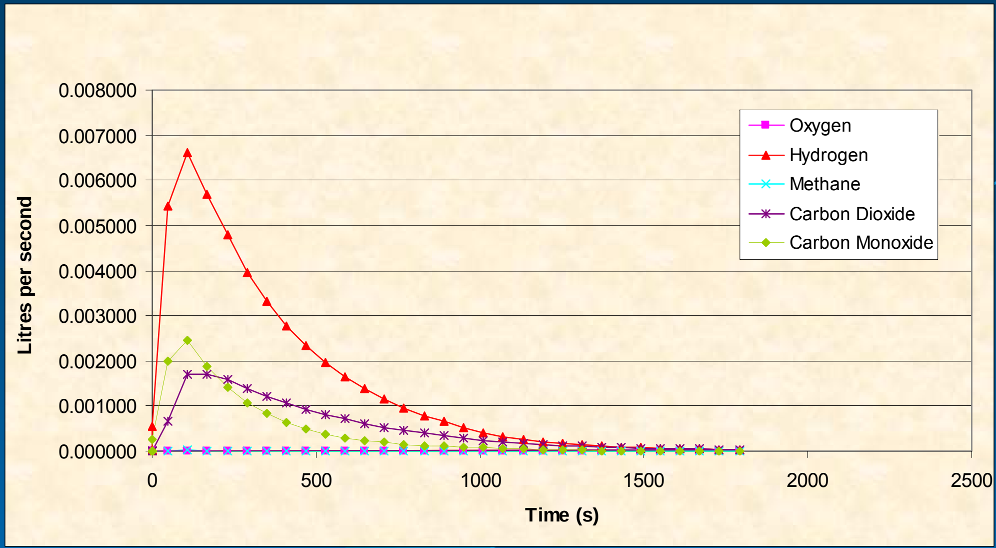
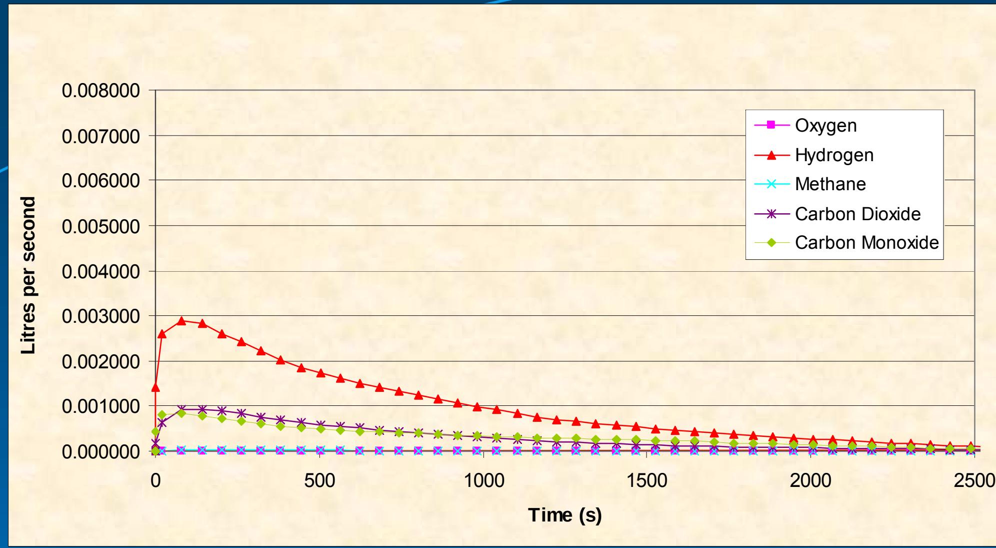
BENCH SCALE GASIFIER





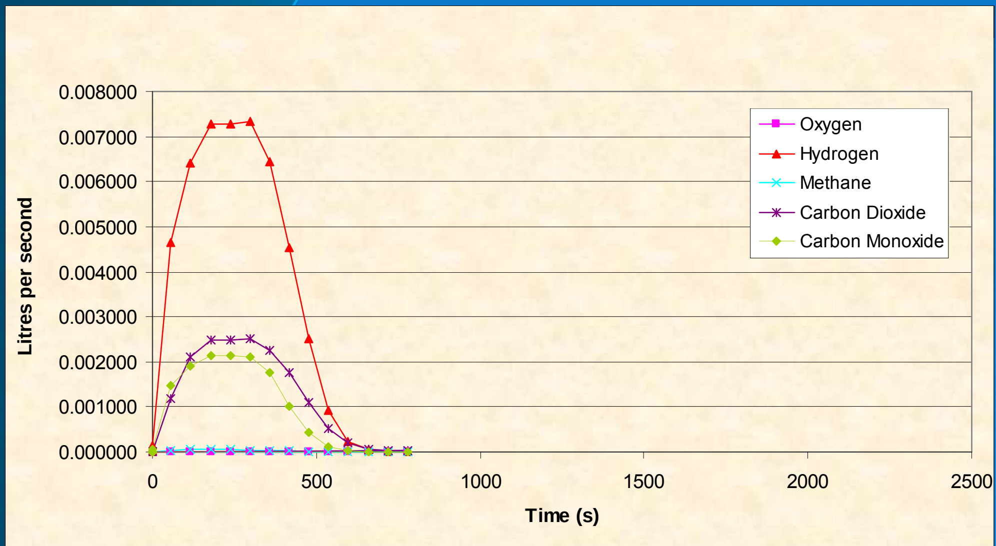


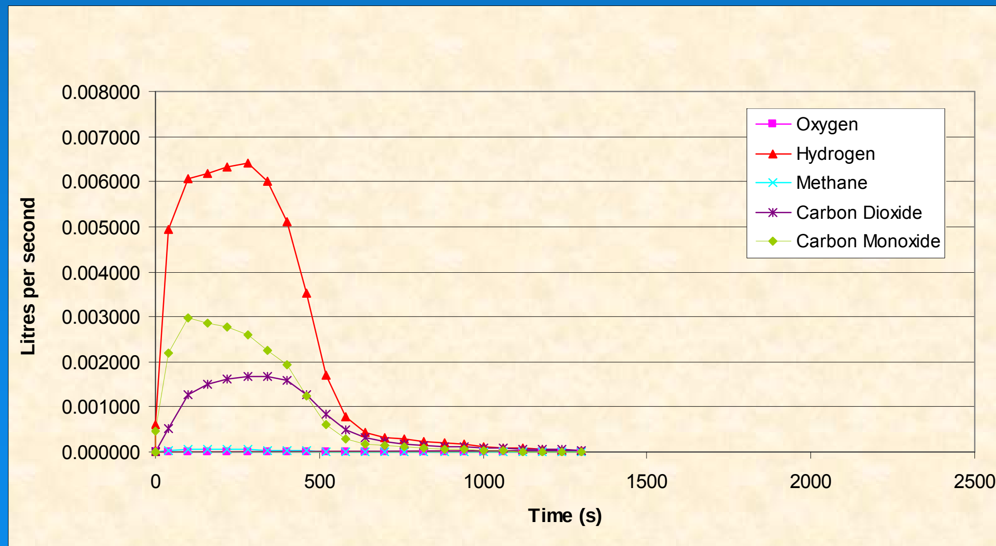
Lignite

Sub-bituminous

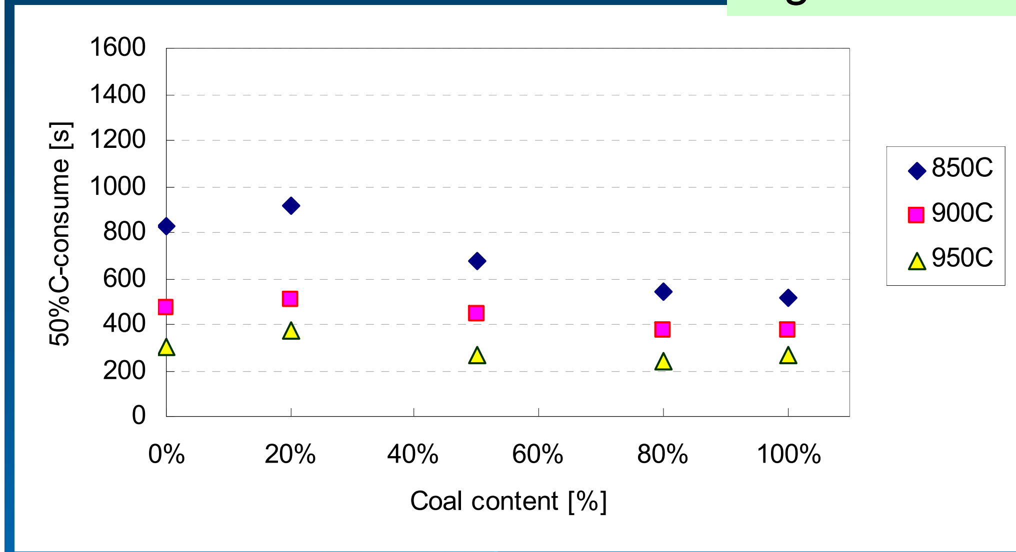
P. radiata

E. nitens

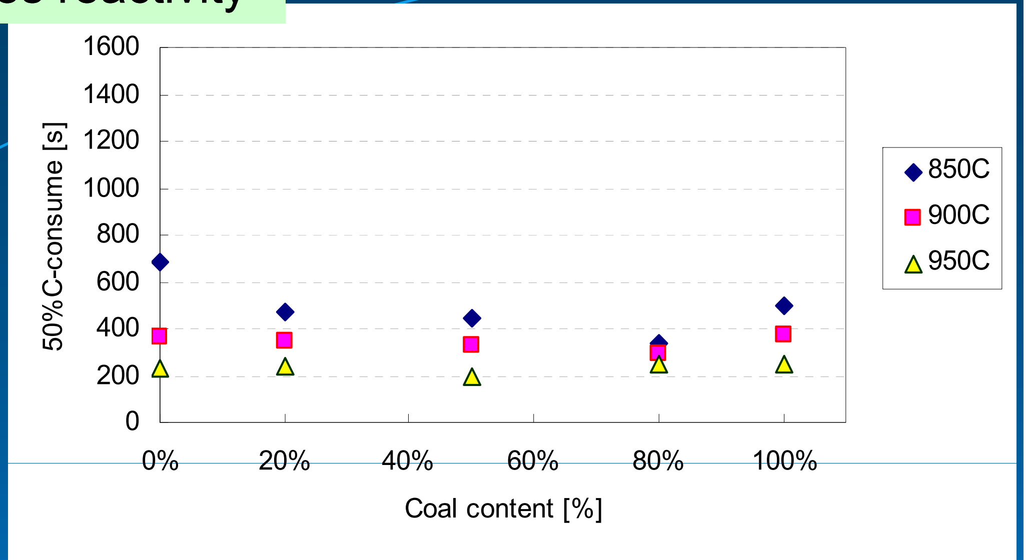




Lignite increases reactivity

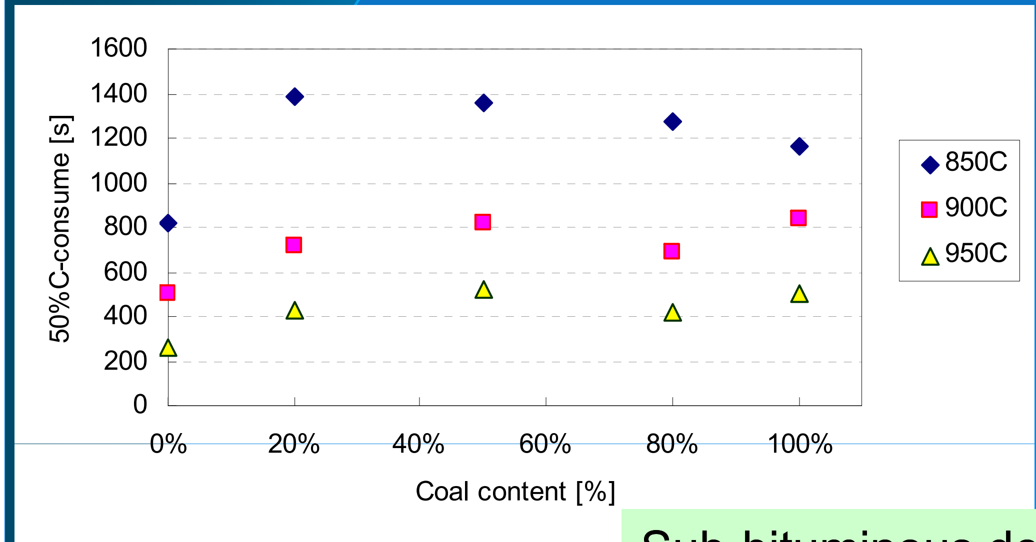


Lignite / *P. radiata*

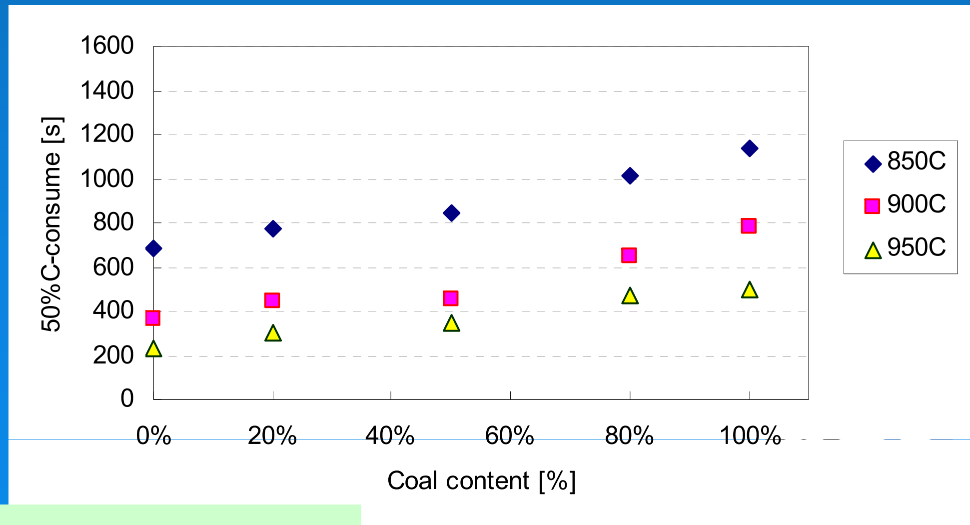


Lignite / *E. nitens*

Sub-bituminous / *P. radiata*



Sub-bituminous / *E. nitens*



Sub-bituminous decreases reactivity

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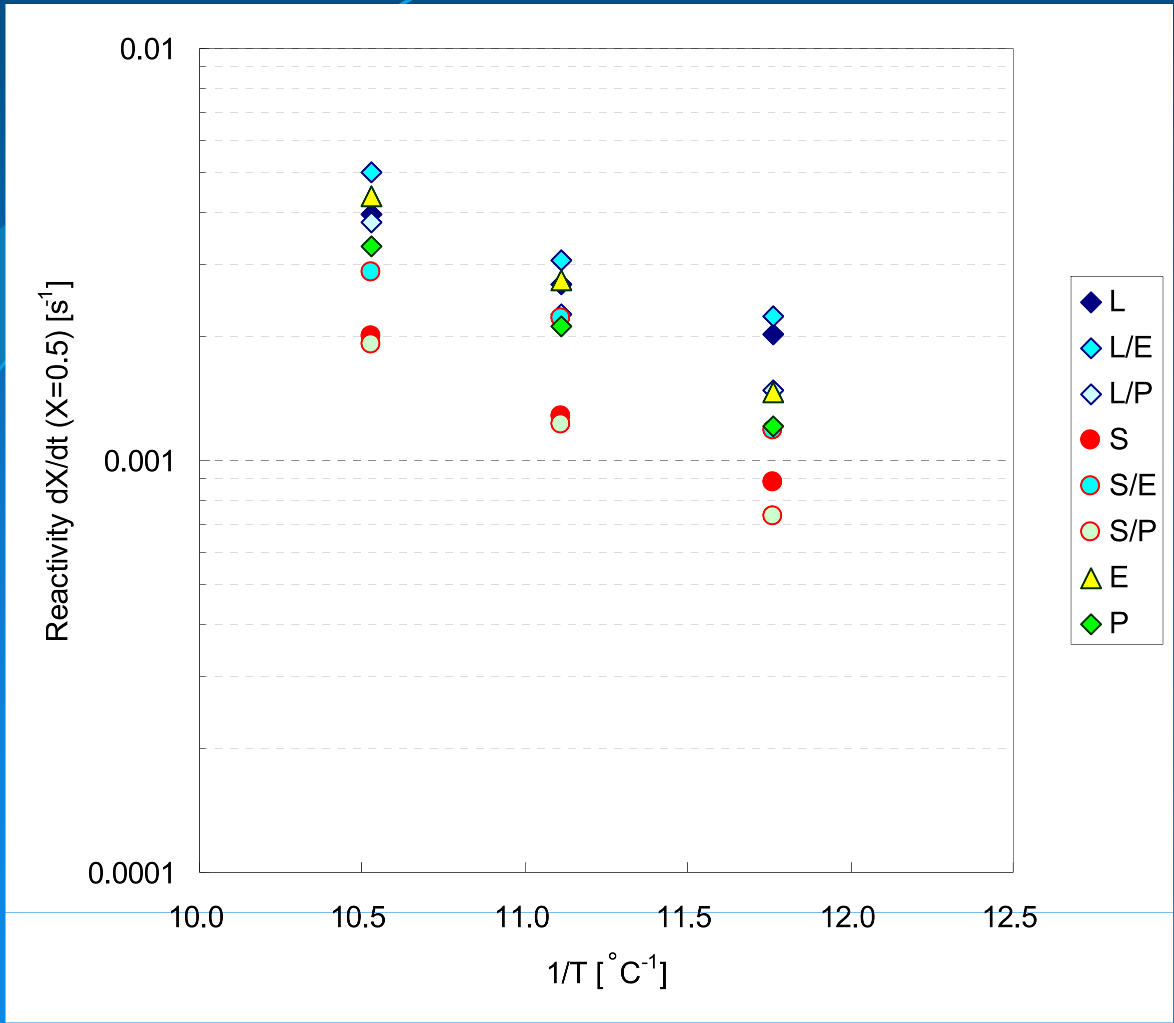
Effect of Gasification Temperature on Reactivity



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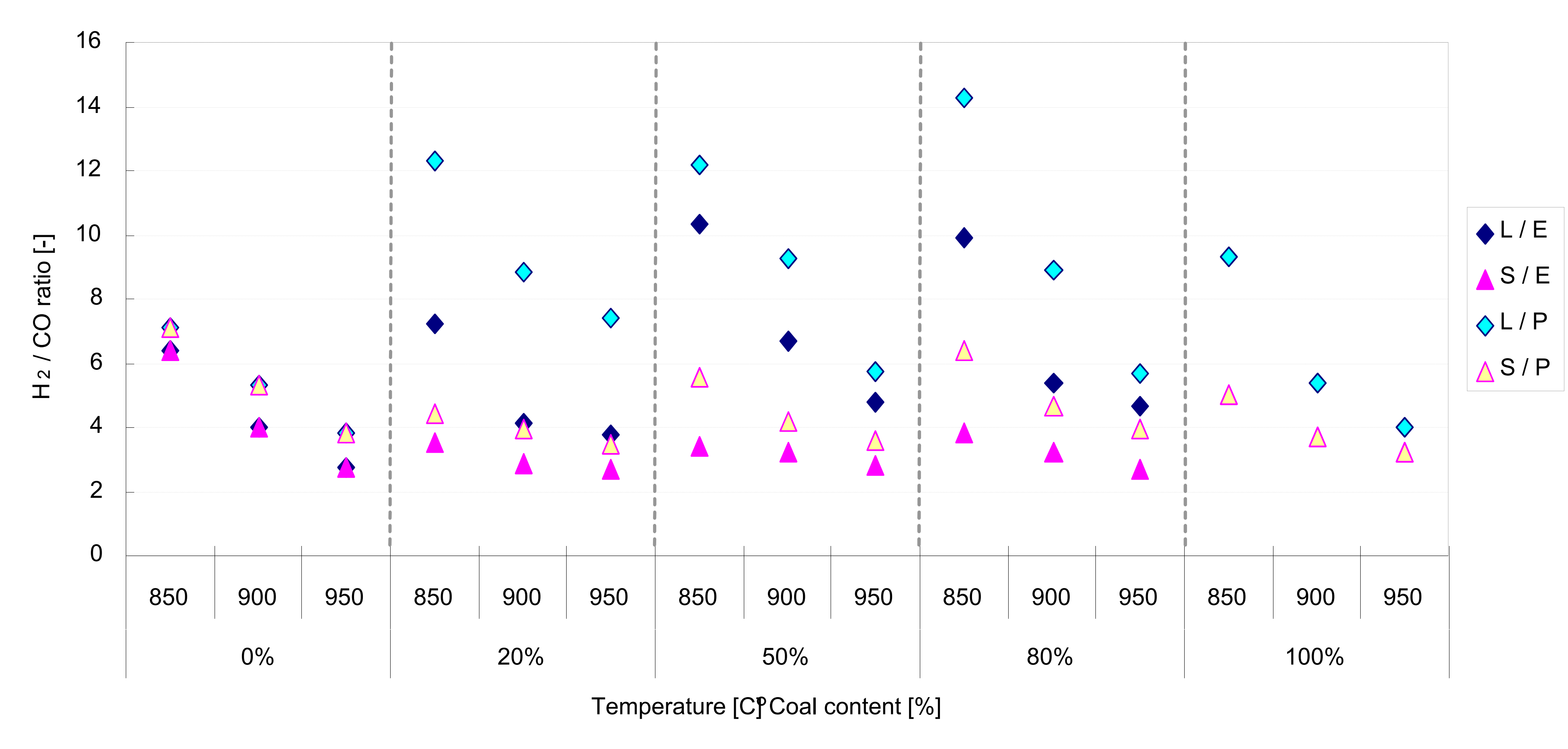
Effect of Gasification Temperature on H_2/CO Ratio



Calcium Effect

Lignite char reactivity is strongly dependent on presence of ionically bound calcium

	T_{50} (min)	
NZ Lignite	22.8	
German Brown Coal	33.5	
Australian Brown Coal	33.4	

	T_{50}(min)		H_2/CO
Lignite	22.8		17
Acid Washed	99.5		2.8
Calcium Reloaded	22.5		17

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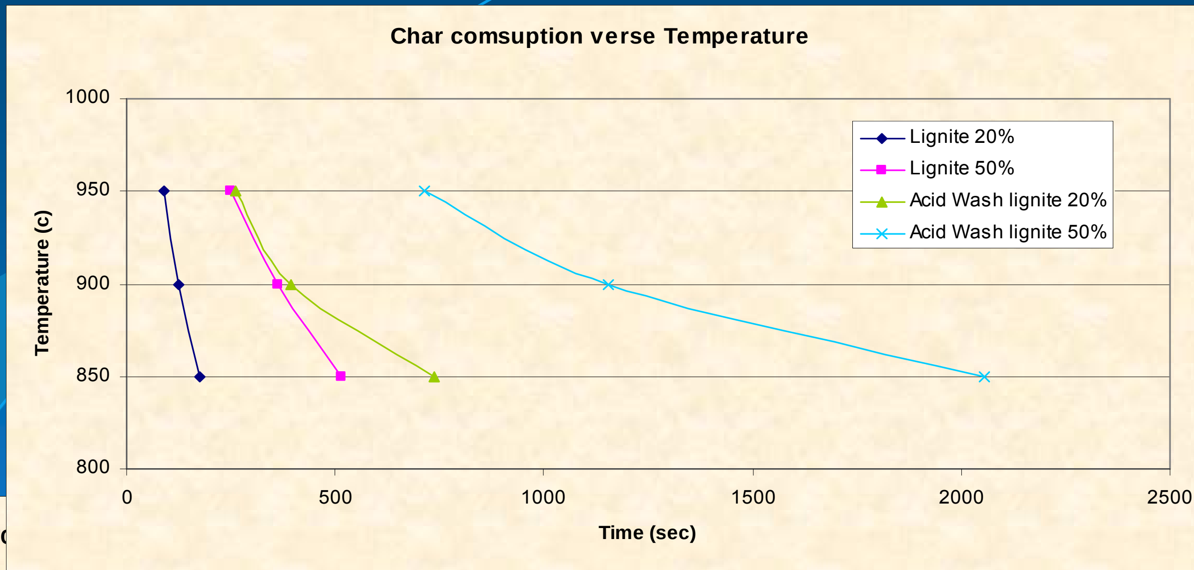
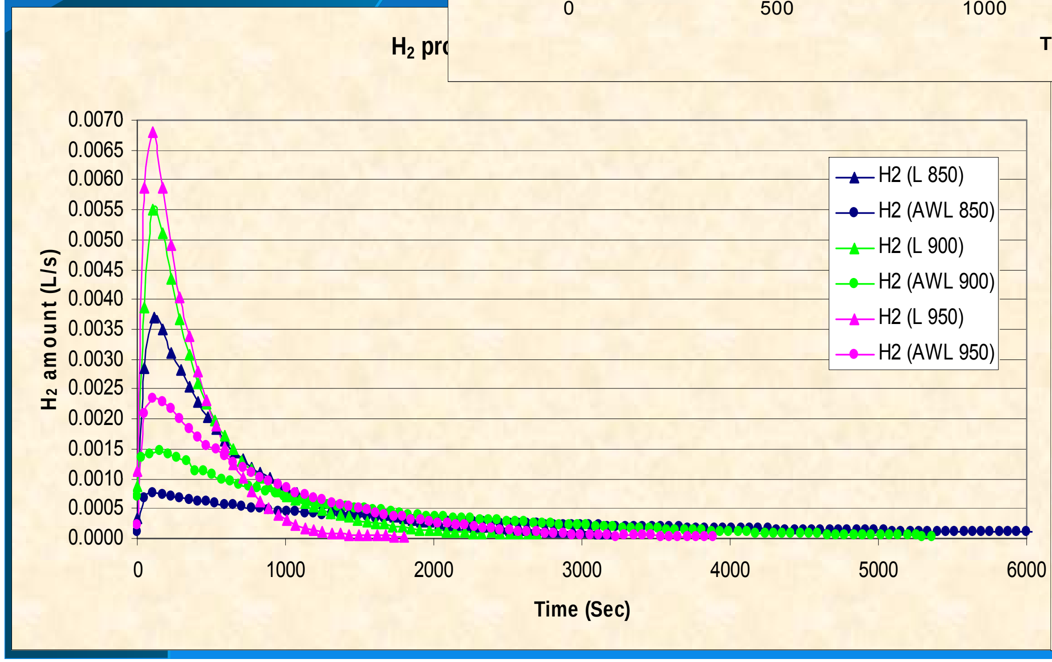
Effect of Calcium on Lignite Reactivity and Syngas Composition

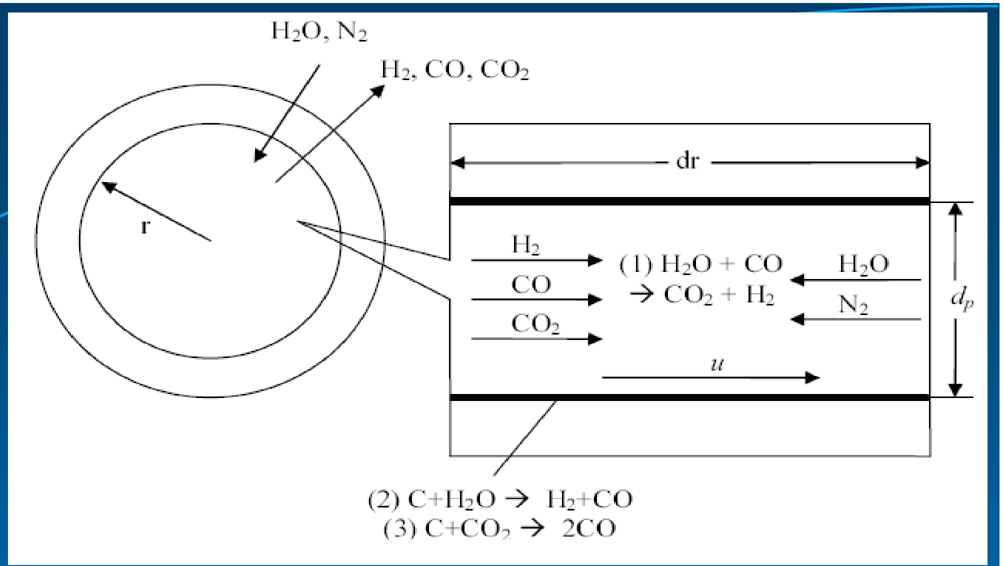


H_2

CO



Modelling Char Reactivity



Model based on:

- Gasification reaction kinetics
- Transportation of gas molecules in char matrix
- Mass balance equations in solid char

Model considers:

- Gasification agent (steam) diffusion into particle through pores
- Chemical reactions among gases (steam, product gases)
- Chemical reactions between gases and char matrix
- Product gas transfer through char

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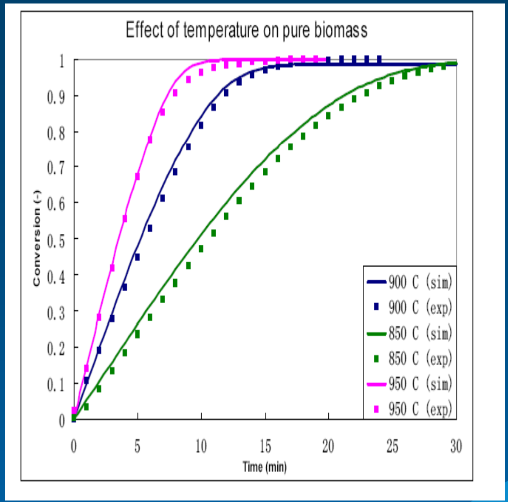
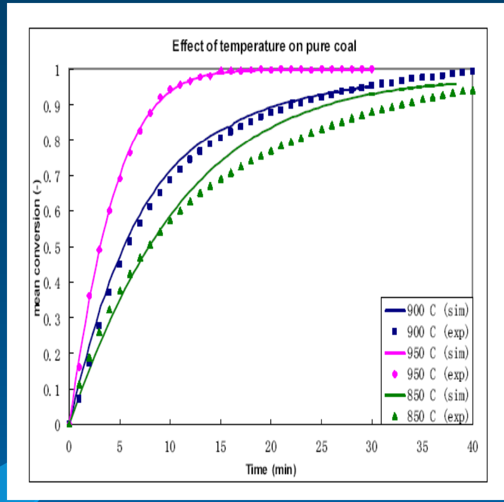
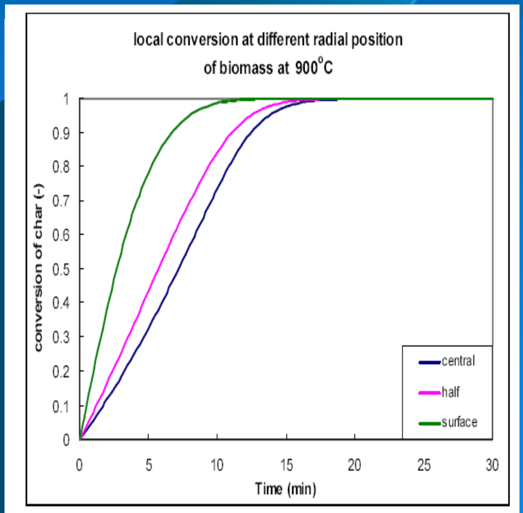
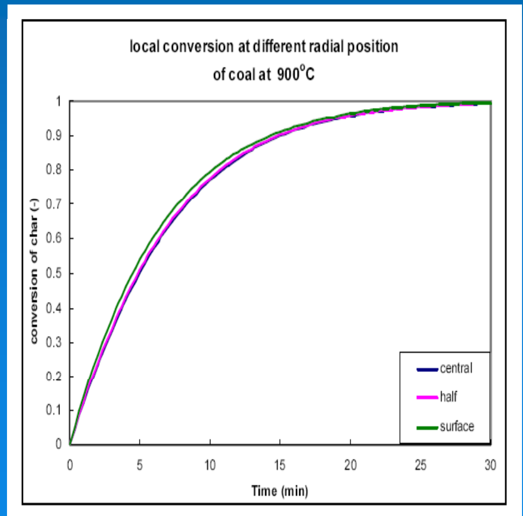




Predicted v Actual Char Conversion





Differences Between Coal & Biomass Char Conversion

- *E. nitens* char reactivity lies between lignite and sub-bituminous coal
- Overall reaction rate ↓ with ↑ in coal:biomass ratio
- Structural properties affect reaction rate
- Internal surface area of lignite char larger (more porous) than *E. nitens*

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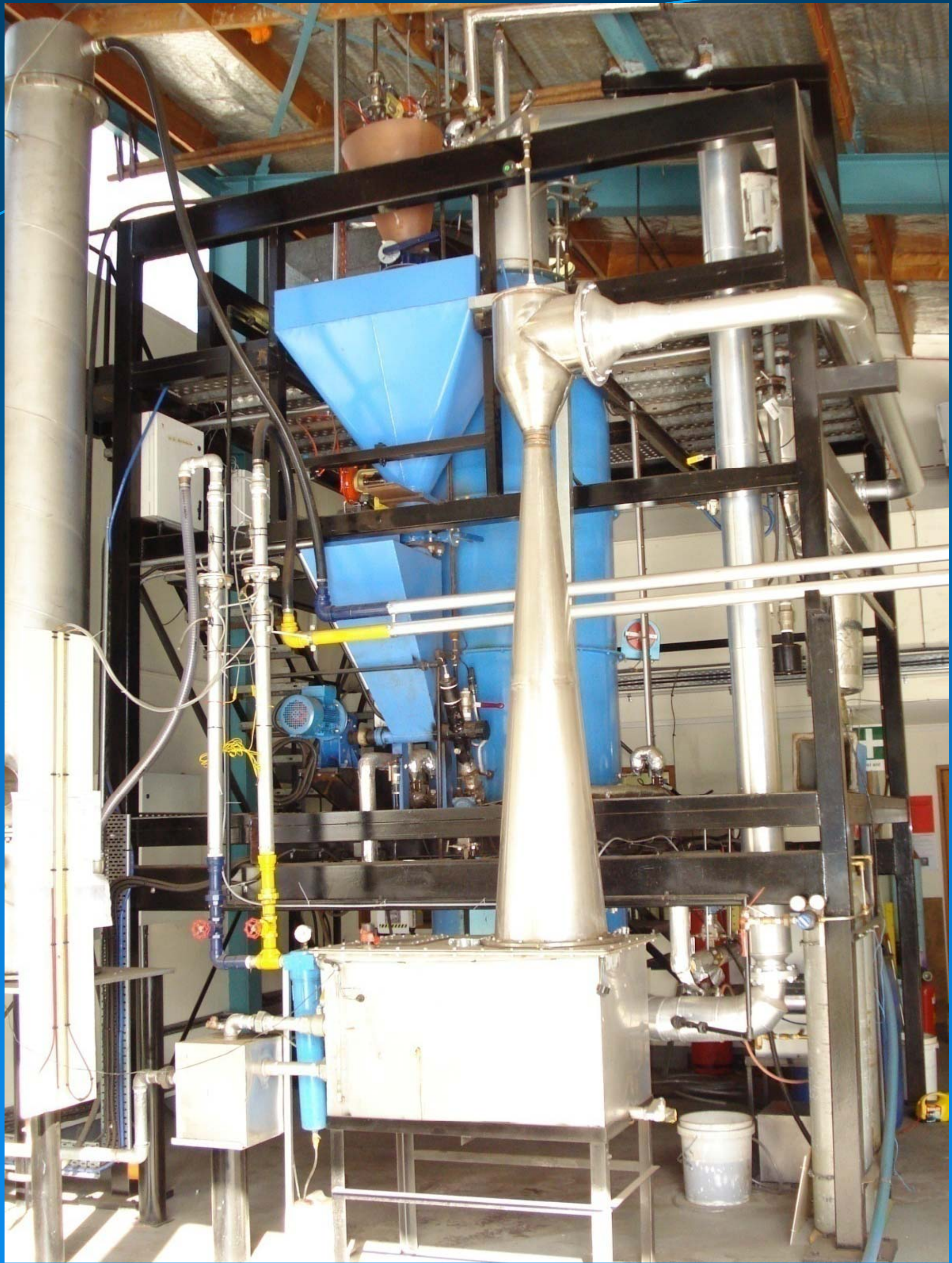
The CRL
Energy Gasifier



Gasifier Detail

Bed: depth of 300 mm

Air flow in: 60 m^3/h

Gas flow gasifier exit: 130m^3/h

Coal size: 3 – 10 mm

Coal feed: 18 kg/h

Steam feed: 5 kg/h

Temperature: 950 – 980 ^oC

Control system: Delta V

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The Fluidised Bed Gasifier

Operation

- Time to steady gasification ~ 2 h
- Reliable optimal operation conditions
- Advanced control system
- Regular quality syngas

  15% H_2, 15% CO_2, 12% CO, <1% CH_4 plus N_2.
- 2000 h + operation
- Continuous (1 week) operation

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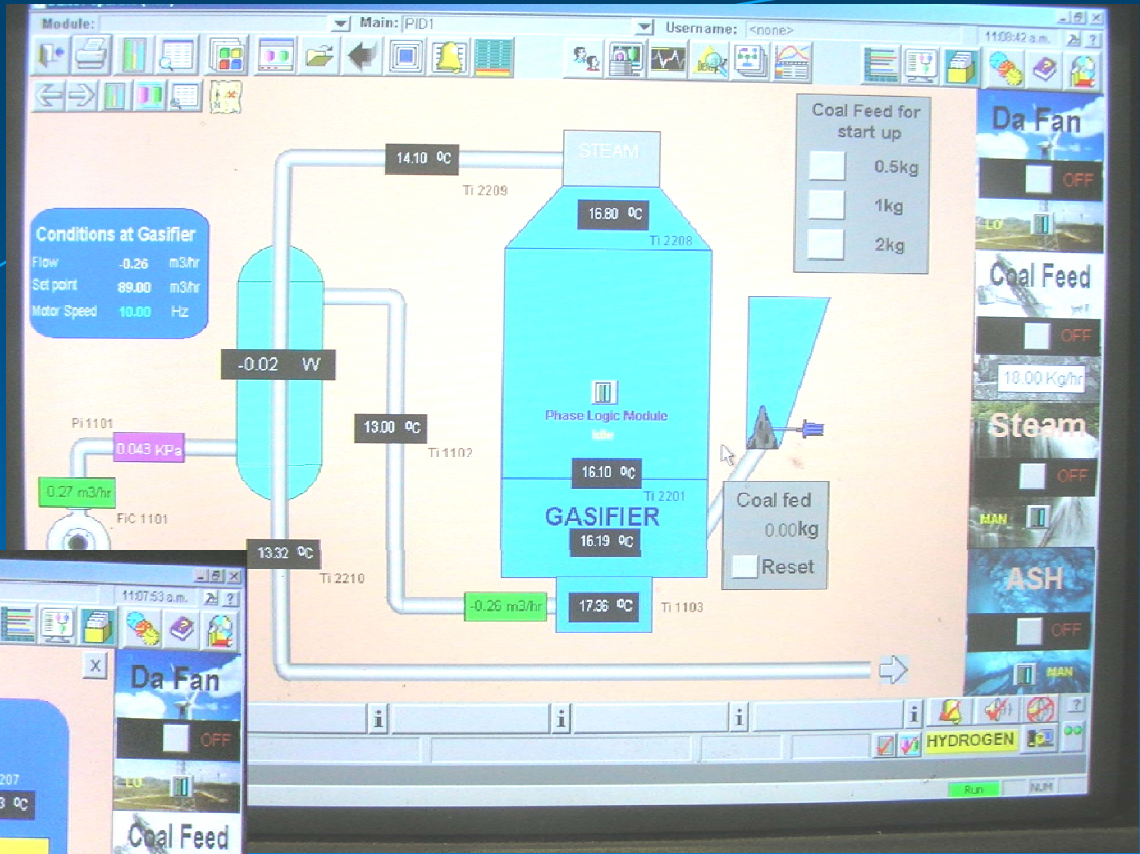
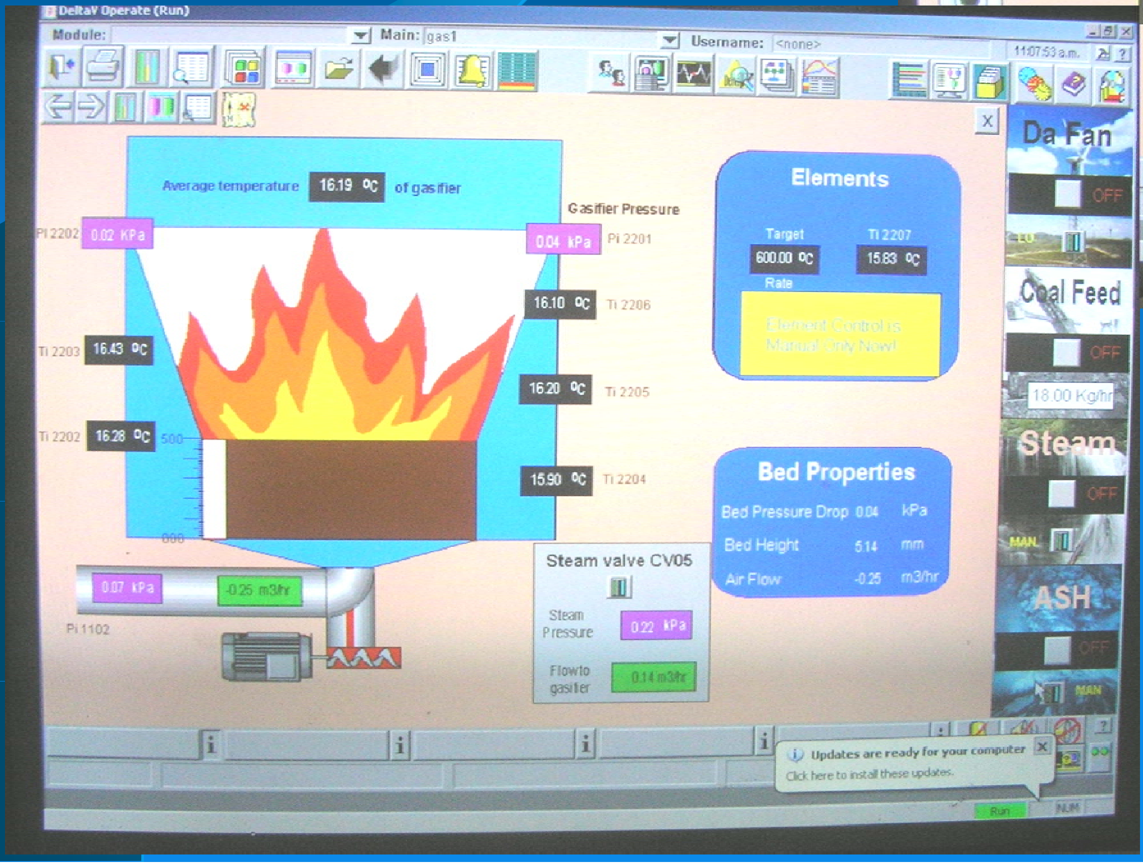
Delta V





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Particulate Removal

2 stage particulate removal system

– High efficiency cyclone (95%)

– Venturi scrubber (5%)

Low yields of tars and condensables recovered

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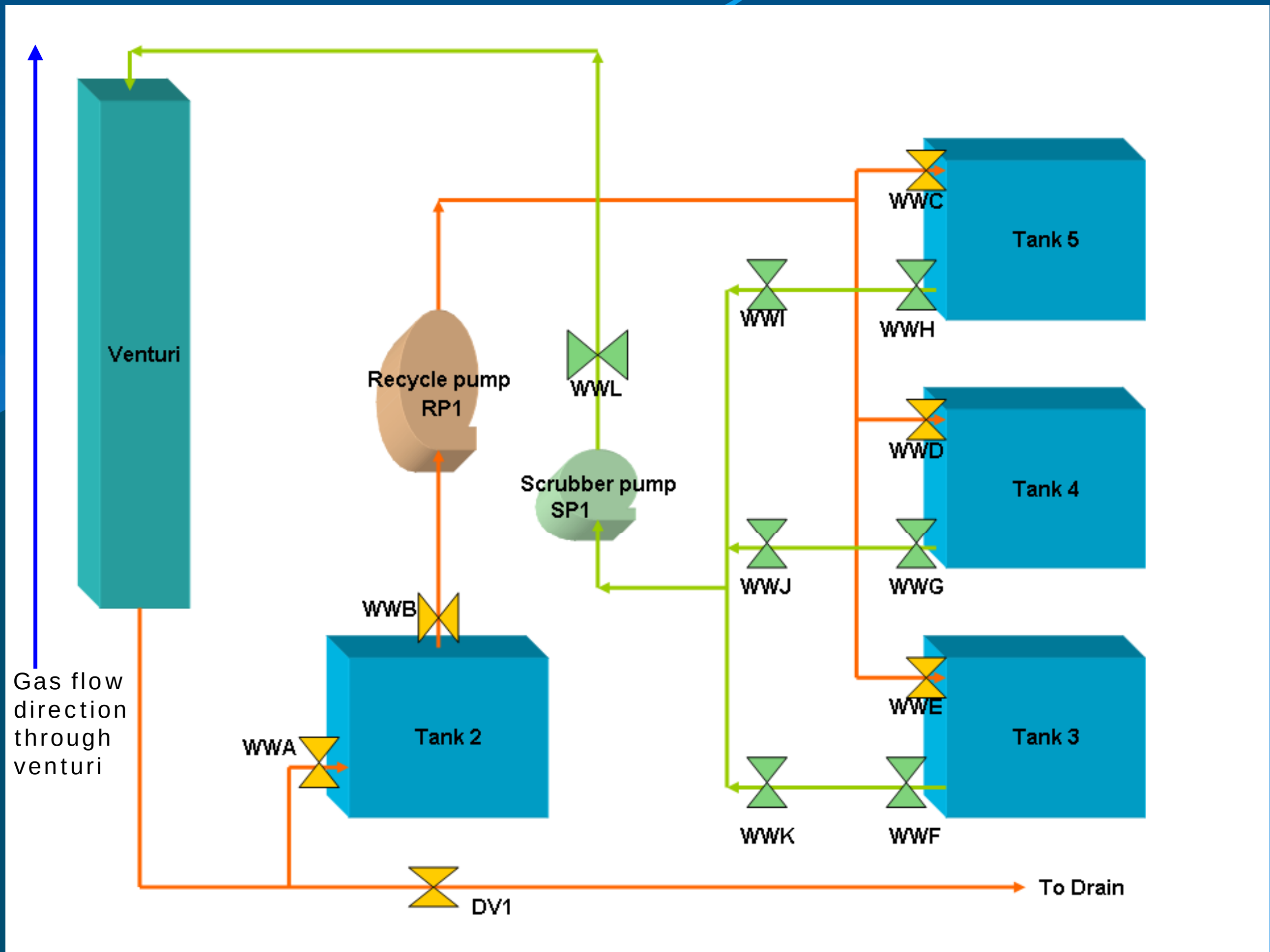
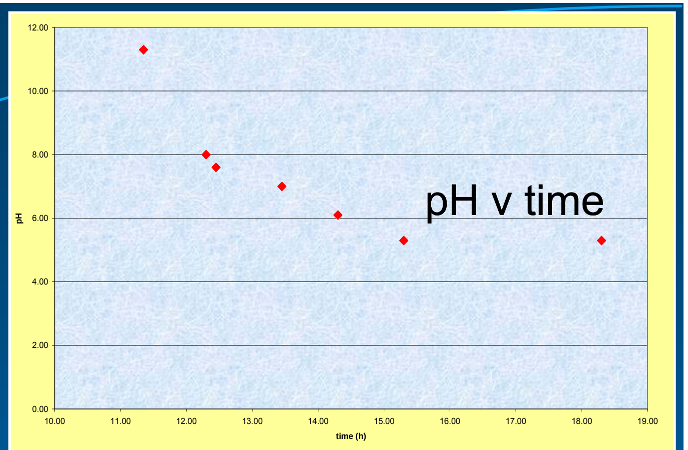
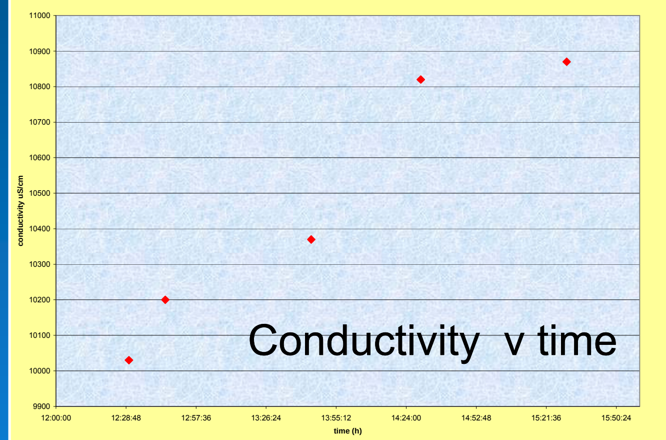
Syngas Clean-up Line
Sulfur Gases

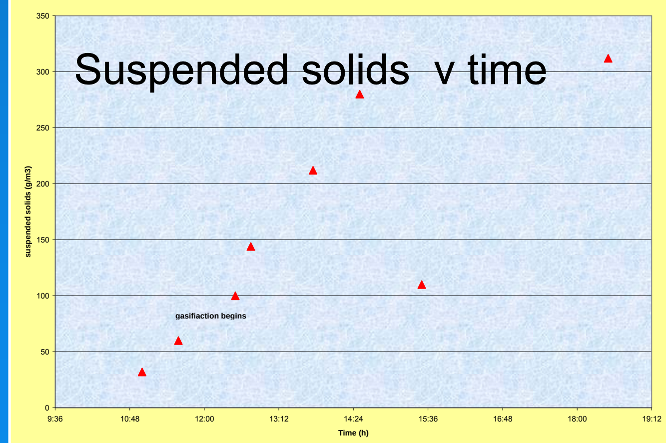
- Amine scrubber (MDEA) x
- Proprietary scavenger x
- Packed column, counter flow caustic wash √

Syngas Clean-up Line



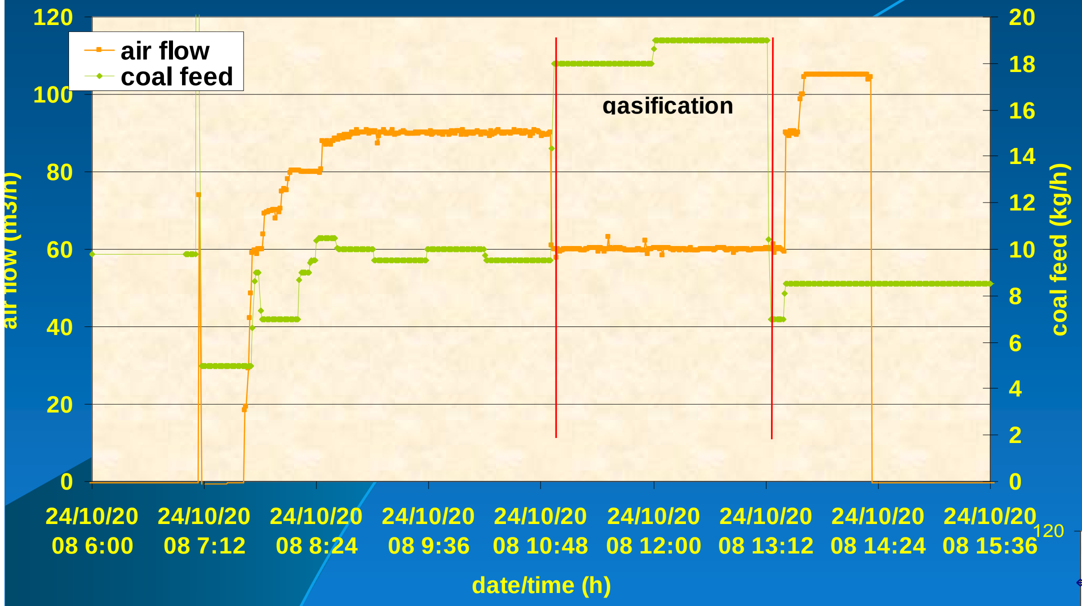






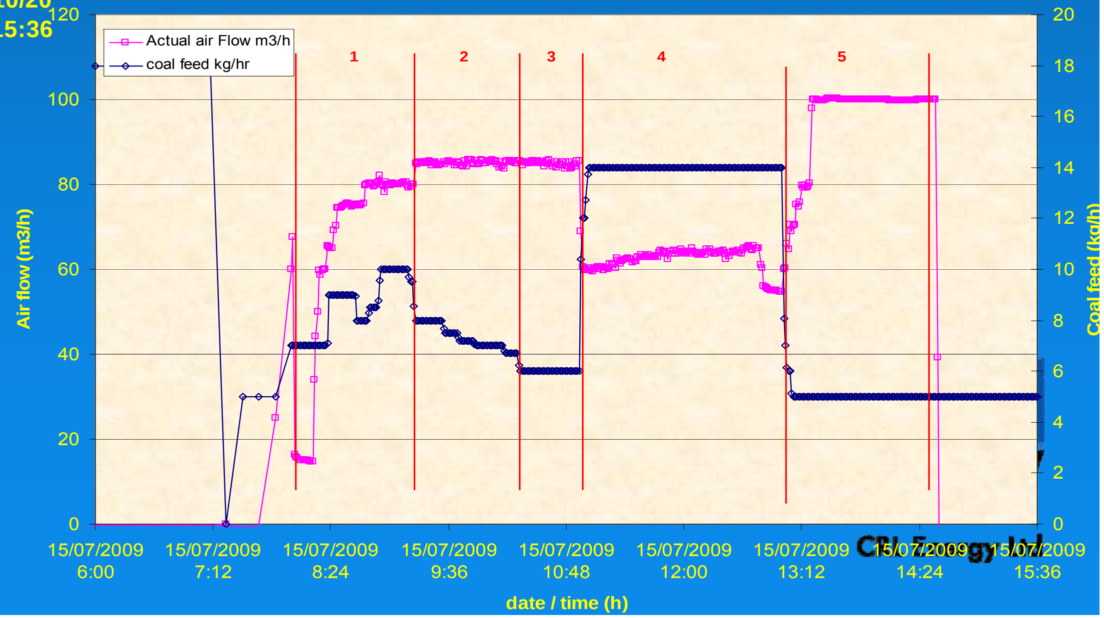
Corrosion

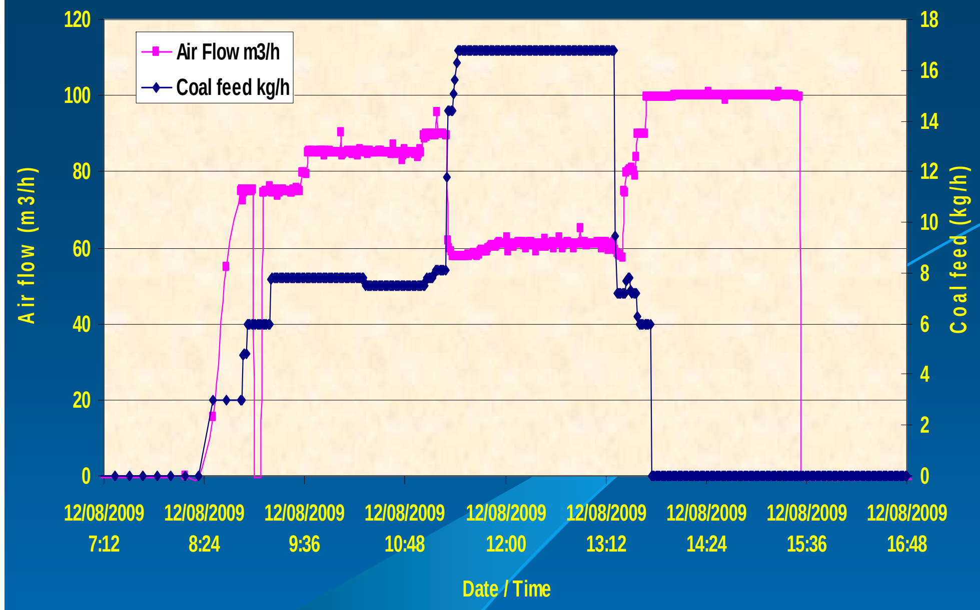
Effect of Biomass Addition on Gasifier Control



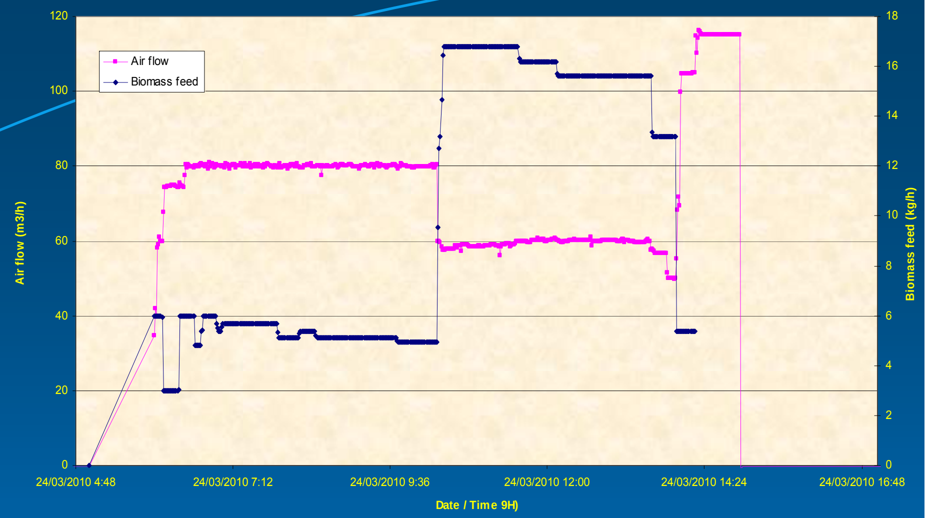
100% lignite

100% sub-bituminous



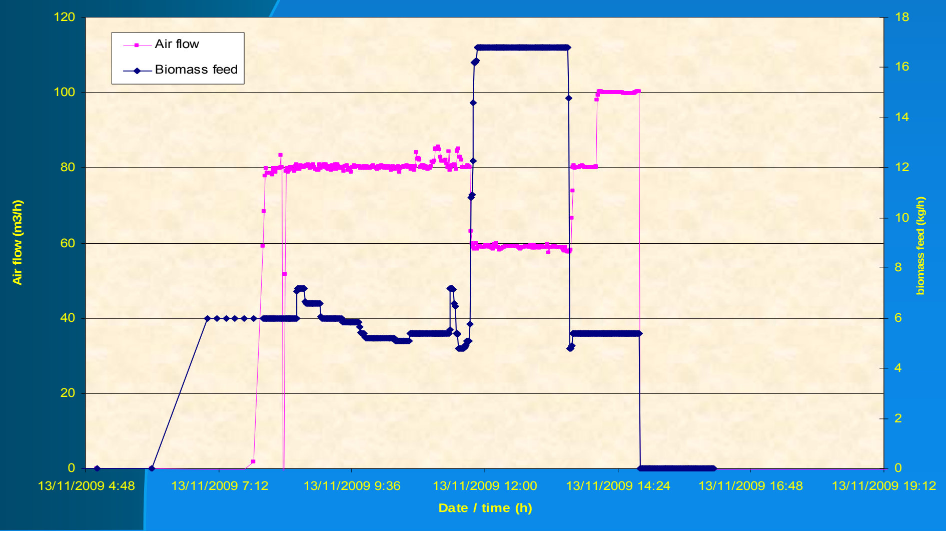


20% *P. radiata* – 80% lignite

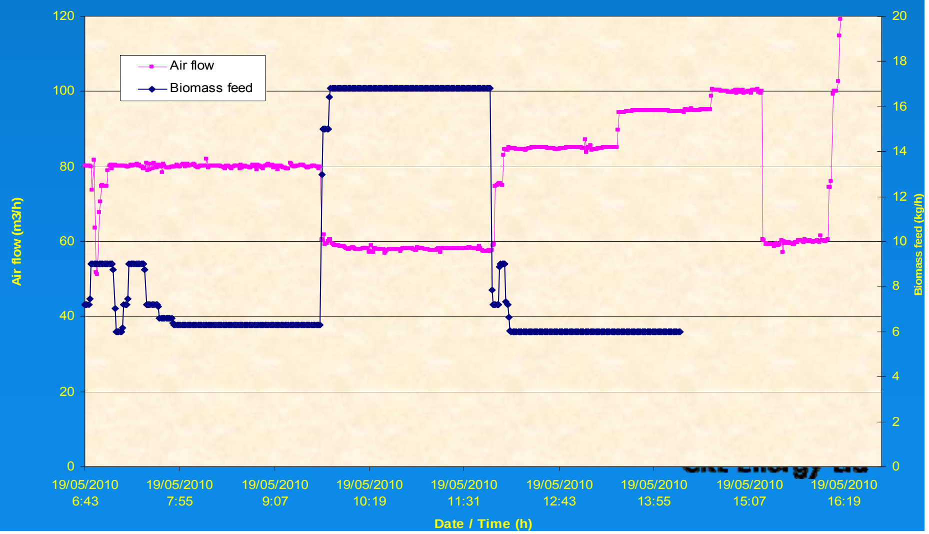


20% *P. radiata* – 80% sub-bituminous

20% *E. nitens* – 80% lignite



20% *E. nitens* – 80% sub-bituminous



Effect of Biomass Addition on Syngas Composition

Fuel	% Gas			
	H_2	CO	CO_2	CH_4
100% lignite	15	12	15	<1
80% lignite – 20% *P. radiata*	9	11	15	1.5
80% lignite – 20% *E. nitens*	8	10	14	1.5
100% sub-bituminous coal	11	15	12	1
80% sub-bituminous coal – 20% *P. radiata*	14	16	13	2
80% sub-bituminous coal – 20% *E. nitens*	11	13	14	1.5

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- Coal/Biomass + O_2 = CO_2 + heat
- Coal/Biomass + heat = C (char) + volatiles

- **$C + H_2O = CO + H_2$**

- $CO_2 + C = 2CO$ (boudouard)
- $CO + 3H_2 = CH_4 + H_2O$ (methanation)
- $CO + H_2O = CO_2 + H_2$ (WGS)
- $CH_4 + H_2O = CO + 3H_2$ (steam reforming)

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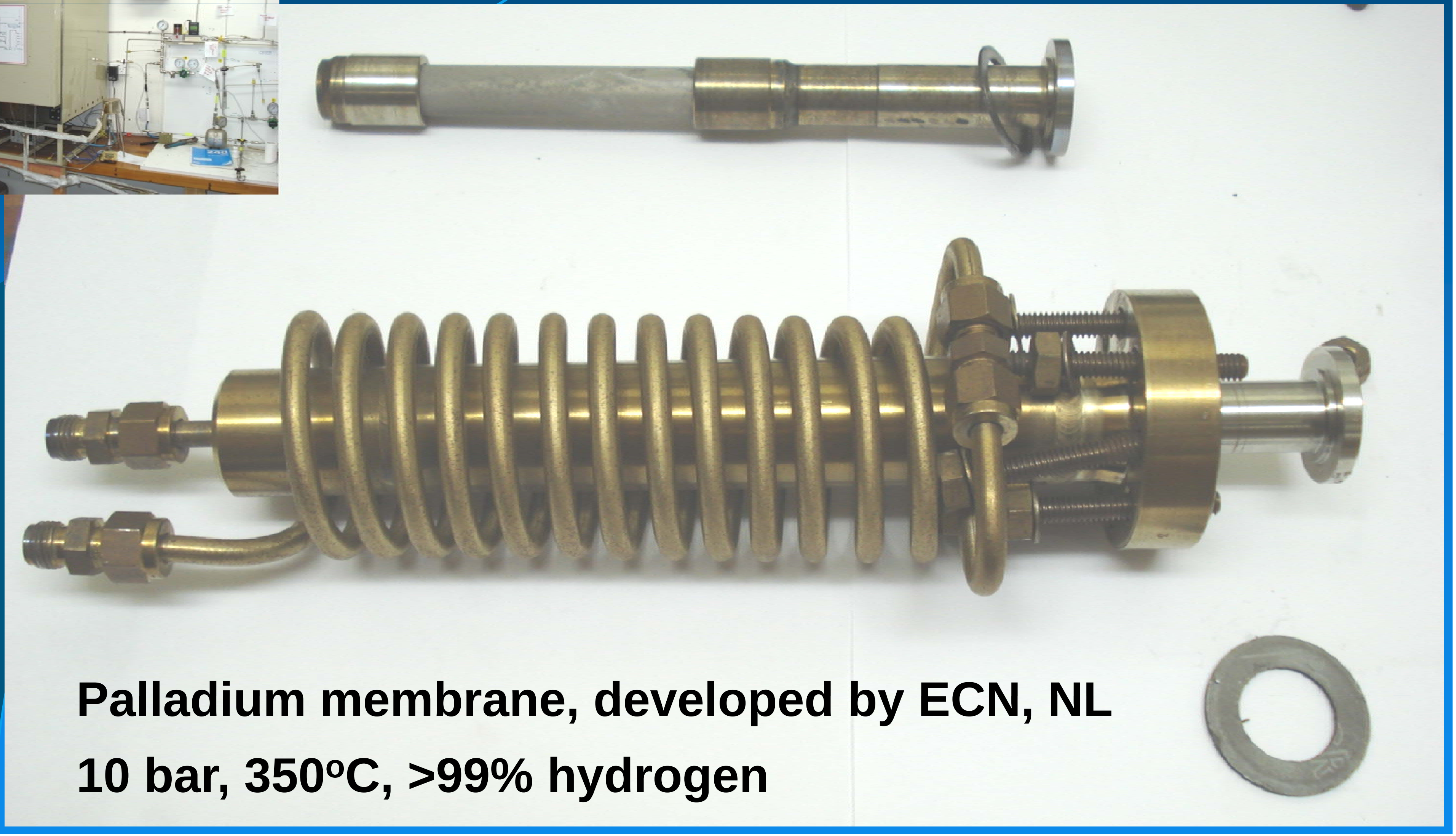
Syngas Clean-up Line
Water Gas Shift Reactor

- $CO + H_2O \leftrightarrow H_2 + CO_2$ ~40 kJ/kg-mol
- Single high temperature catalyst bed (340 to 360°C)
- Iron Oxide Catalyst
- Gas flow rate 5.0 - 2.4 m^3/h
- Regular quality syngas
  - 22% H_2, 20% CO_2, 5% CO, <1% CH_4

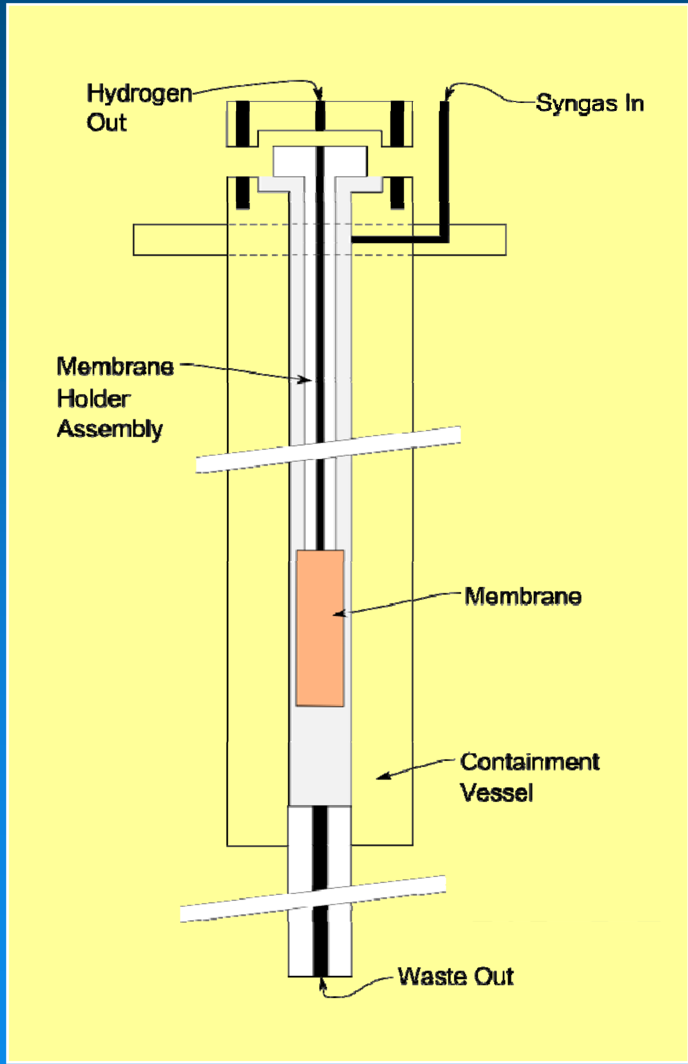
Syngas Clean-up Line
Hydrogen Purification



Palladium membrane, developed by ECN, NL

10 bar, 350°C, >99% hydrogen

Syngas Clean-up Line
High Pressure High Temperature Gas Separation Unit



Fuel Cell

- Alkaline fuel cell (2.5 kW) assembled
- Developed by IRL, NZ
- 2 bar H_2 buffer storage system feed
- Overall electrical conversion efficiencies 50% HHV

- Fuel (H_2) is fed into the anode
- Oxidant (O_2 air) is fed into cathode
- React in presence of KOH
- H_2 -> 2H+ + 2e-
- 2H+ + 2e- + O_2 -> H_2O

O_2 Blown Fluidized Bed Gasifier with Integrated Electrolyser

Develop new technology of oxygen blown co-fired gasifier with integrated electrolyser for production of low carbon footprint syngas, synfuels and H_2 from New Zealand's coal and biomass resources

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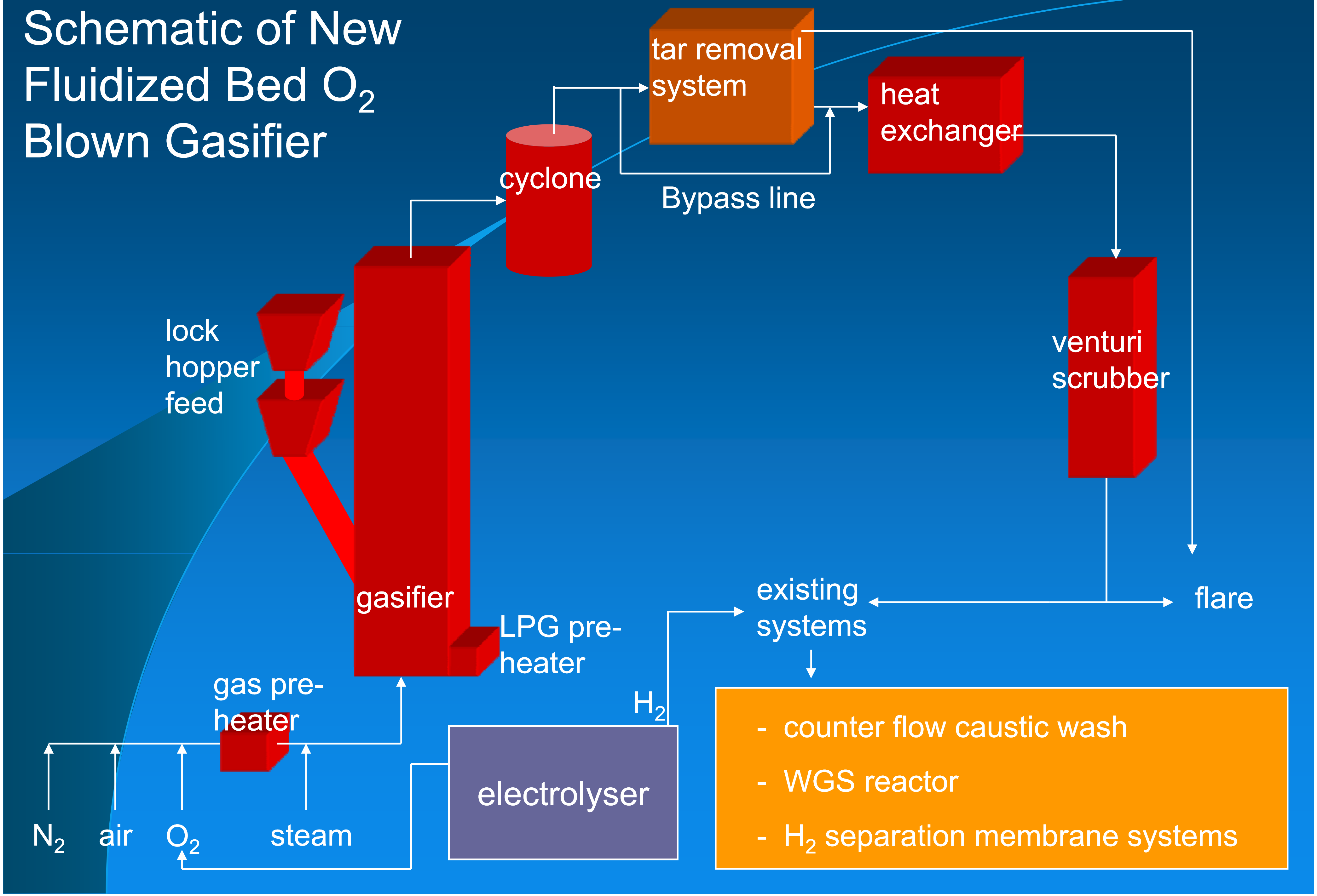
Schematic of New Fluidized Bed O_2 Blown Gasifier



Specifications

50kw unit

Fluidized bed

O_2 or air blown

Biomass capability (up to 45%)

Modular design

Max working temperature 1000^{o}C

Ambient pressure system

Regular quality syngas (> 20% H_2)

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WHY?

- ASU 15-20% electrical output
- Roaring 40s
- Use of green H_2 and O_2 with biomass and coal interesting
- Green input - reduce process emissions
- If CCS high - minimise CO to CO_2 shift and produce as much H_2 for optimum FT

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Benefits and Barriers

- Electrolysis provides a relatively simple means of producing high purity O_2 and H_2 in a ratio of 1:2

- The technology is expensive
- The cost of feedstock (electricity) is high
- The production efficiency is presently of the order of only 60% HHV.

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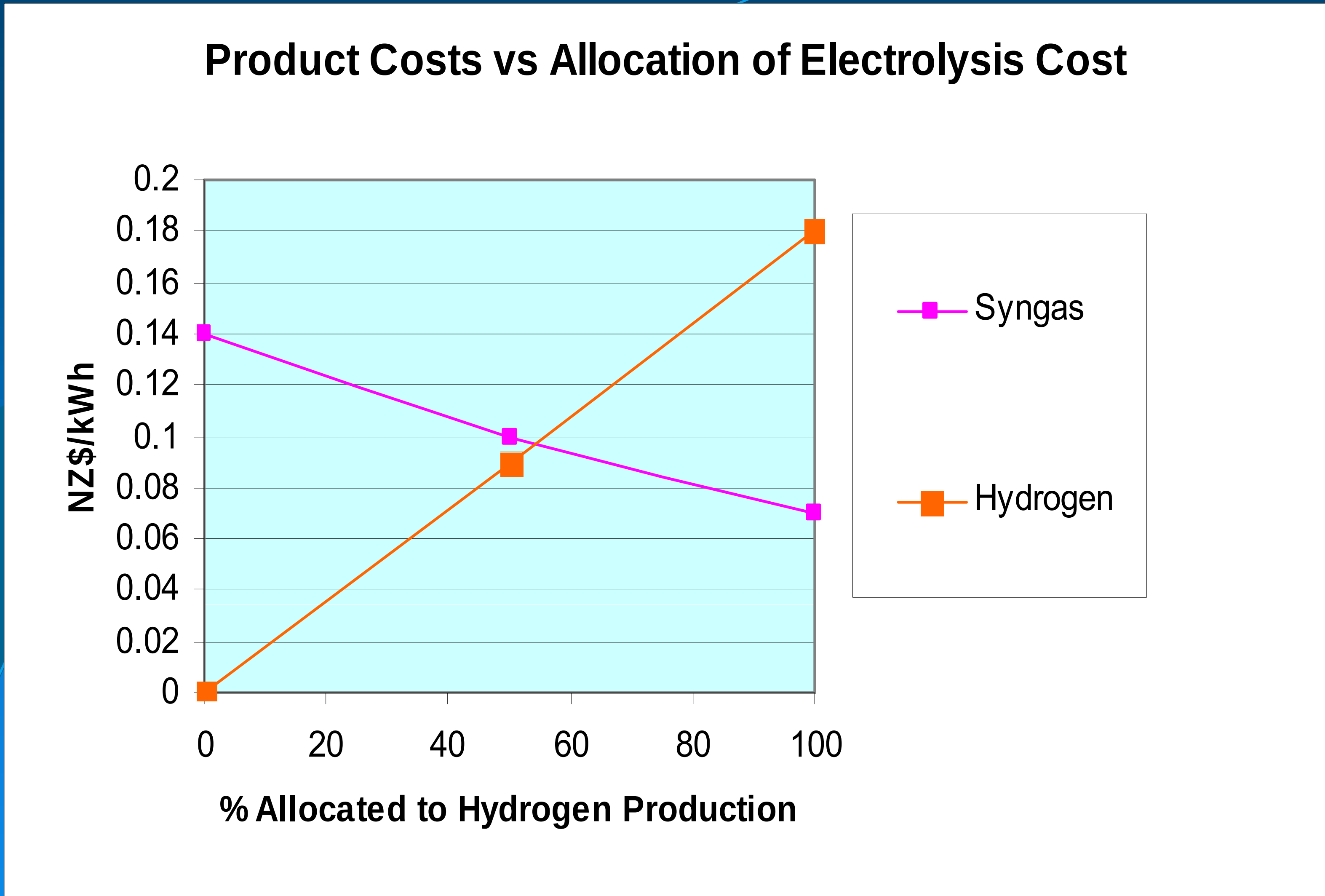

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Benefits and Barriers

- Recent advances in materials technology can potentially reduce these barriers
- Changing environment of electricity supply + improvements could alter economics in high value O_2 and H_2 applications

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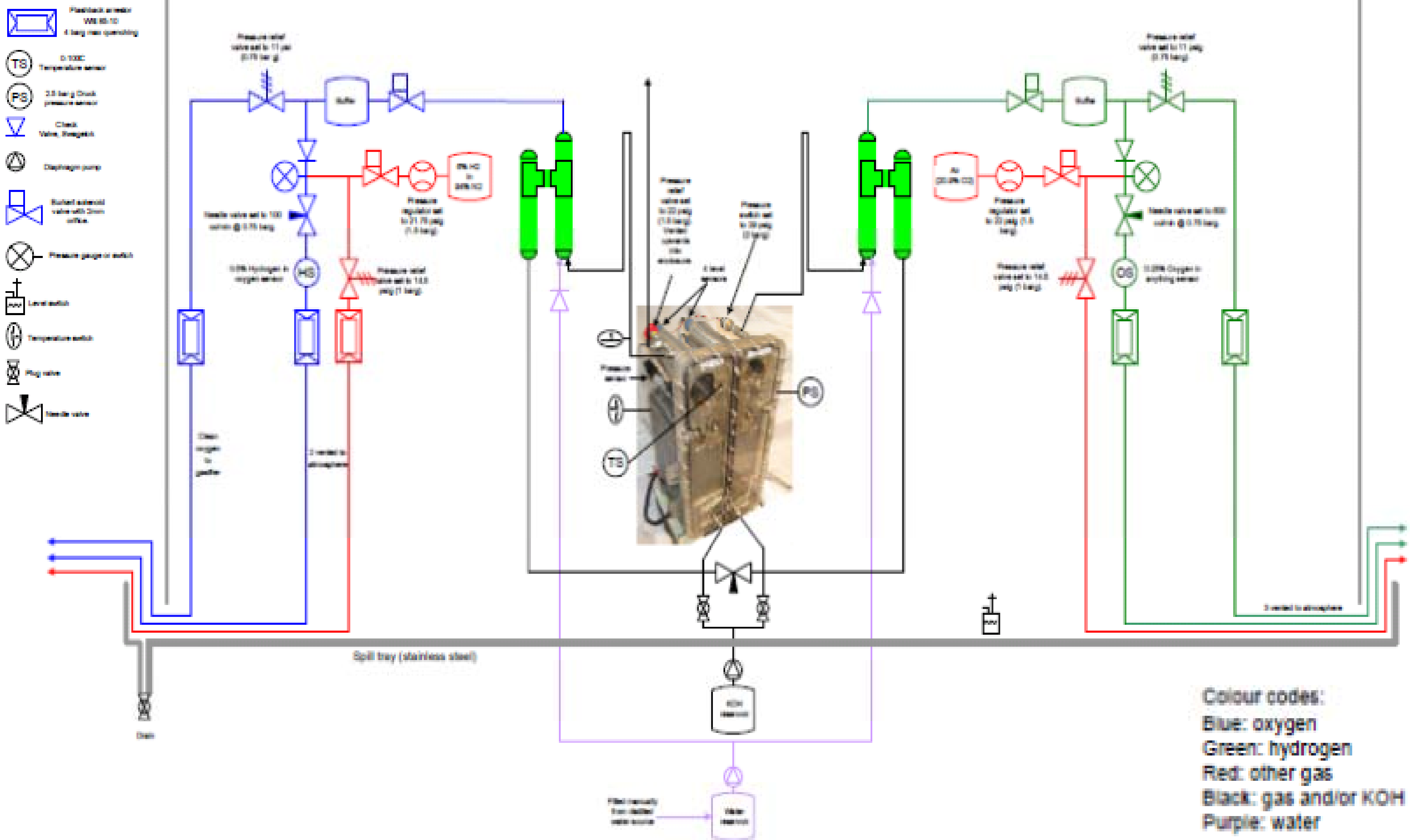
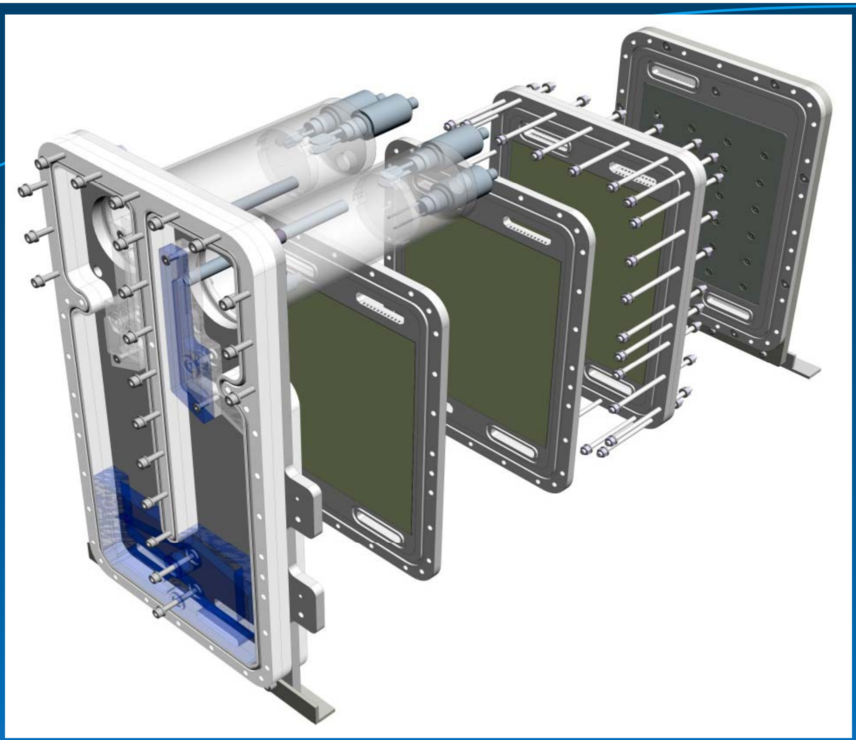
Integrated Electrolyser



Integrated Electrolyser



- Operates at nominal 50Vdc
- Fully self contained
- Wide operating range
- Fast turn-up and turn-down
- O_2 and H_2 at required quality
- Produces 0.4 Nm^3/hr O_2 (0.8Nm^3 H_2)
- Very low peripheral power demand
- Efficiency of 70% HHV without any special electrode surface preparation
- Target module level efficiency of > 80%HHV

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2009 - To Date

- PhD student
- Masters Student

- 2 Journal papers
- 4 Conference papers and presentations
- 3 Workshops

- Developed several international collaborations

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Future Work

- Prove concept - complete gasifier-electrolyser integration
- Complete test run schedule with 100% O_2 and 45% biomass
- Develop new test programme

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Acknowledgements

- Ministry for Science and Innovation, New Zealand
- Industrial Research Limited, New Zealand
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- ECN, The Netherlands
- Argonne National Laboratory, USA
- Solid Energy, New Zealand
- Genesis Energy, New Zealand
- Carter Holt Harvey, New Zealand
- BP, New Zealand

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How Much Hydrogen will we Need?

- 1.2 – 1.75 million tonnes of hydrogen p.a. by 2050 (144 – 210 PJ) to meet predicted land transport demand

- Primary domestic energy sources
  - Coal
  - Natural Gas
  - Renewables

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Gasification – The Key Enabling Technology

- New Zealand lignites very well suited to new advanced efficient gasification process
- Generation of 1.2 to 1.7 million tonnes of hydrogen requires gasification of 10 to 15 million tonnes of lignite.

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