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

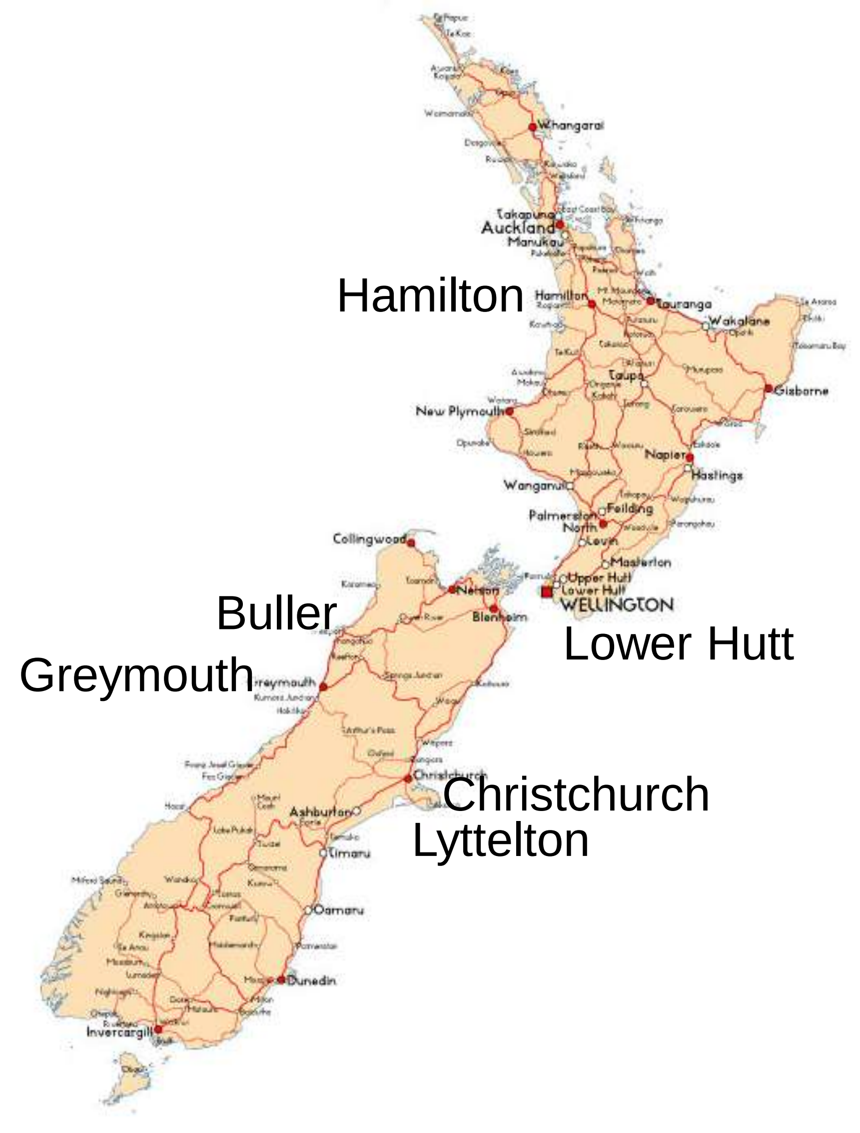
Tana Levi

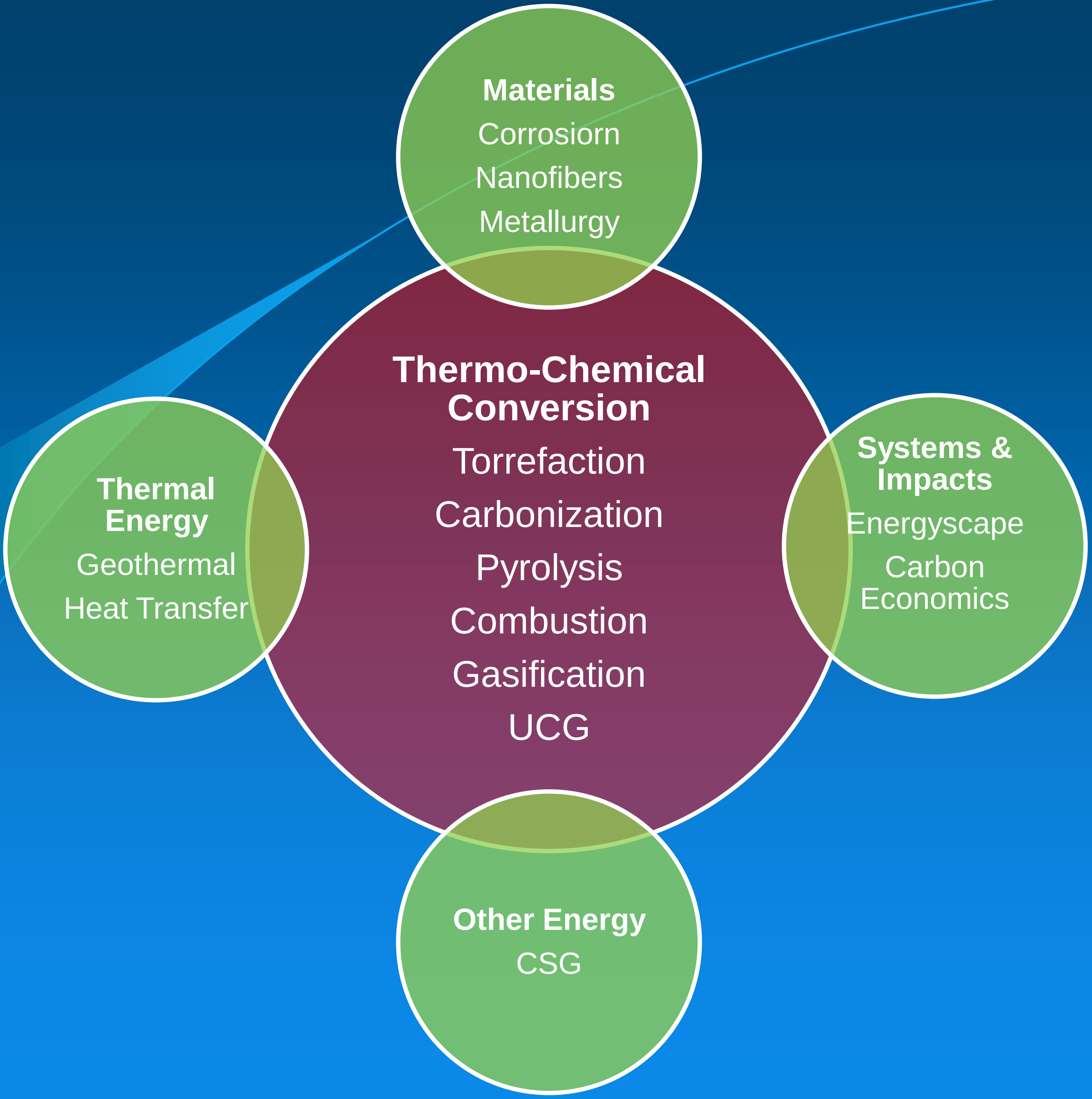
IEA Workshop - Bioenergy Task 33
14th April 2011

CRL Energy Ltd

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





Materials
Corrosiorn
Nanofibers
Metallurgy

Thermal Energy
Geothermal
Heat Transfer

Thermo-Chemical Conversion
Torrefaction
Carbonization
Pyrolysis
Combustion
Gasification
UCG

Systems & Impacts
Energyscape
Carbon Economics

Other Energy
CSG

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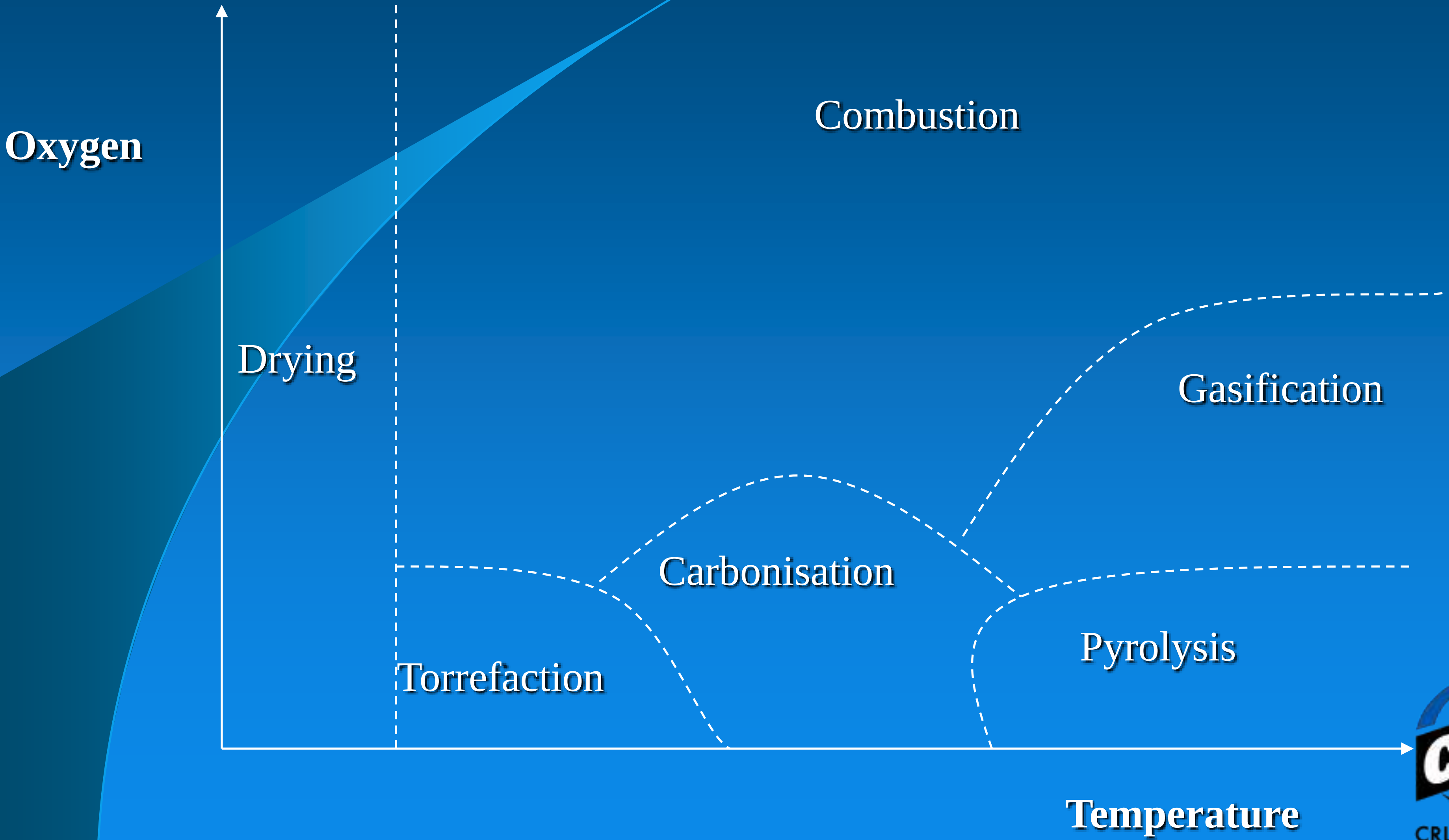
Thermo-chemical Conversion Methods



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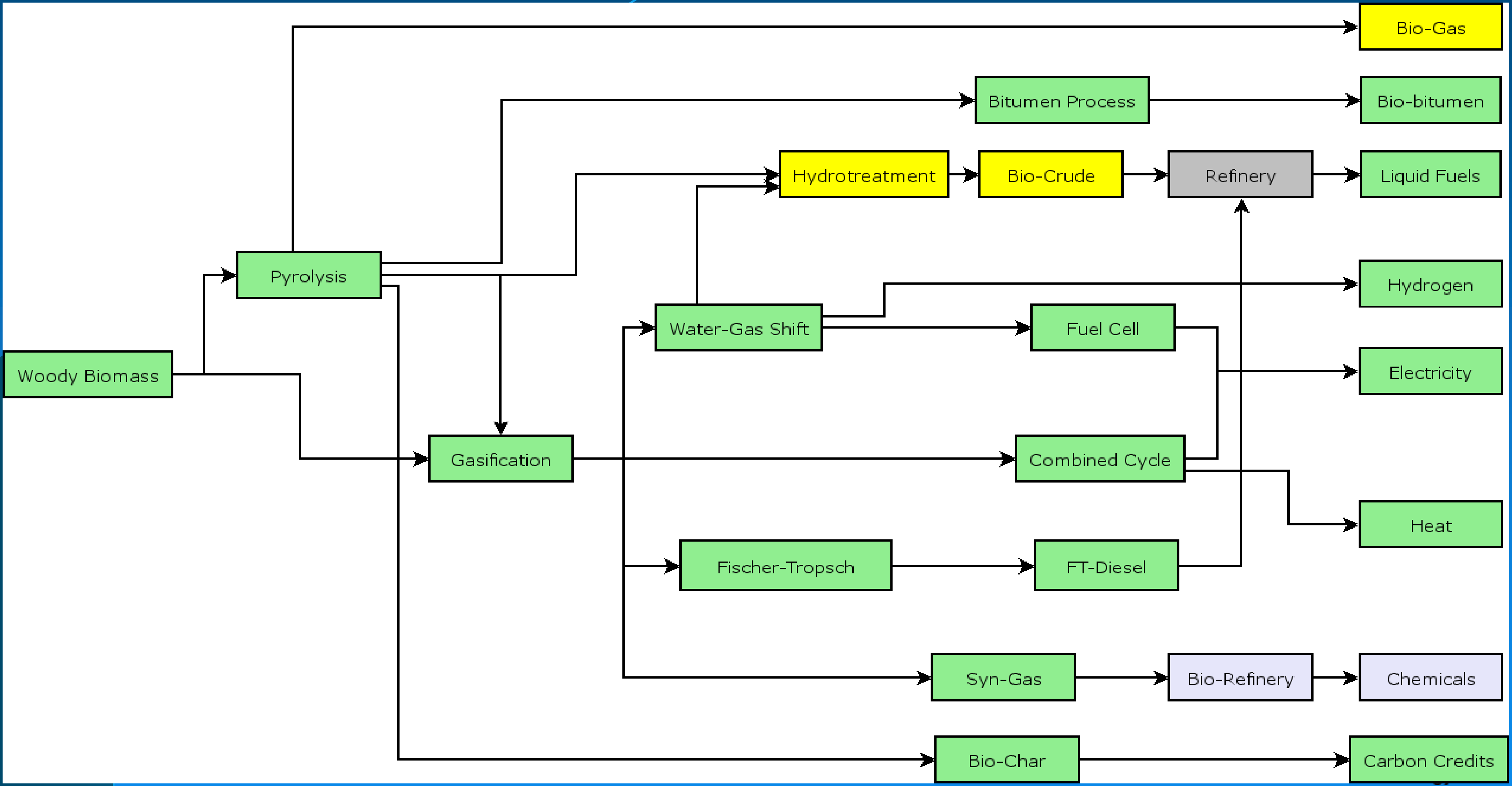
Thermo-chemical Conversion Pathways



Woody Biomass

Pyrolysis

Gasification

Water-Gas Shift

Fischer-Tropsch

Hydrotreatment

Bitumen Process

Bio-Crude

Refinery

Fuel Cell

Combined Cycle

FT-Diesel

Syn-Gas

Bio-Refinery

Bio-Char

Bio-Gas

Bio-bitumen

Liquid Fuels

Hydrogen

Electricity

Heat

Chemicals

Carbon Credits

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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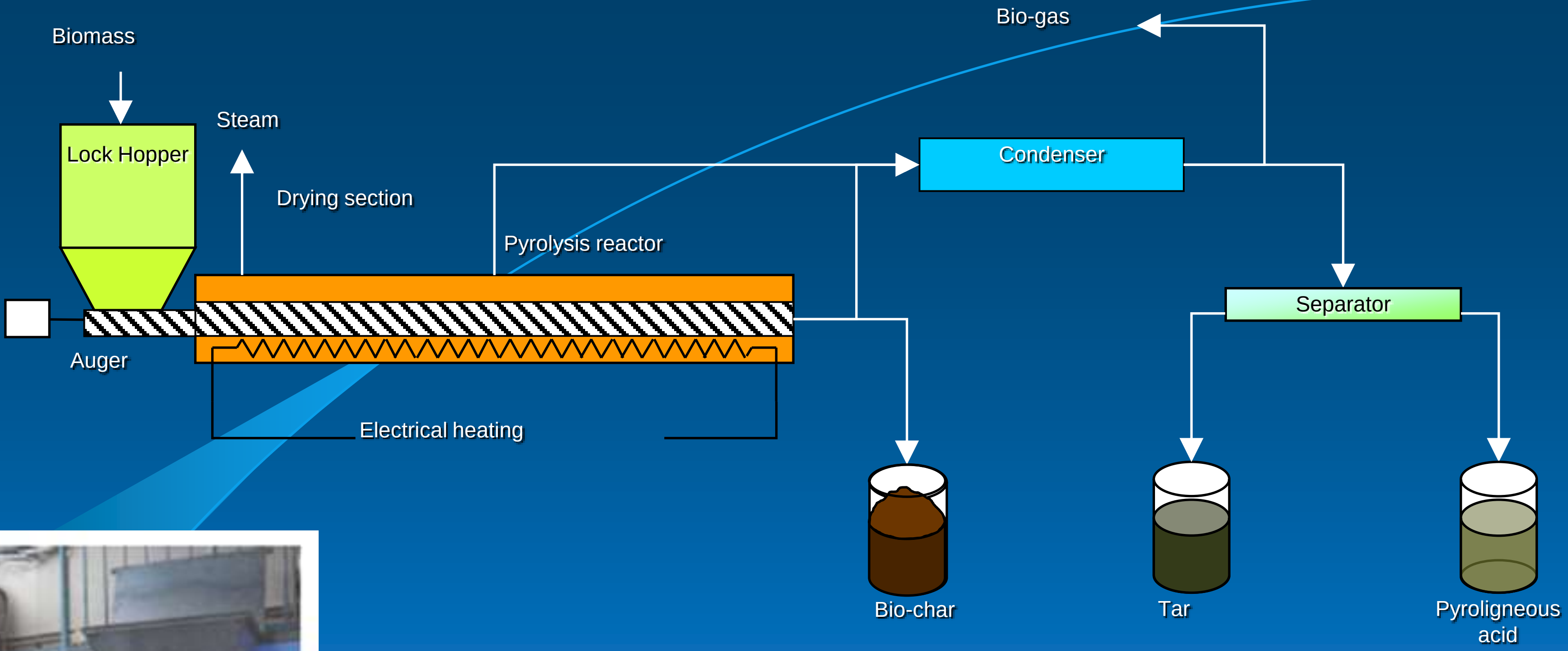
Carbonisation

- 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



- 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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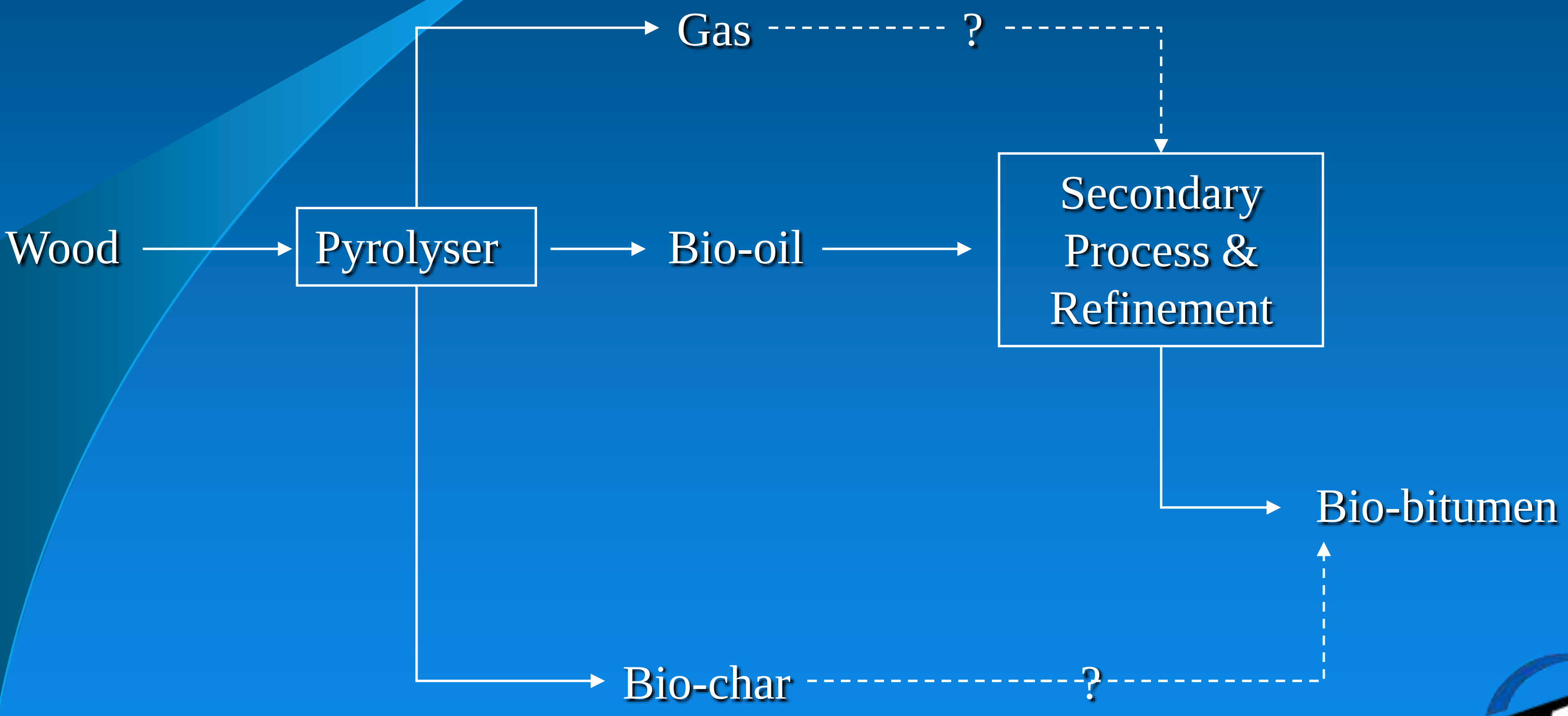
Bio-bitumen Pathway



Wood

Pyrolyser

Gas

?

Bio-oil

Secondary Process & Refinement

Bio-bitumen

Bio-char

?

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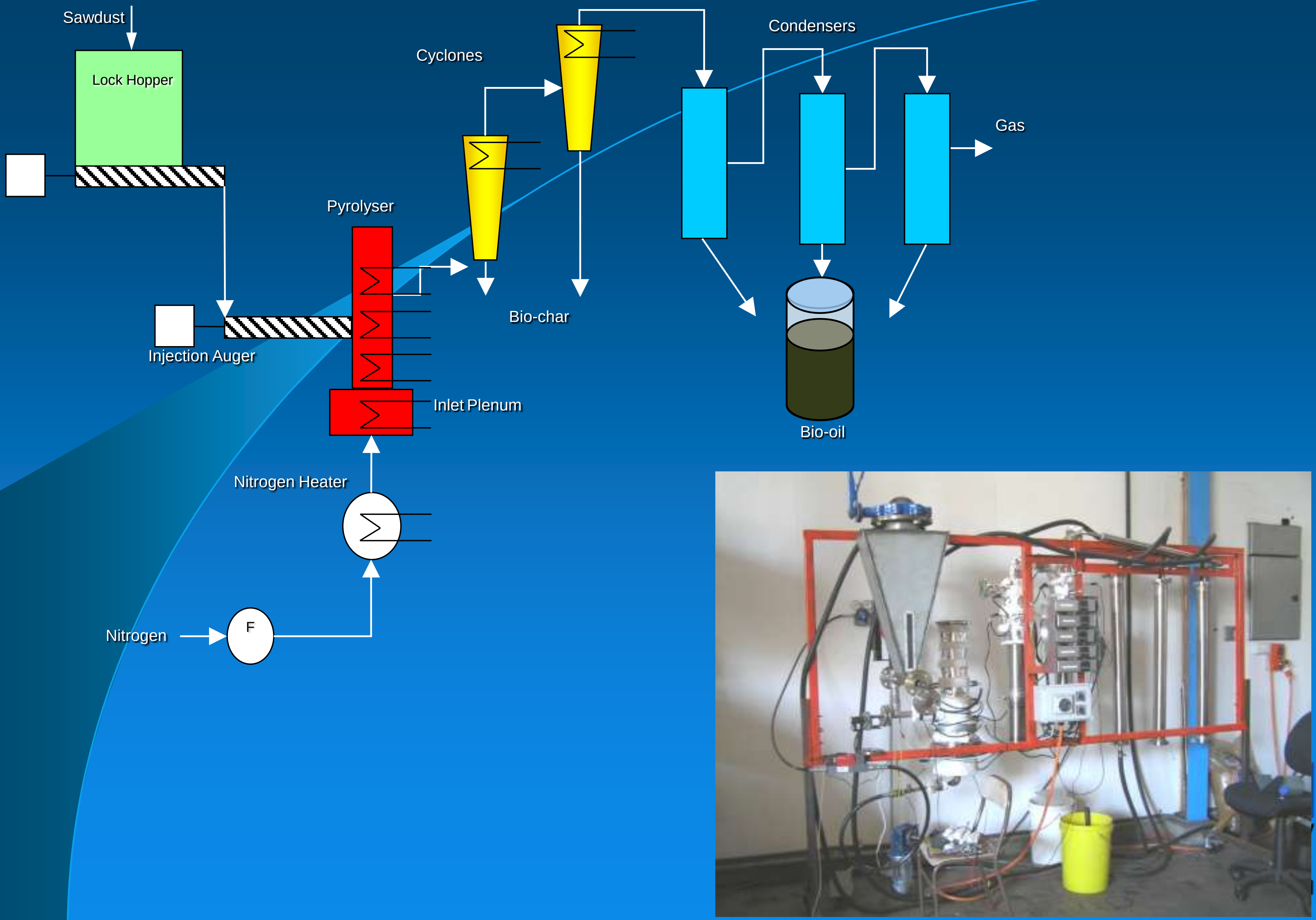

Sawdust

Lock Hopper

Injection Auger

Pyrolyser

Inlet Plenum

Nitrogen Heater

Nitrogen

F

Cyclones

Bio-char

Condensers

Gas

Bio-oil

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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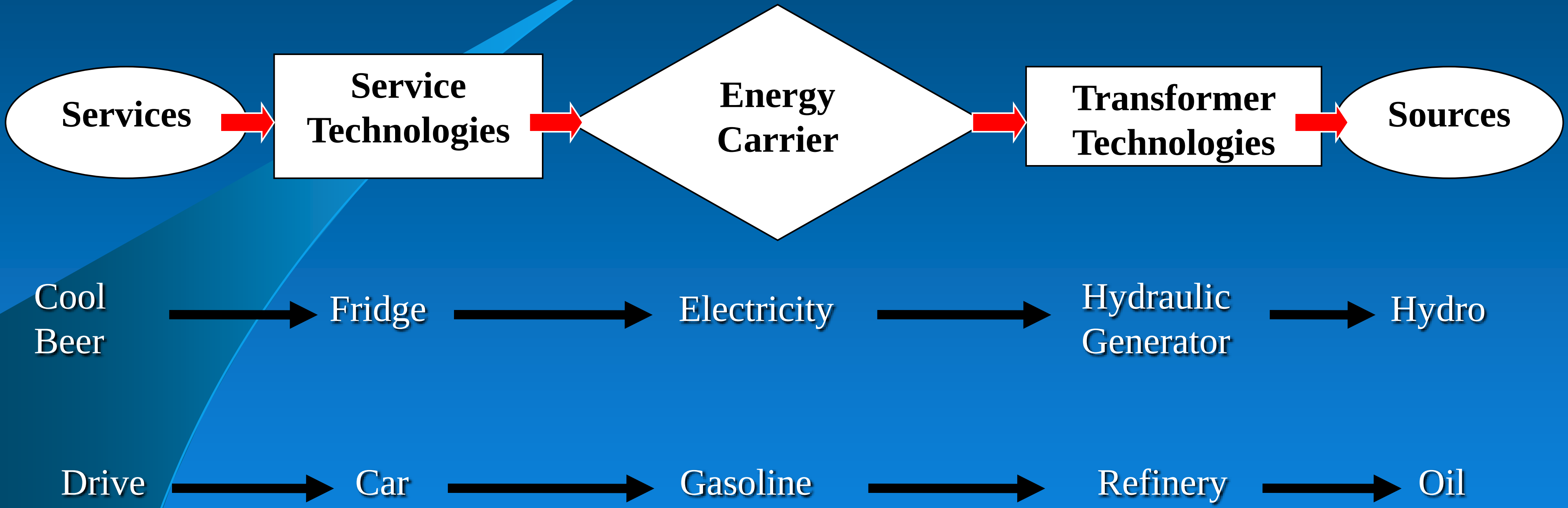
The Current Energy System



Services → Service Technologies → Energy Carrier → Transformer Technologies → Sources

Cool Beer → Fridge → Electricity → Hydraulic Generator → Hydro

Drive → Car → Gasoline → Refinery → Oil

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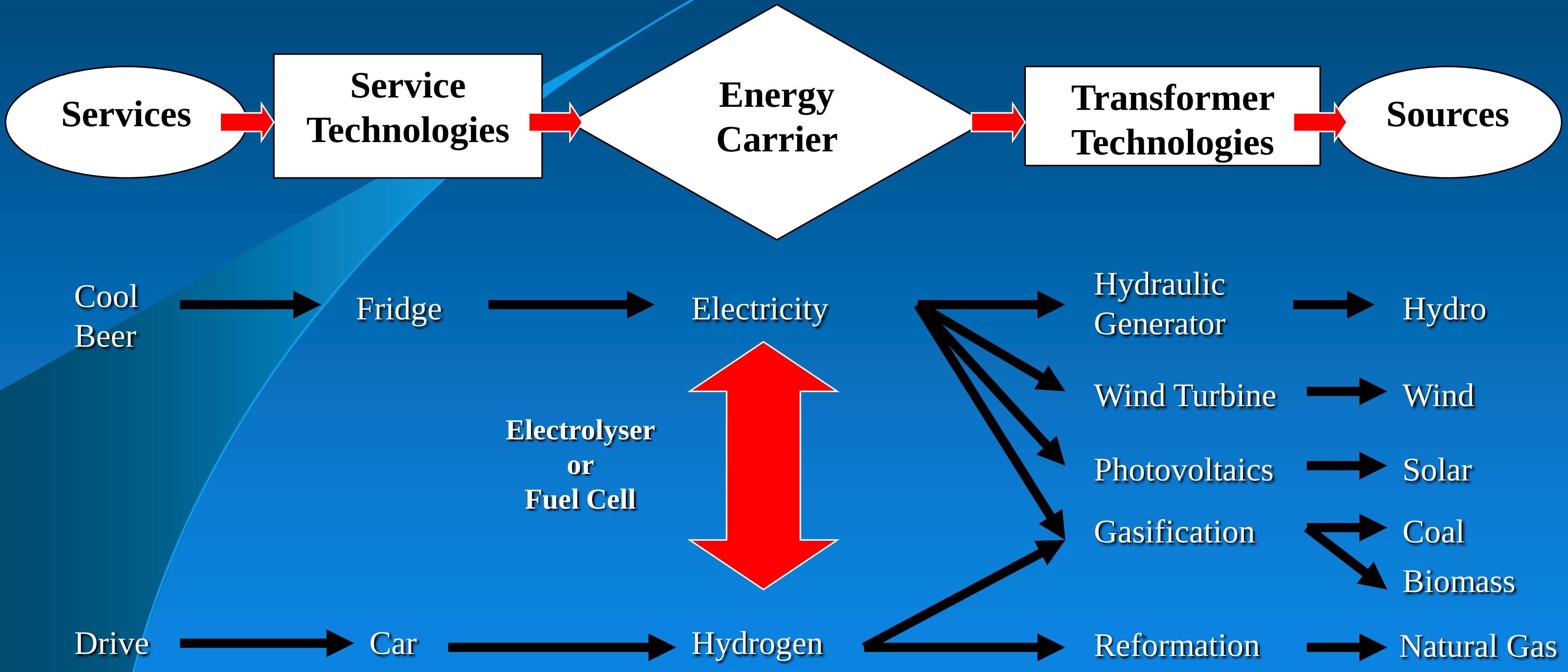
An Energy System With Hydrogen



Services → Service Technologies → Energy Carrier → Transformer Technologies → Sources

Cool Beer → Fridge → Electricity

Electrolyser
or
Fuel Cell

Drive → Car → Hydrogen

Electricity → Hydraulic Generator → Hydro

Electricity → Wind Turbine → Wind

Electricity → Photovoltaics → Solar

Electricity → Gasification → Coal

Hydrogen → Gasification → Biomass

Hydrogen → Reformation → Natural Gas

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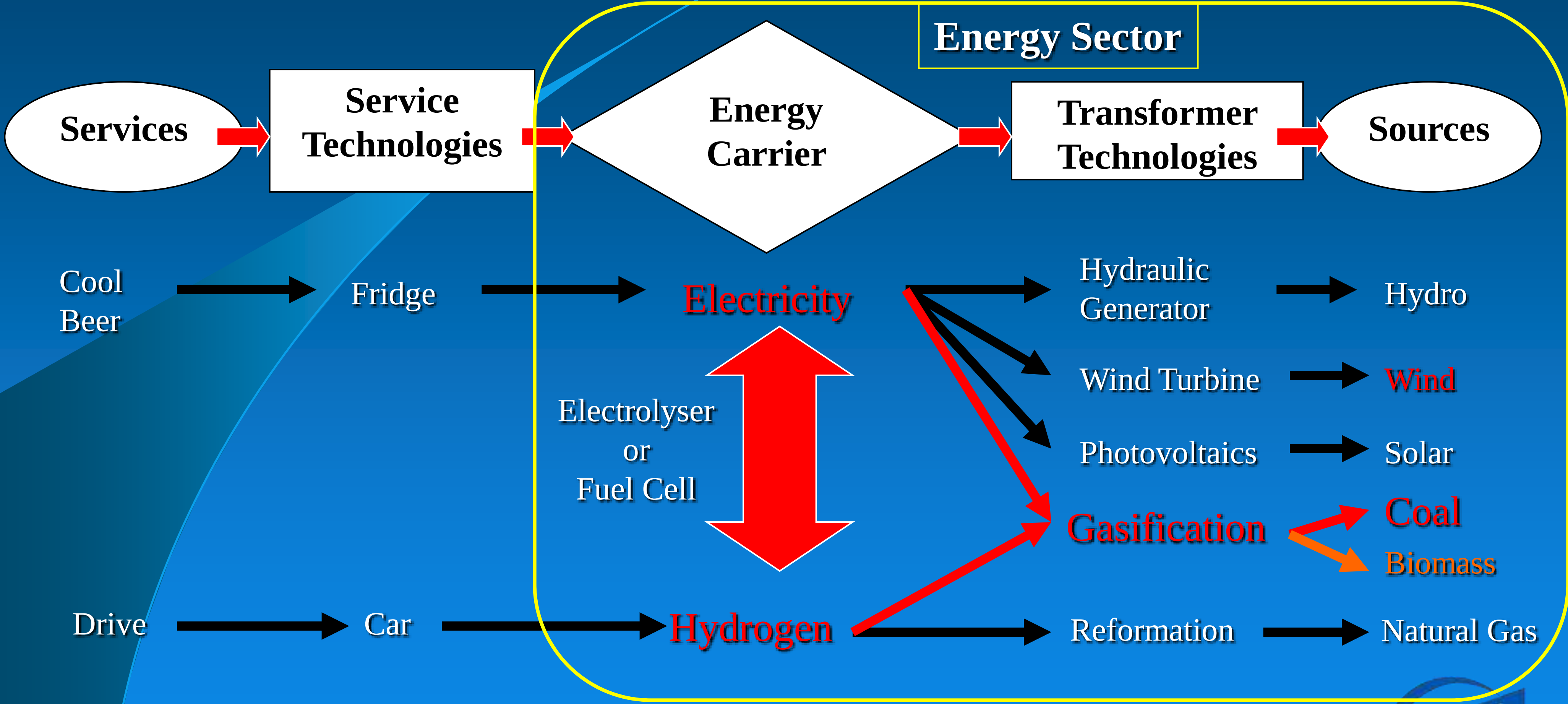
Alignment of CRL Energy's Research Programmes



Energy Sector

Services → Service Technologies → Energy Carrier → Transformer Technologies → Sources

Cool Beer → Fridge → Electricity

Electricity → Hydraulic Generator → Hydro

Electricity → Wind Turbine → Wind

Electricity → Photovoltaics → Solar

Electricity → Gasification

Electrolyser or Fuel Cell (Electricity ↔ Hydrogen)

Drive → Car → Hydrogen

Hydrogen → Gasification → Coal, Biomass

Hydrogen → Reformation → Natural Gas

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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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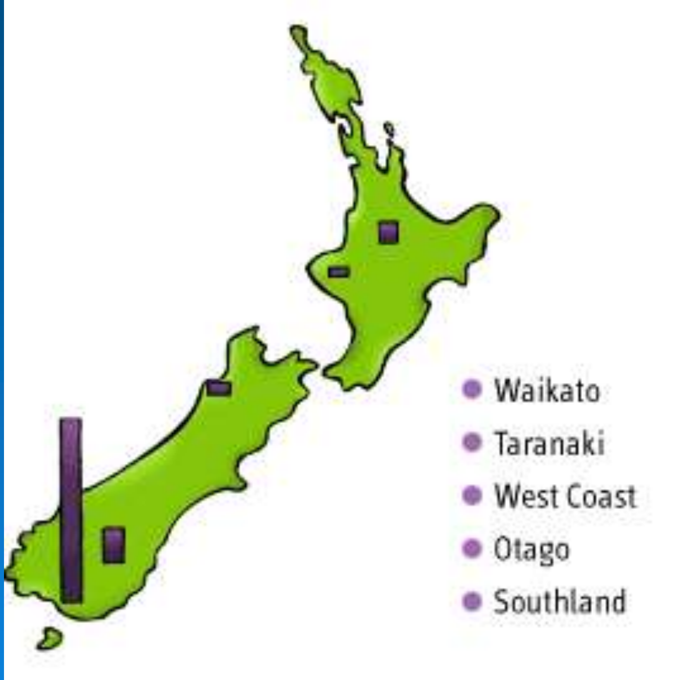
New Zealand Coal Resources

- 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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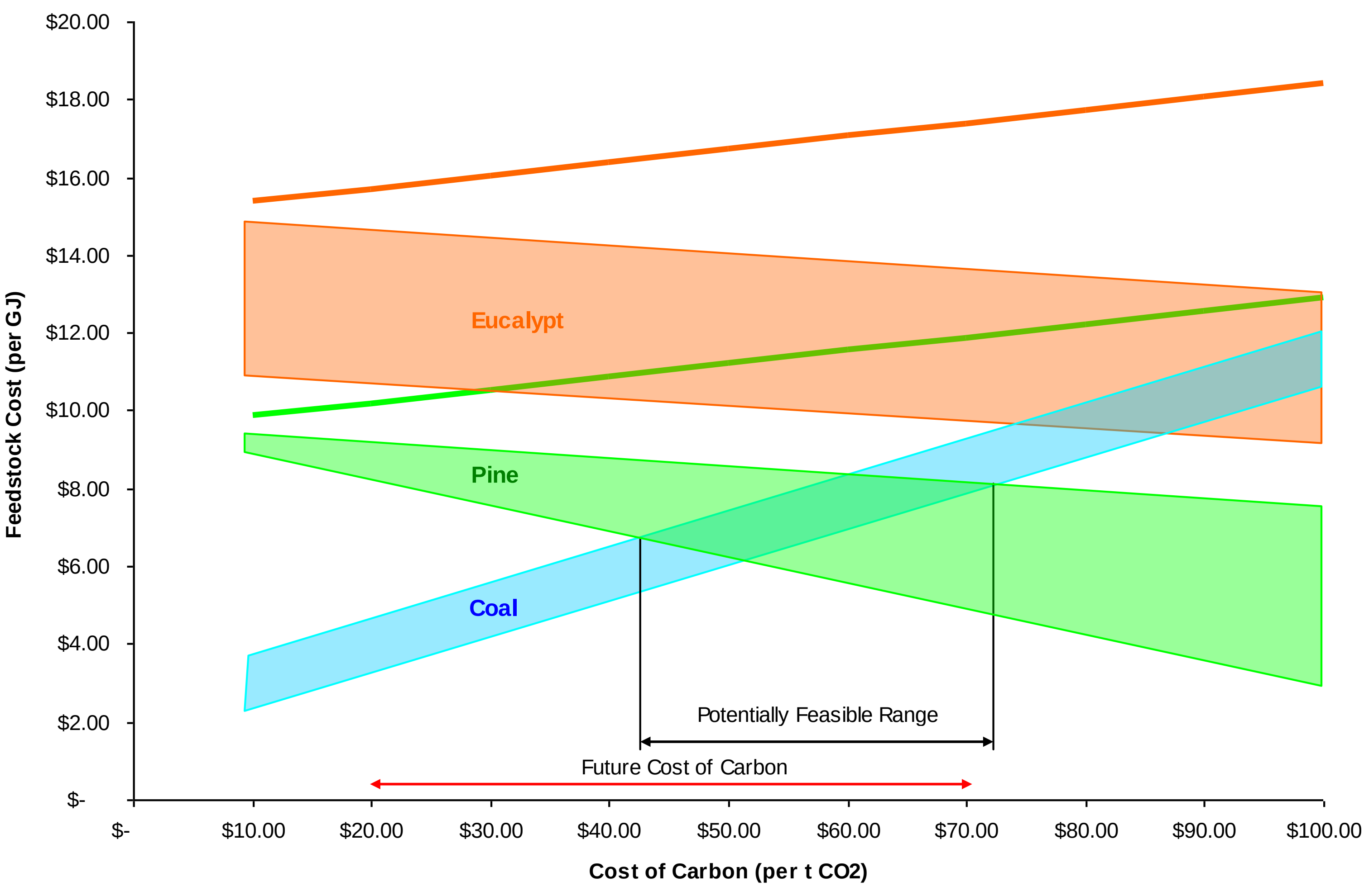
Feasibility of Biomass



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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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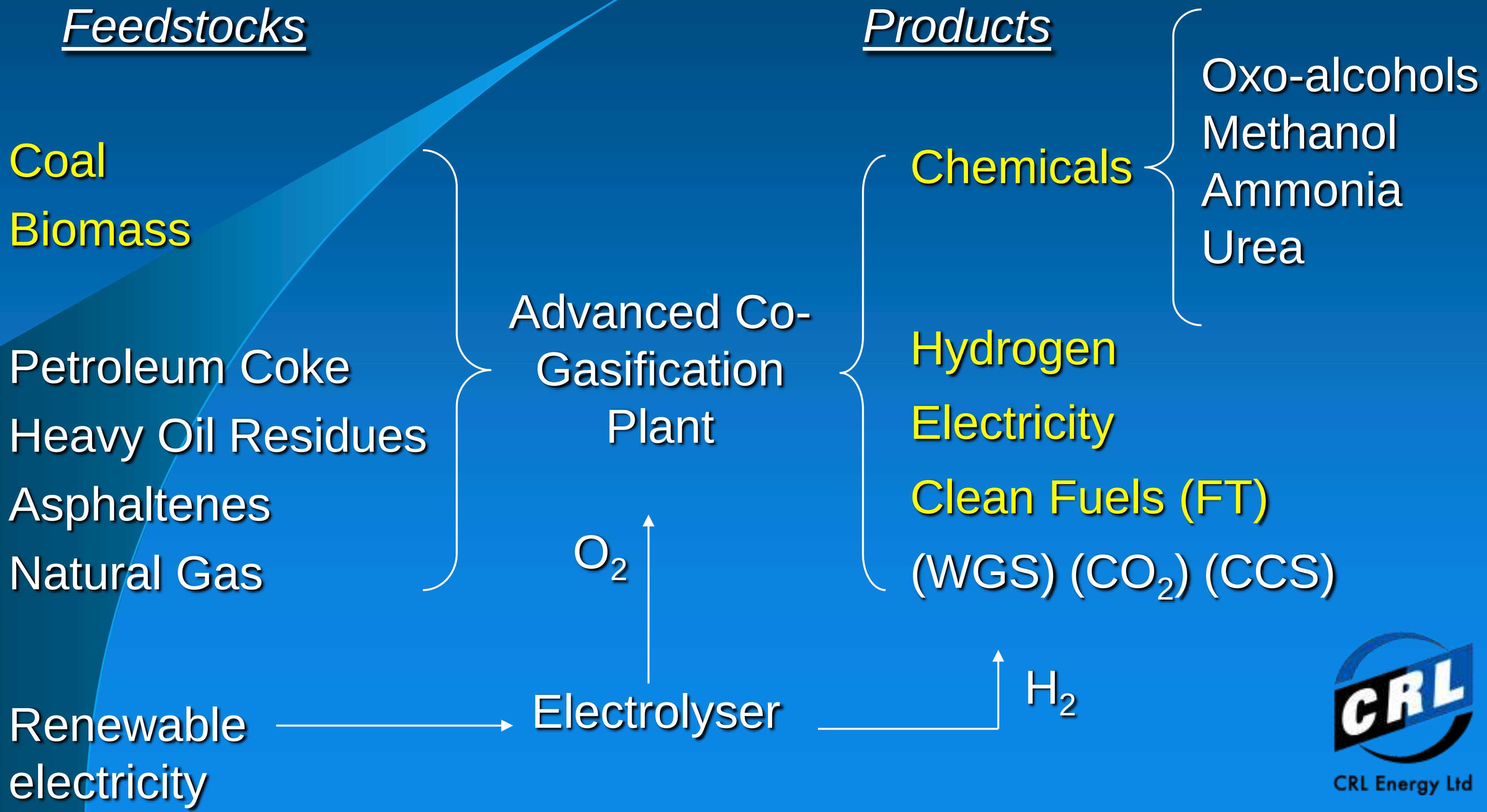
Hydrogen and Syngas – Flexible, Valuable Products



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

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

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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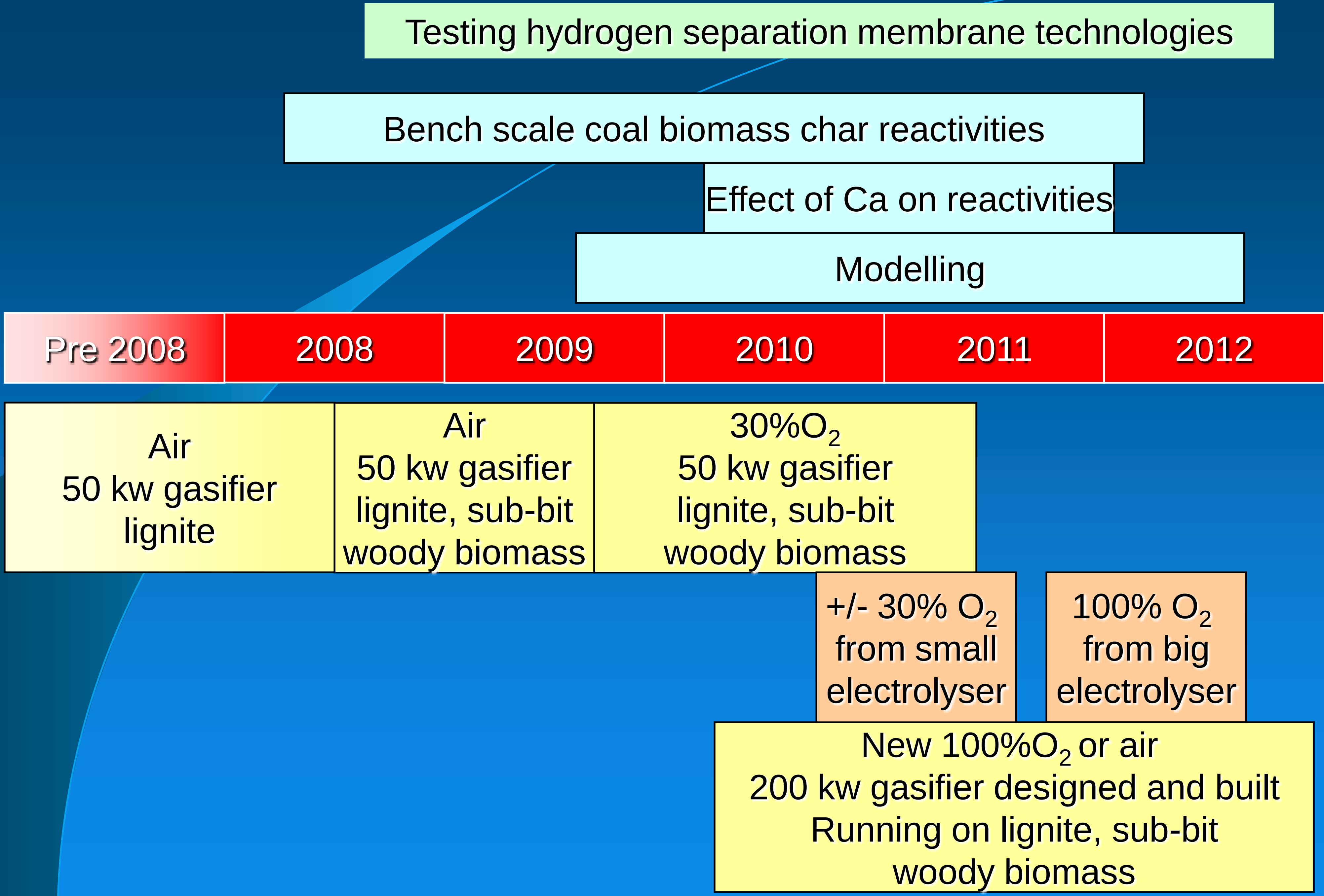

Testing hydrogen separation membrane technologies

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

Scale

constraints

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

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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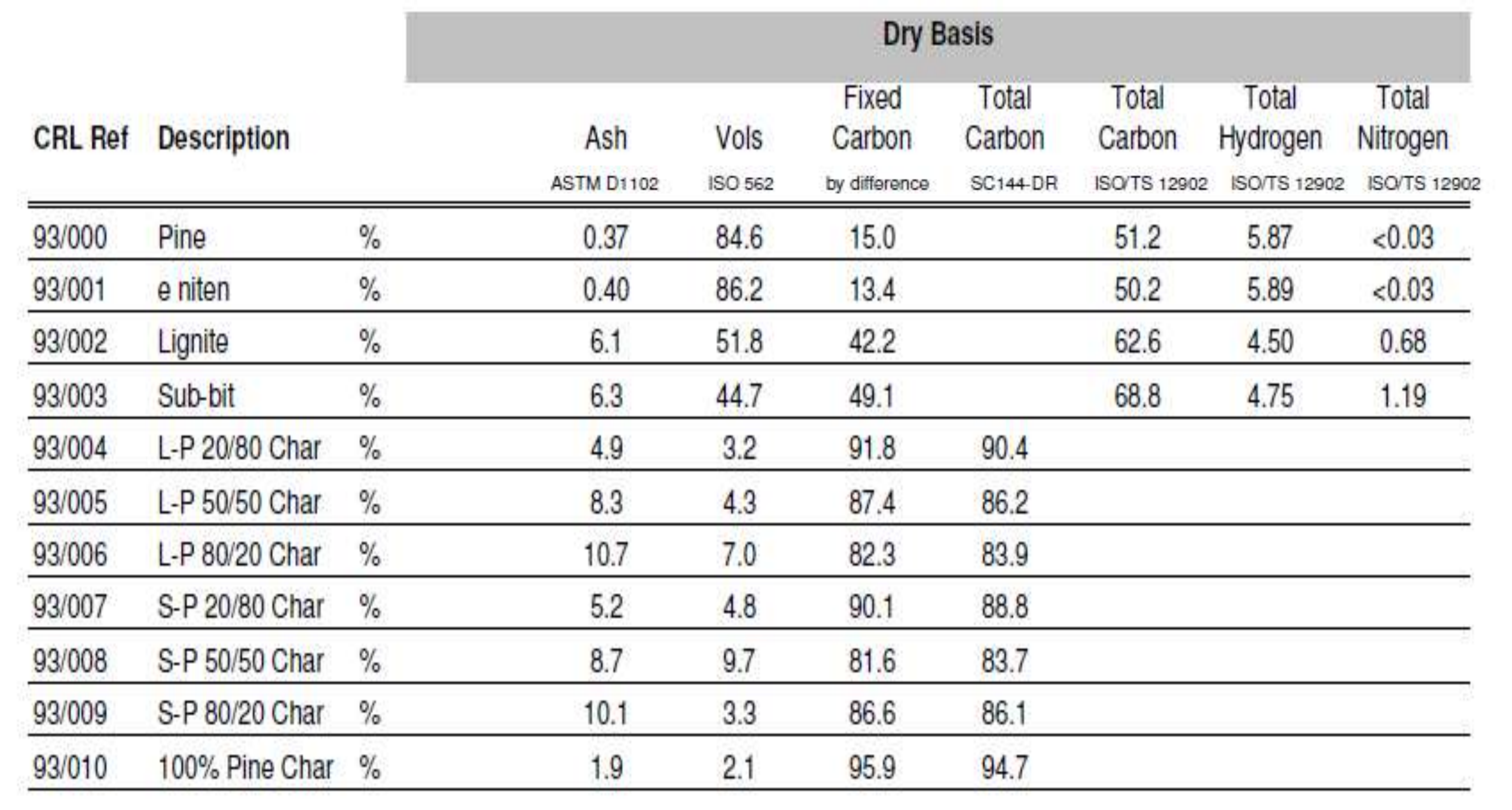
Things did not always go quite to plan !!!

Analysis of Feed Stocks



			Dry Basis						
CRL Ref	Description		Ash	Vols	Fixed Carbon	Total Carbon	Total Carbon	Total Hydrogen	Total Nitrogen
			ASTM D1102	ISO 562	by difference	SC144-DR	ISO/TS 12902	ISO/TS 12902	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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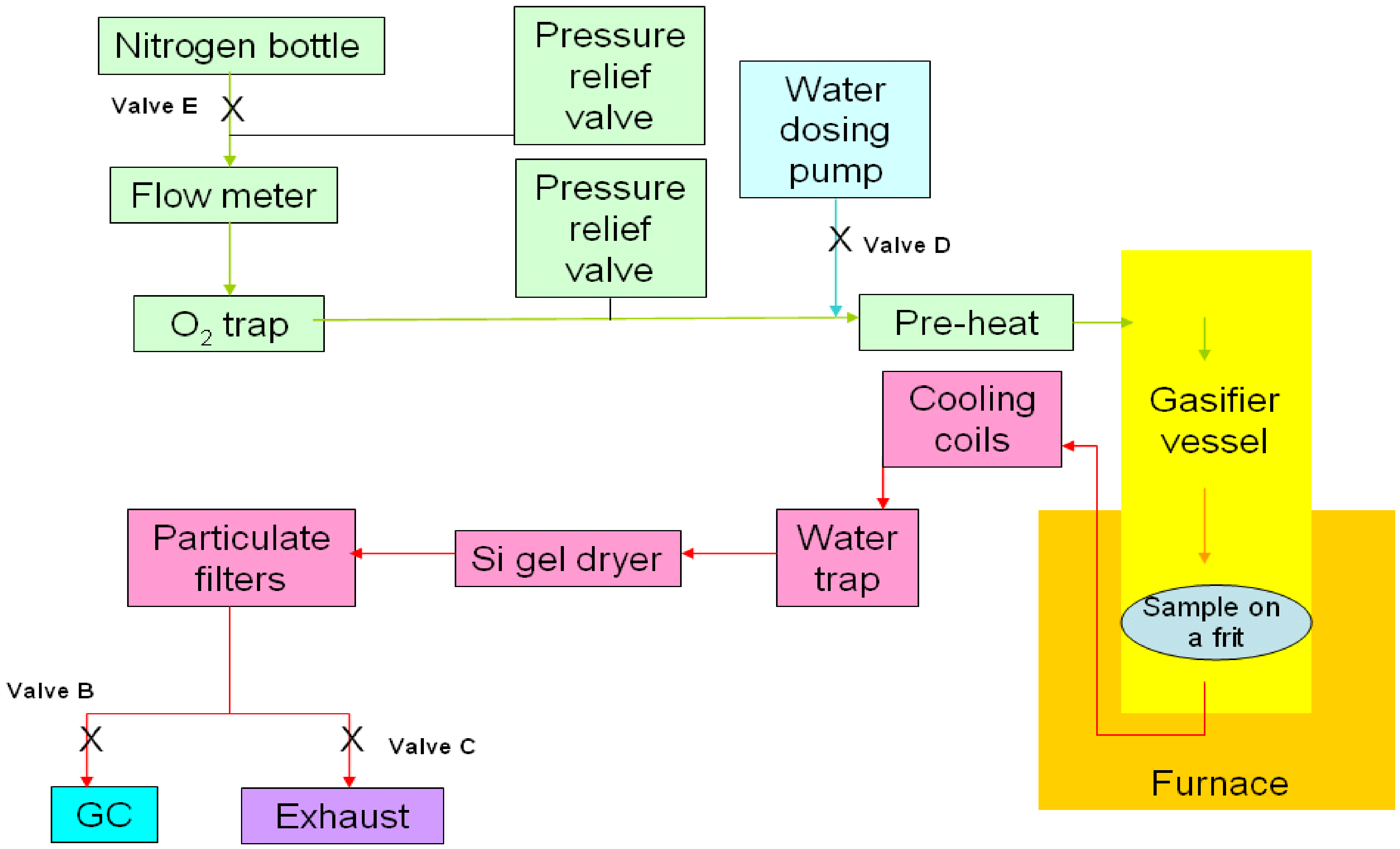
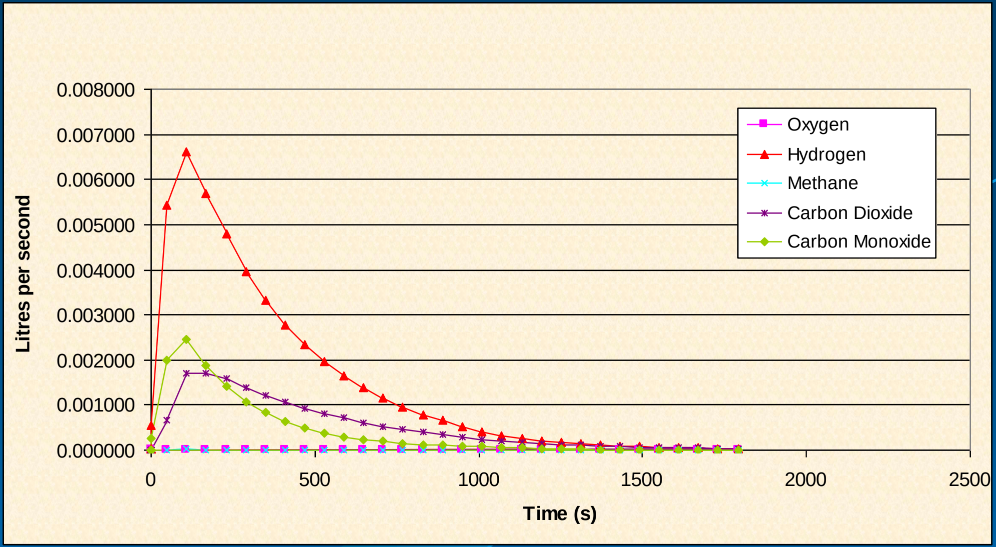
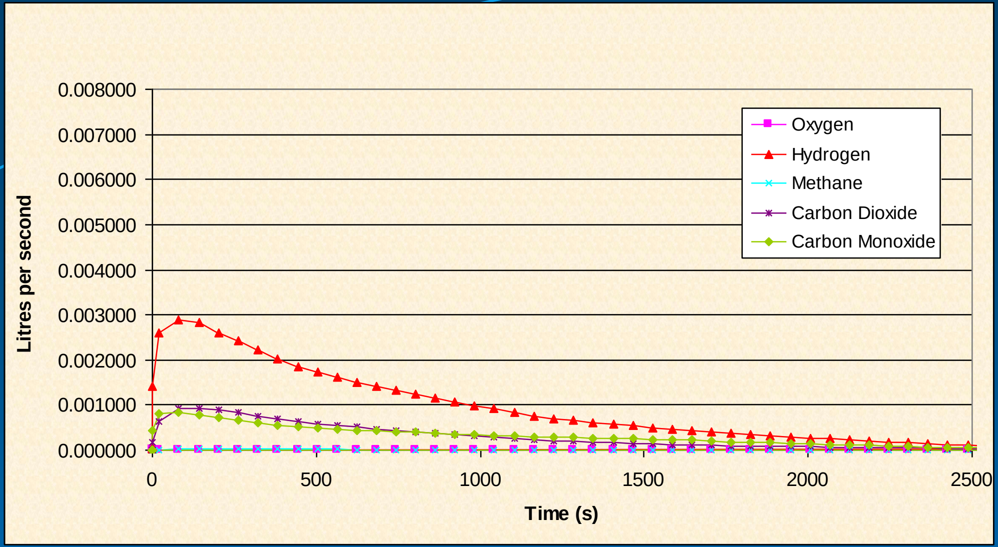
BENCH SCALE GASIFIER





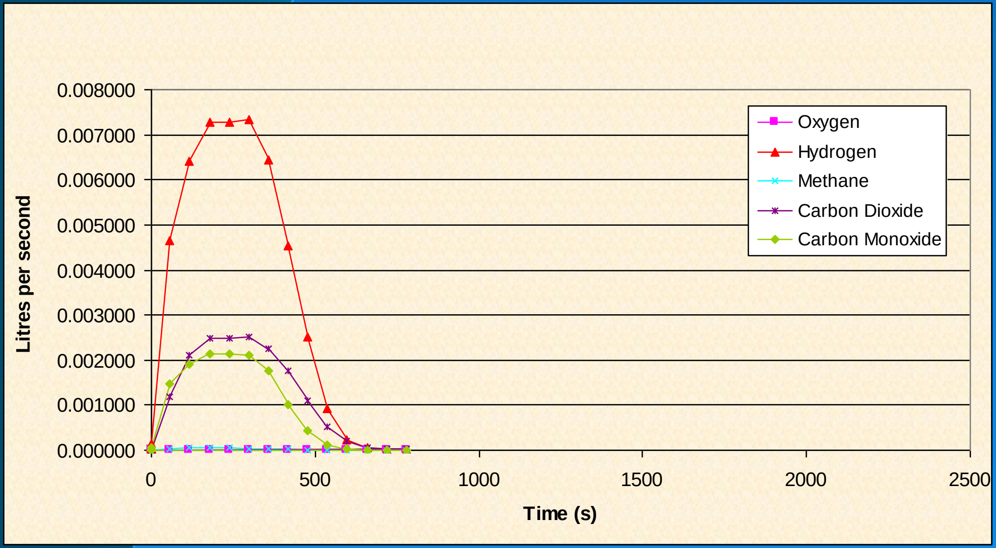


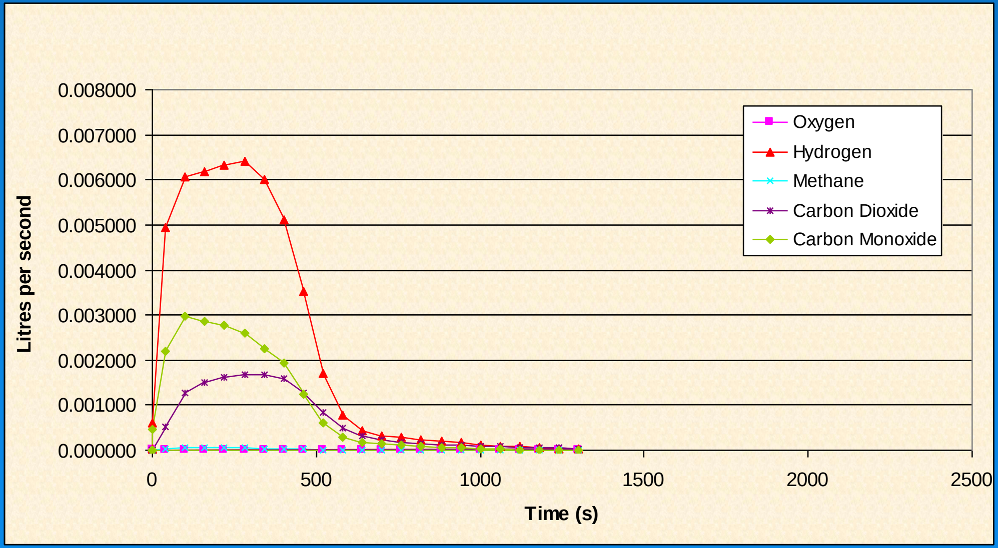
Lignite

Sub-bituminous

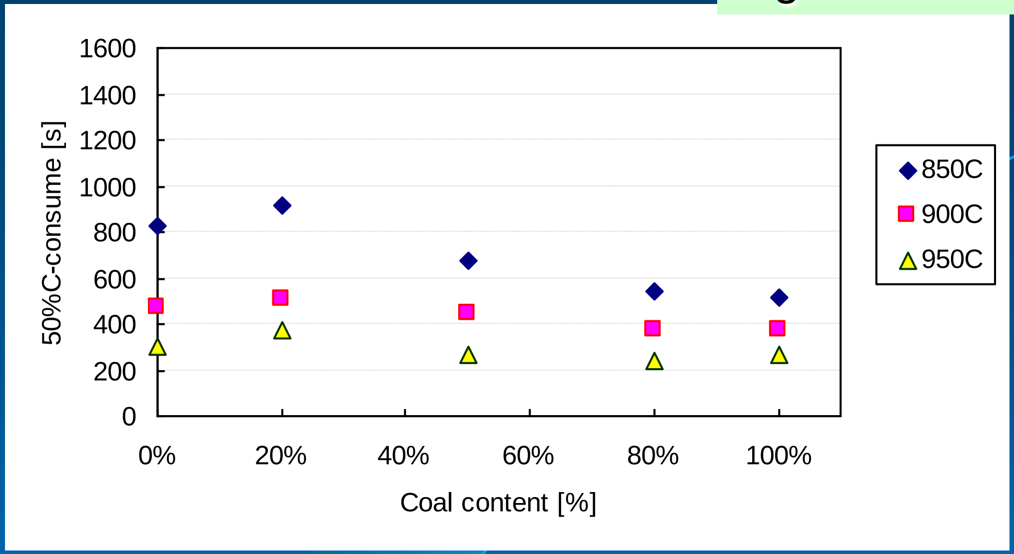
P. radiata

E. nitens

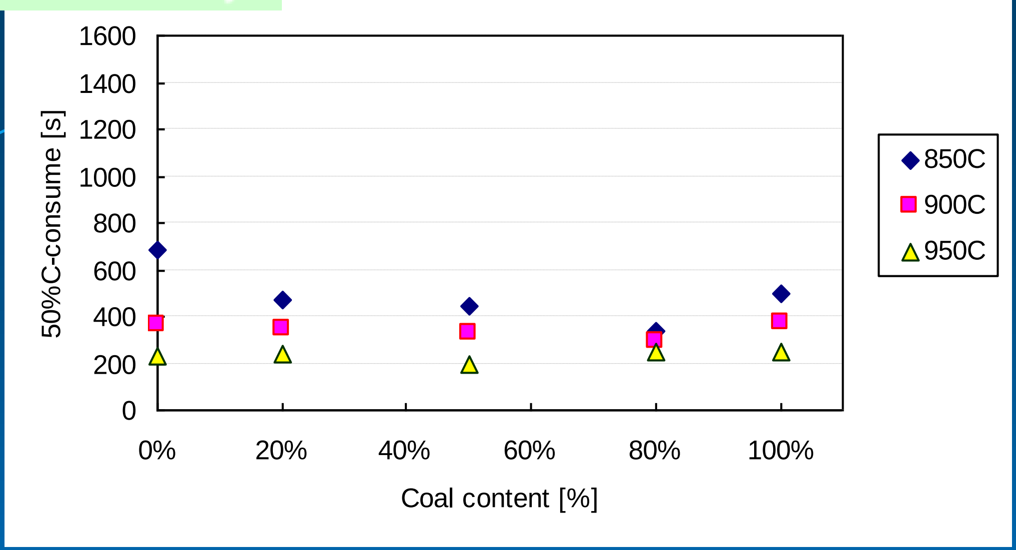




Lignite increases reactivity

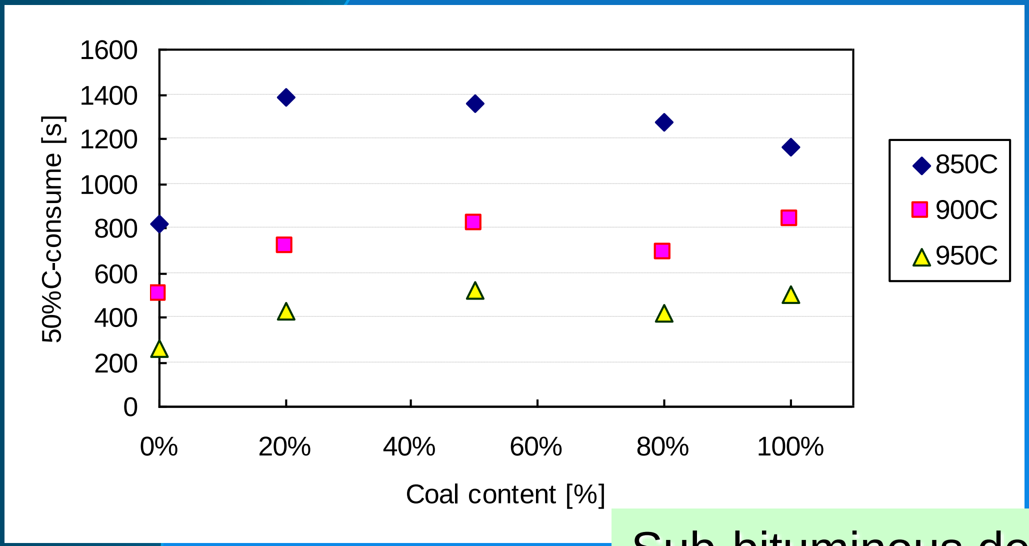


Lignite / *P. radiata*

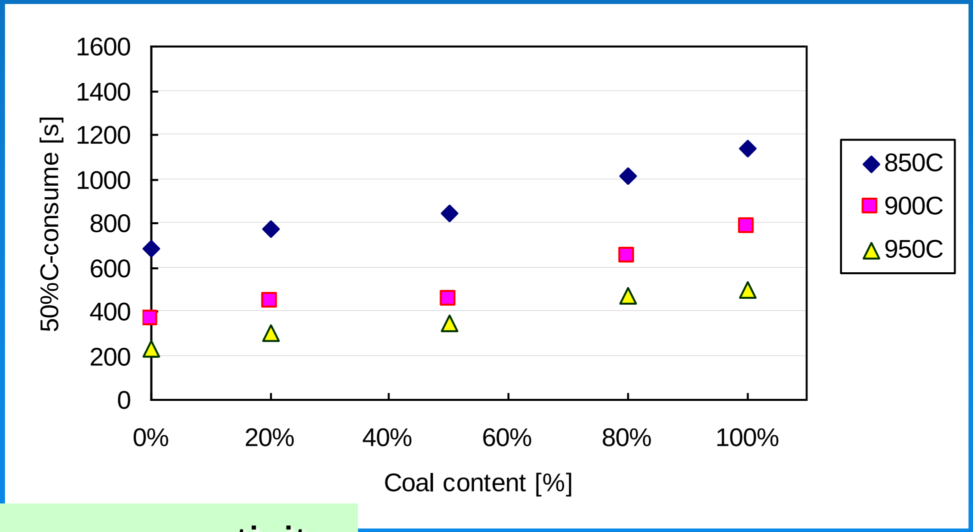


Lignite / *E. nitens*

Sub-bituminous / *P. radiata*



Sub-bituminous / *E. nitens*



Sub-bituminous decreases reactivity

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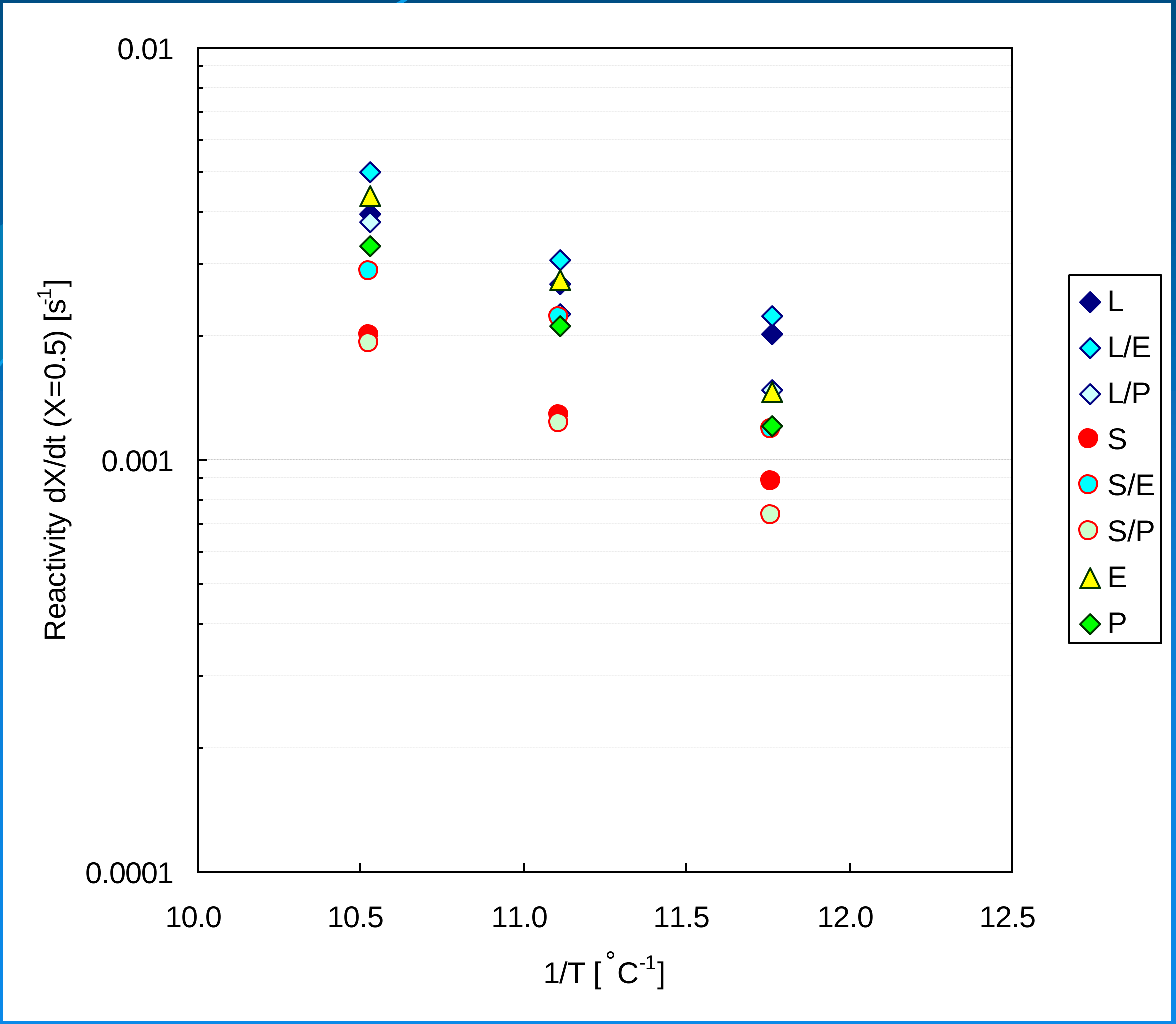
Effect of Gasification Temperature on Reactivity



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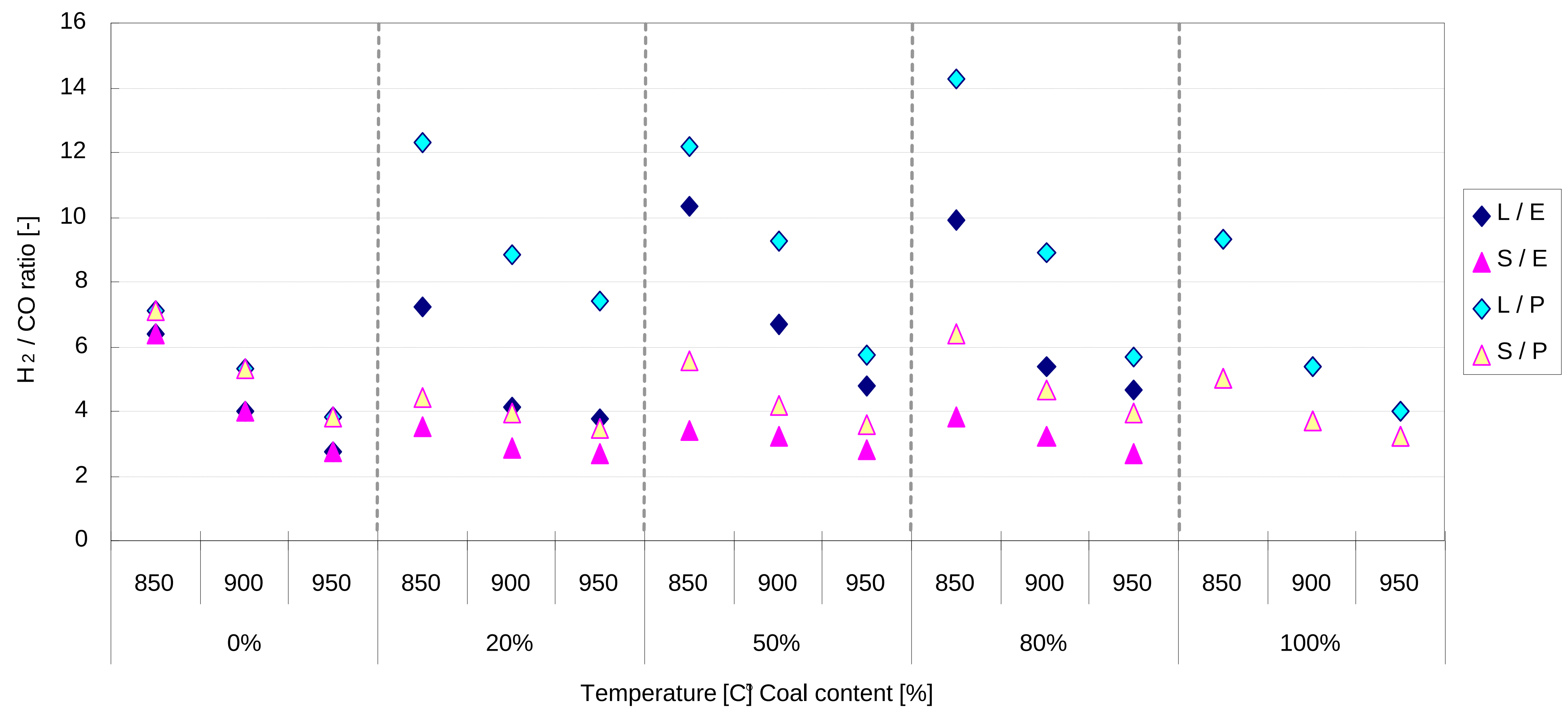
Effect of Gasification Temperature on H_2/CO Ratio



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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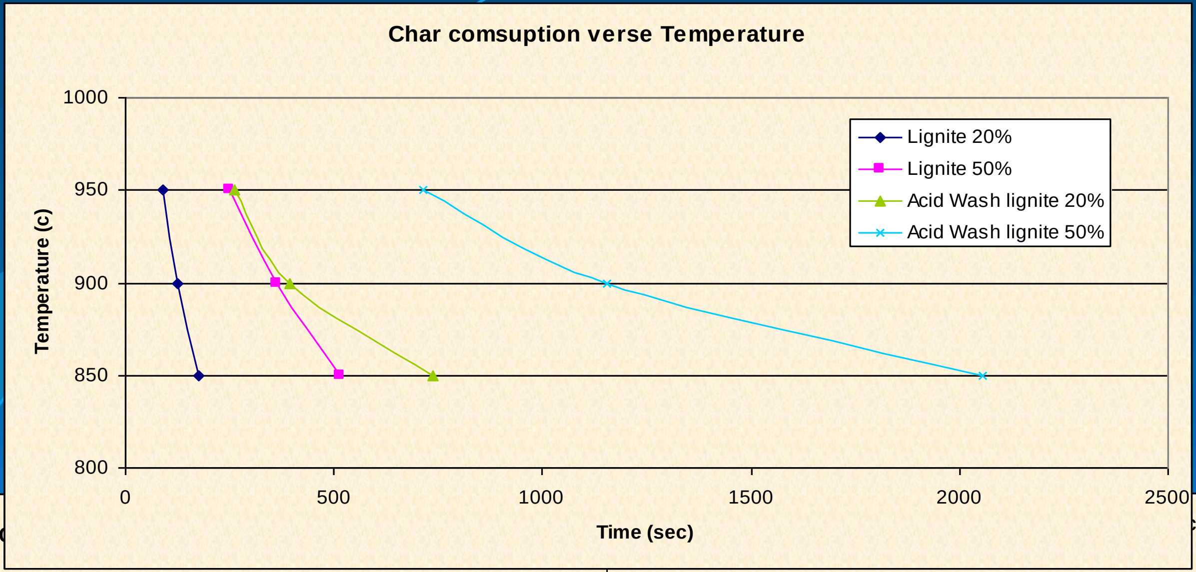
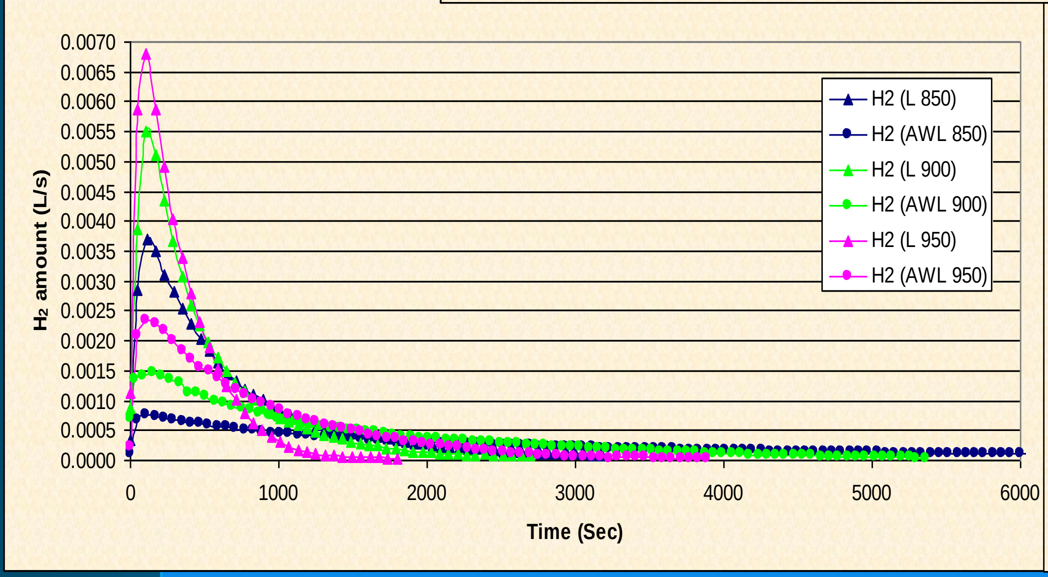
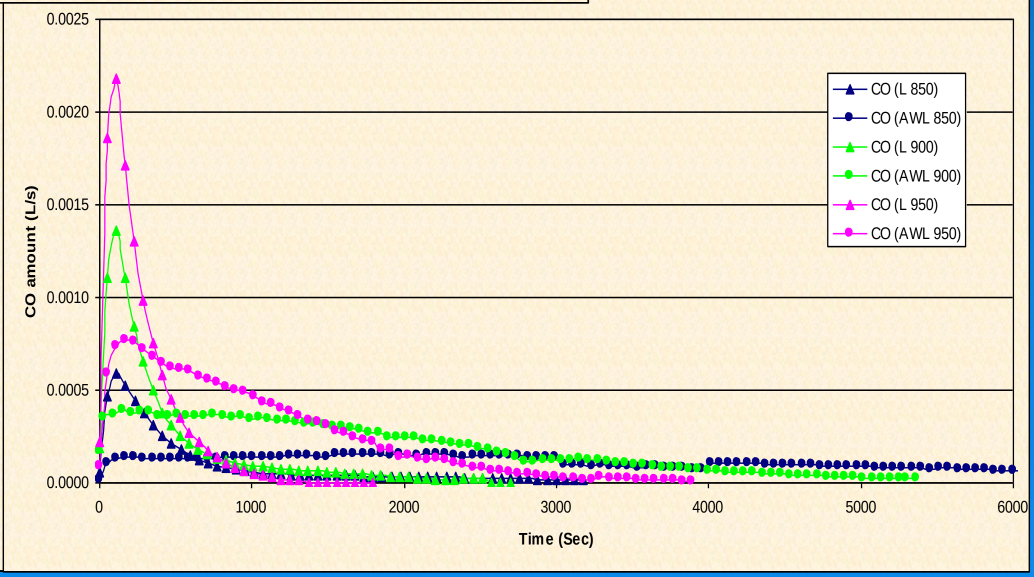
Effect of Calcium on Lignite Reactivity and Syngas Composition



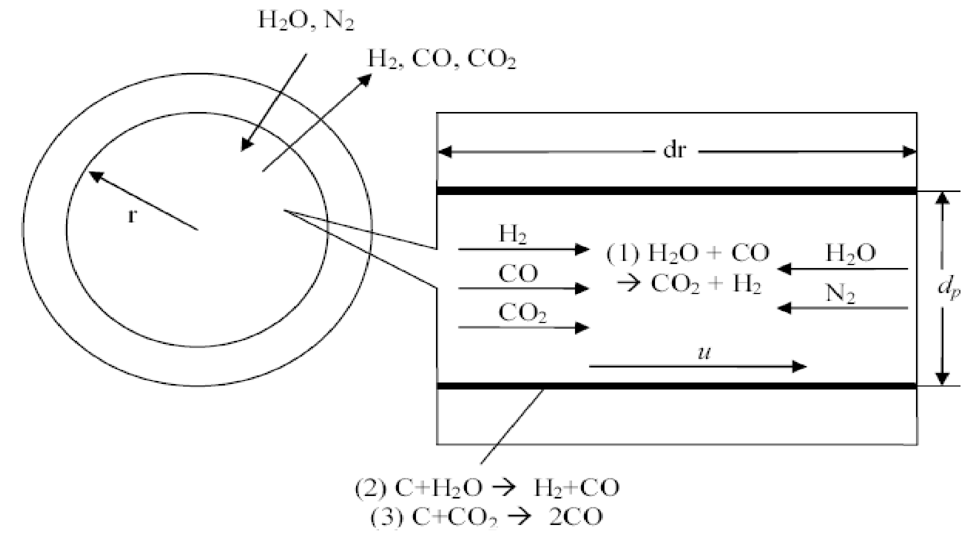
H_2



CO



Modelling Char Reactivity

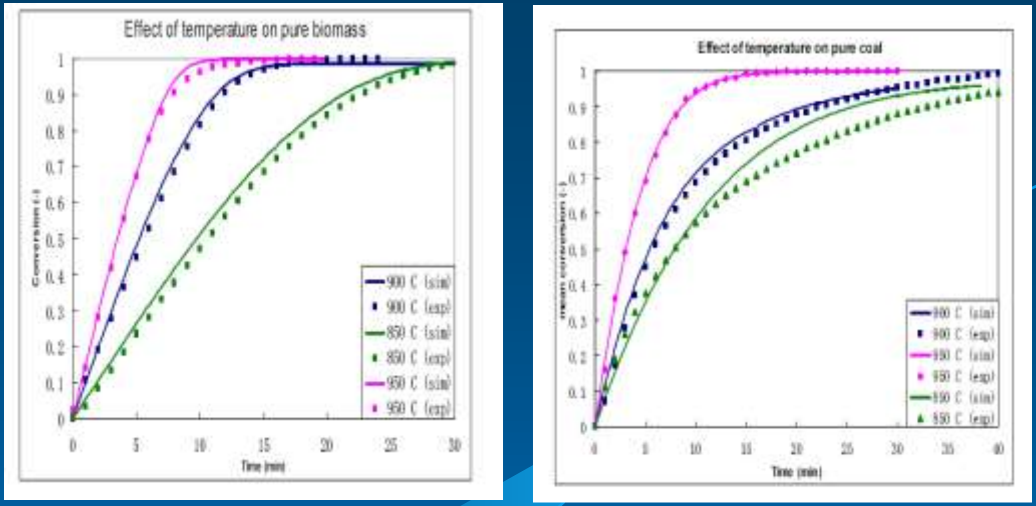


Model based on:

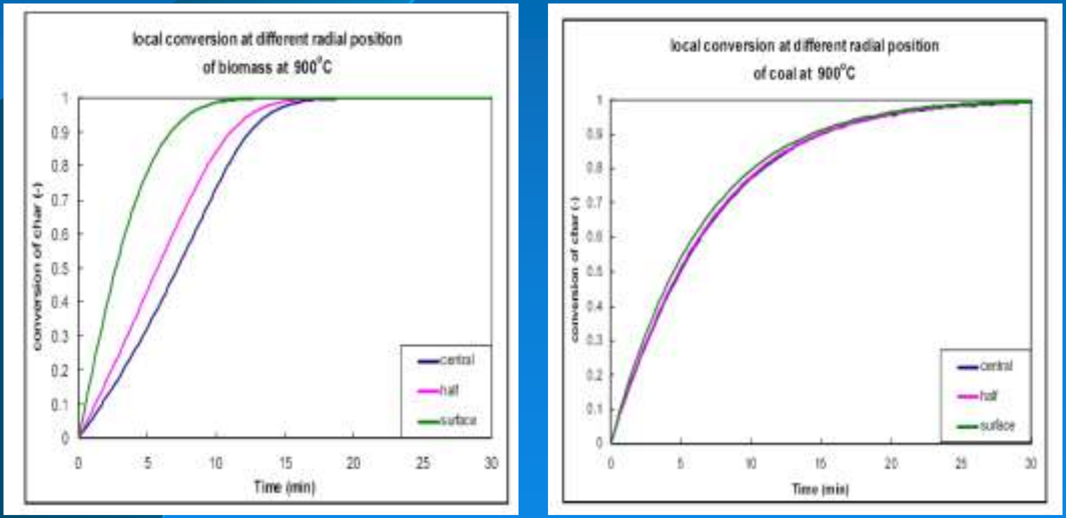
- Gasification reaction kinetics
- Transportation of gas molecules in char matrix
- Mass balance equations in solid char

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



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 ^{o}C

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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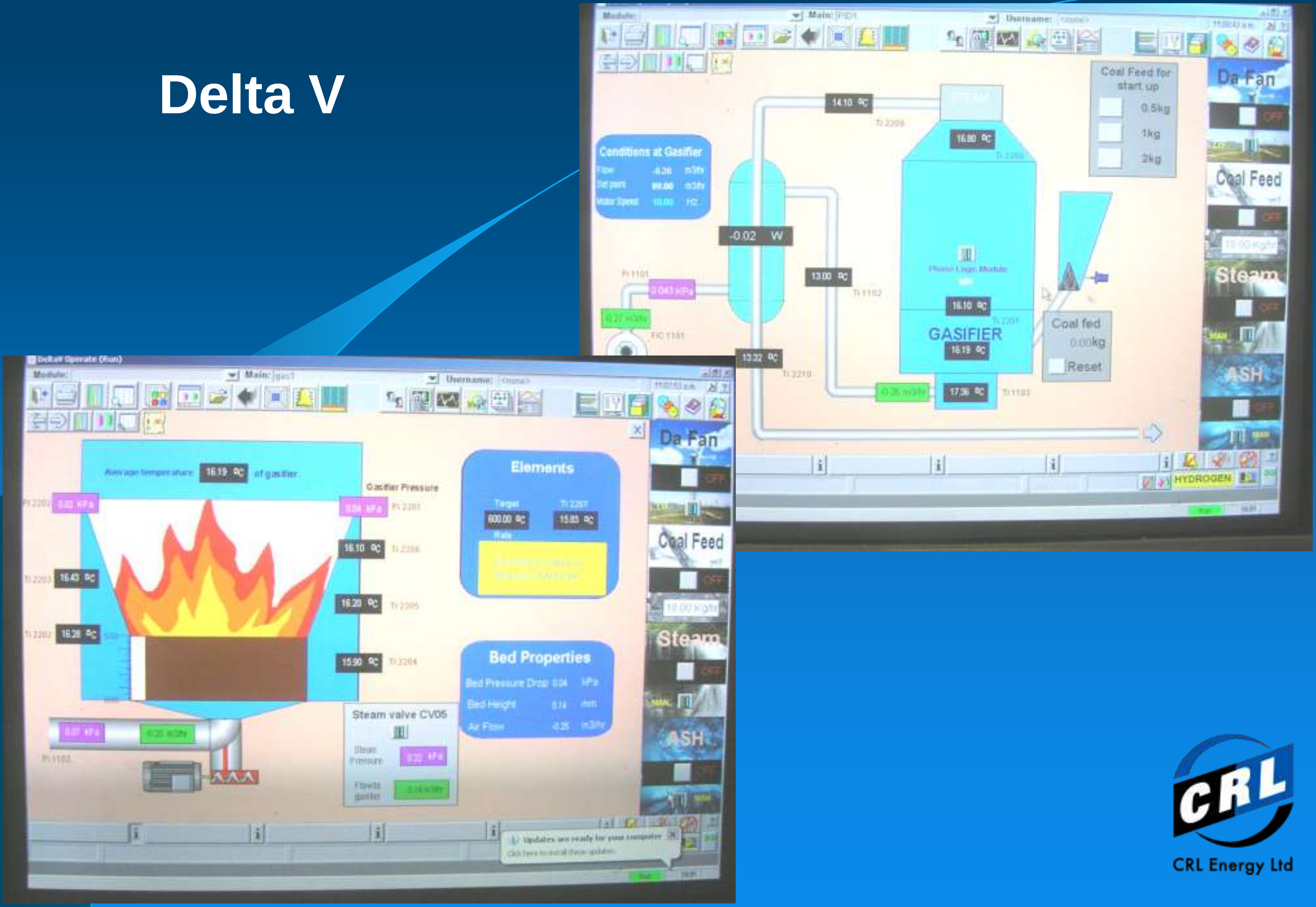
Delta V



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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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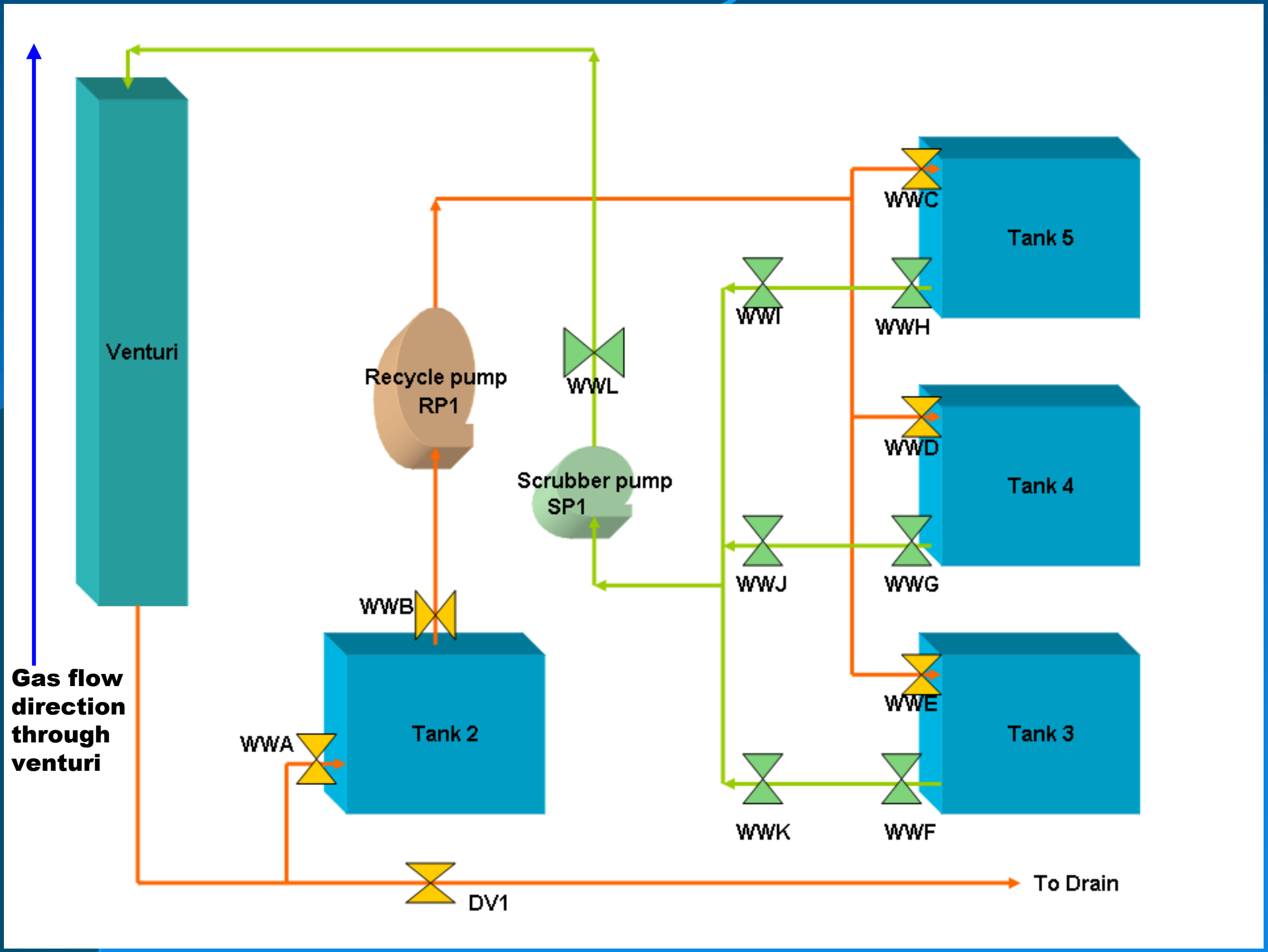
Syngas Clean-up Line
Sulfur Gases

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

Syngas Clean-up Line



Venturi

Recycle pump
RP1

WWL

Scrubber pump
SP1

WWB

Tank 2

WWA

DV1

To Drain

WWC

Tank 5

WWI

WWH

WWD

Tank 4

WWJ

WWG

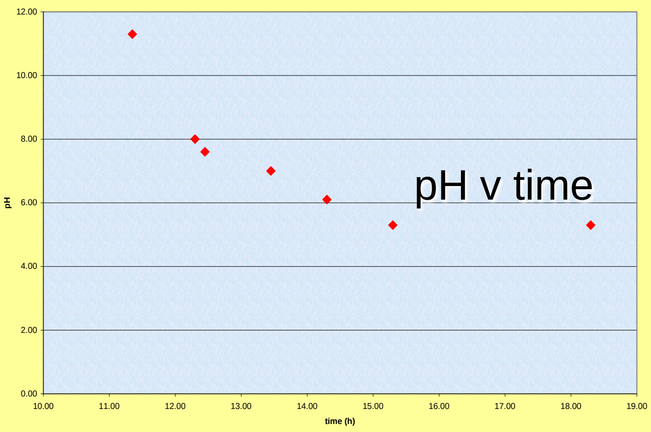
WWE

Tank 3

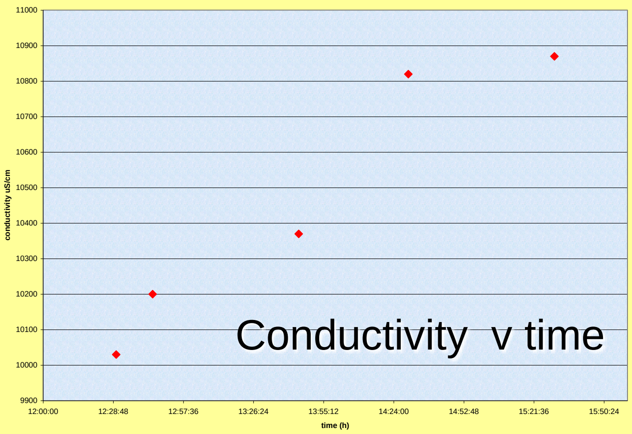
WWK

WWF

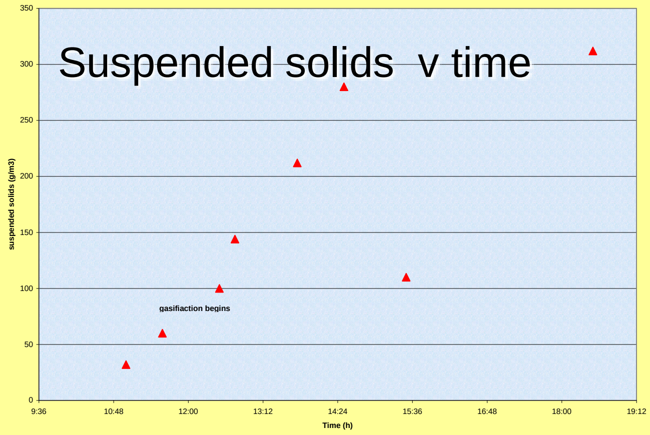
Gas flow direction through venturi



pH v time



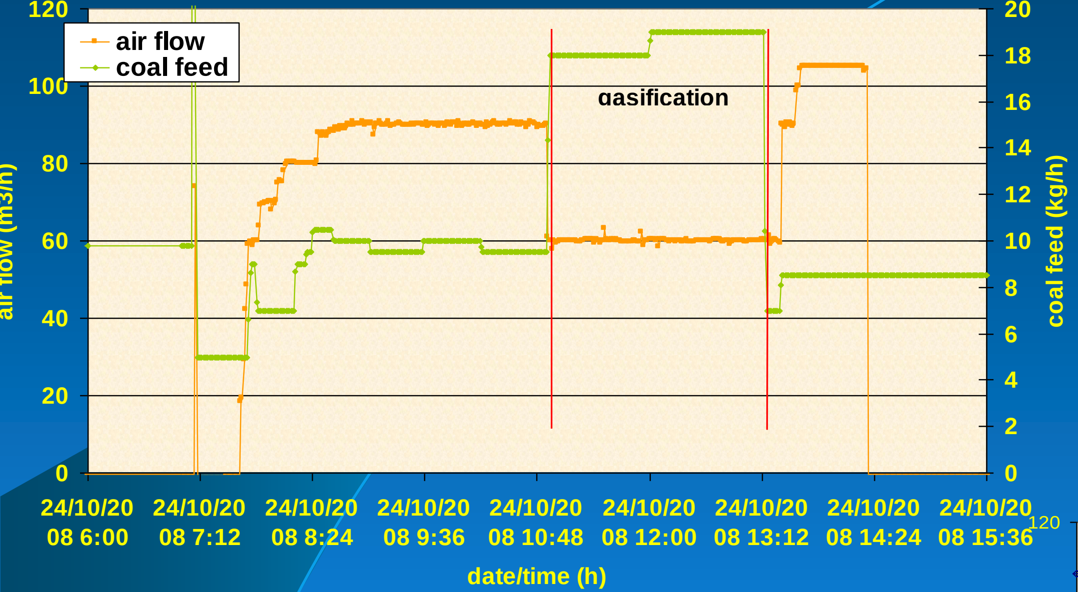
Conductivity v time



Suspended solids v time

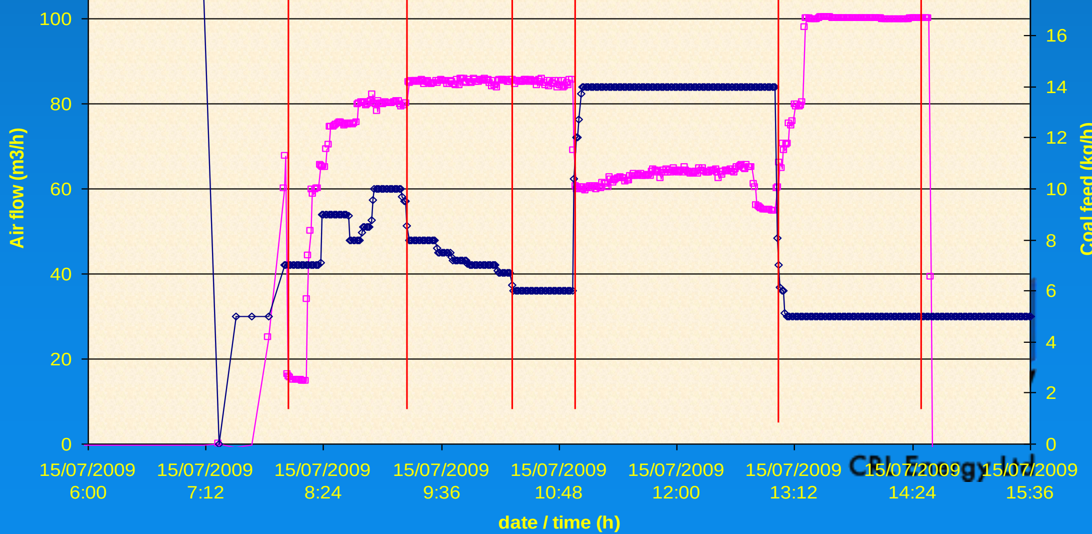
Corrosion

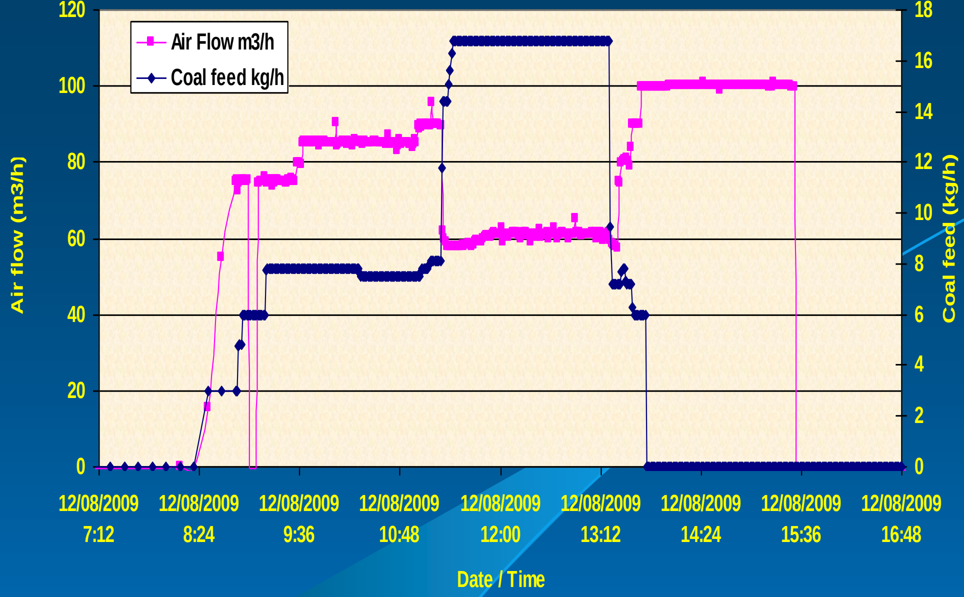
Effect of Biomass Addition on Gasifier Control



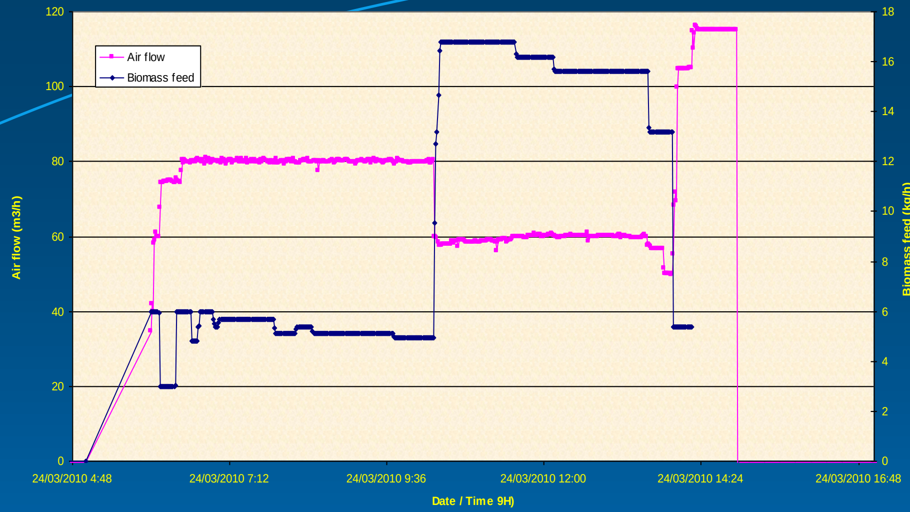
100% lignite

100% sub-bituminous



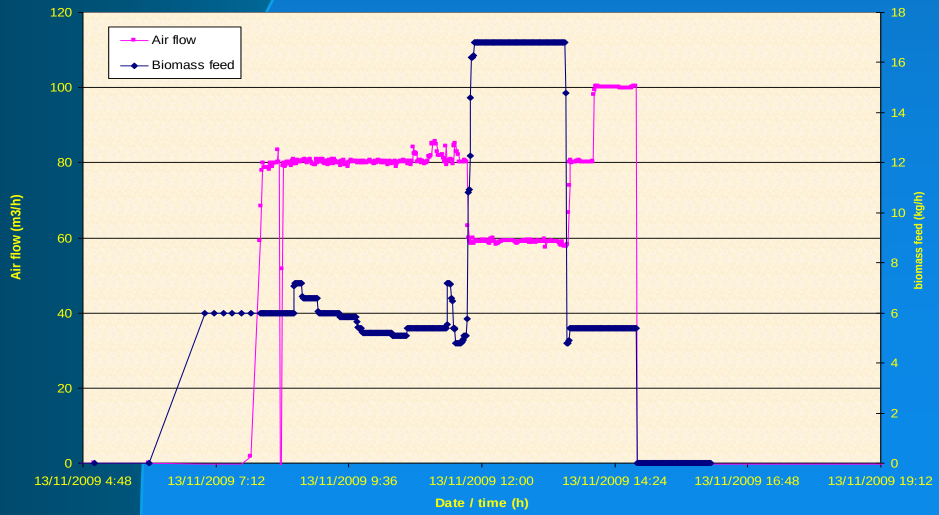


20% *P. radiata* – 80% lignite

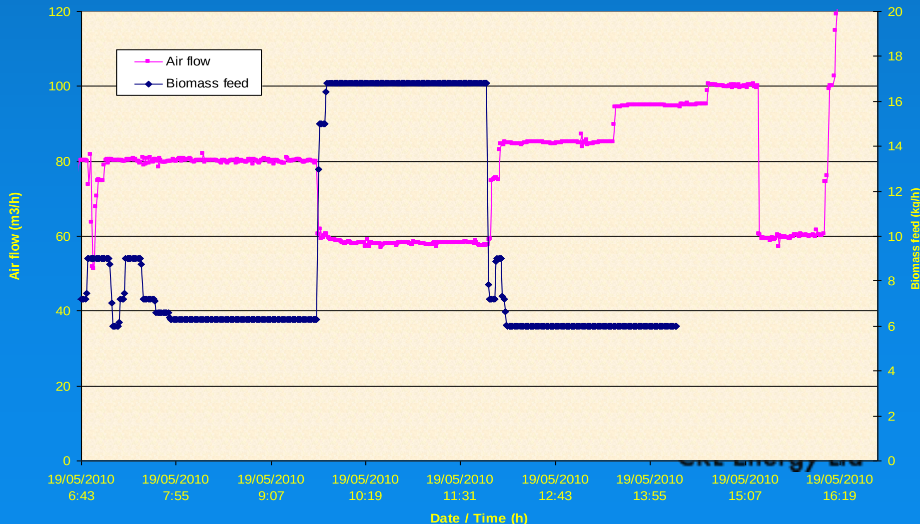


20% *P. radiata* – 80% sub-bituminous

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

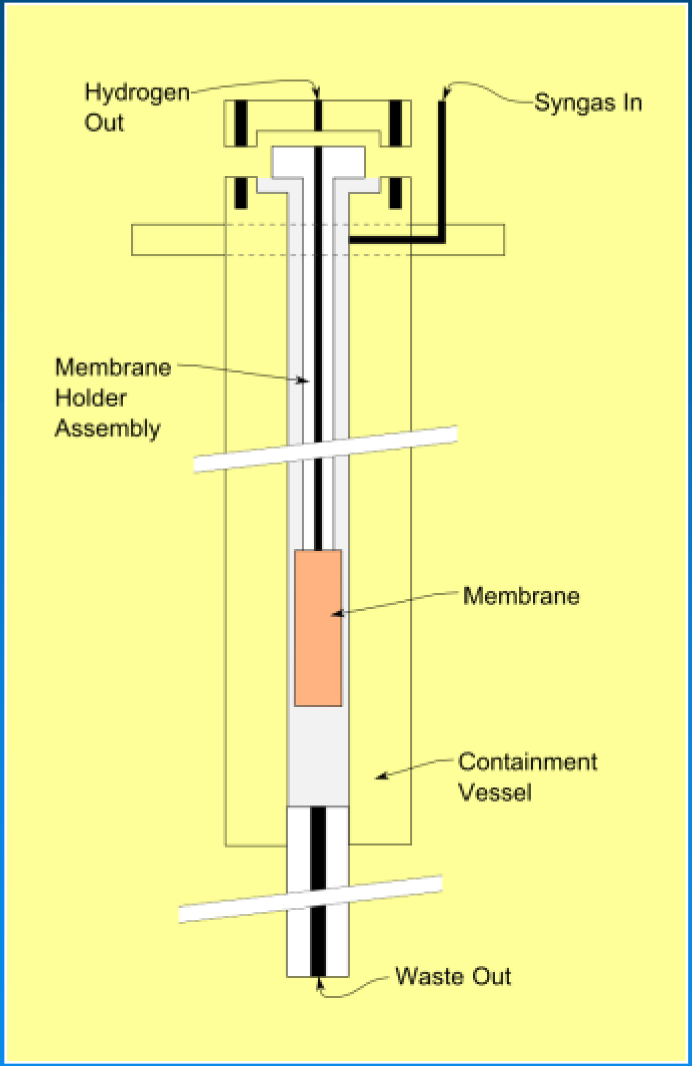
- $CO + H_2O \leftrightarrow H_2 + CO_2$ ~40 kJ/kg-mol
- Single high temperature catalyst bed (340 to 360°C)
- Iron Oxide Catalyst
- Gas flow rate 5.0 - 2.4 m^3/h
- Regular quality syngas
  - 22% H_2, 20% CO_2, 5% CO, <1% CH_4

Syngas Clean-up Line Hydrogen Purification

Palladium membrane, developed by ECN, NL

10 bar, 350^{o}C, >99% hydrogen

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



Fuel Cell

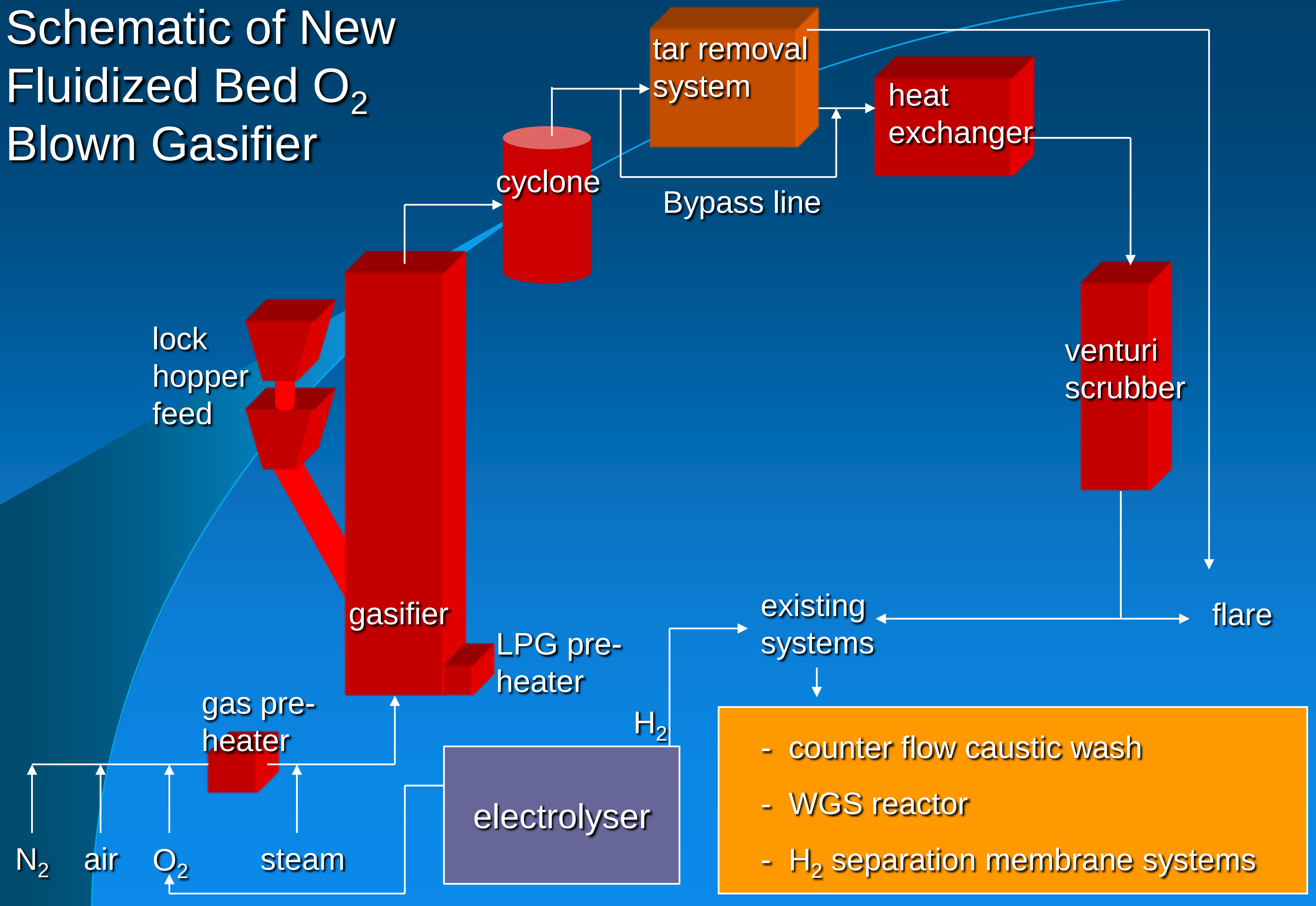
- Alkaline fuel cell (2.5 kW) assembled
- Developed by IRL, NZ
- 2 bar H_2 buffer storage system feed
- Overall electrical conversion efficiencies 50% HHV

- 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

Schematic of New Fluidized Bed O_2 Blown Gasifier



- counter flow caustic wash
- WGS reactor
- H_2 separation membrane systems

Specifications

50kw unit

Fluidized bed

O_2 or air blown

Biomass capability (up to 45%)

Modular design

Max working temperature 1000ºC

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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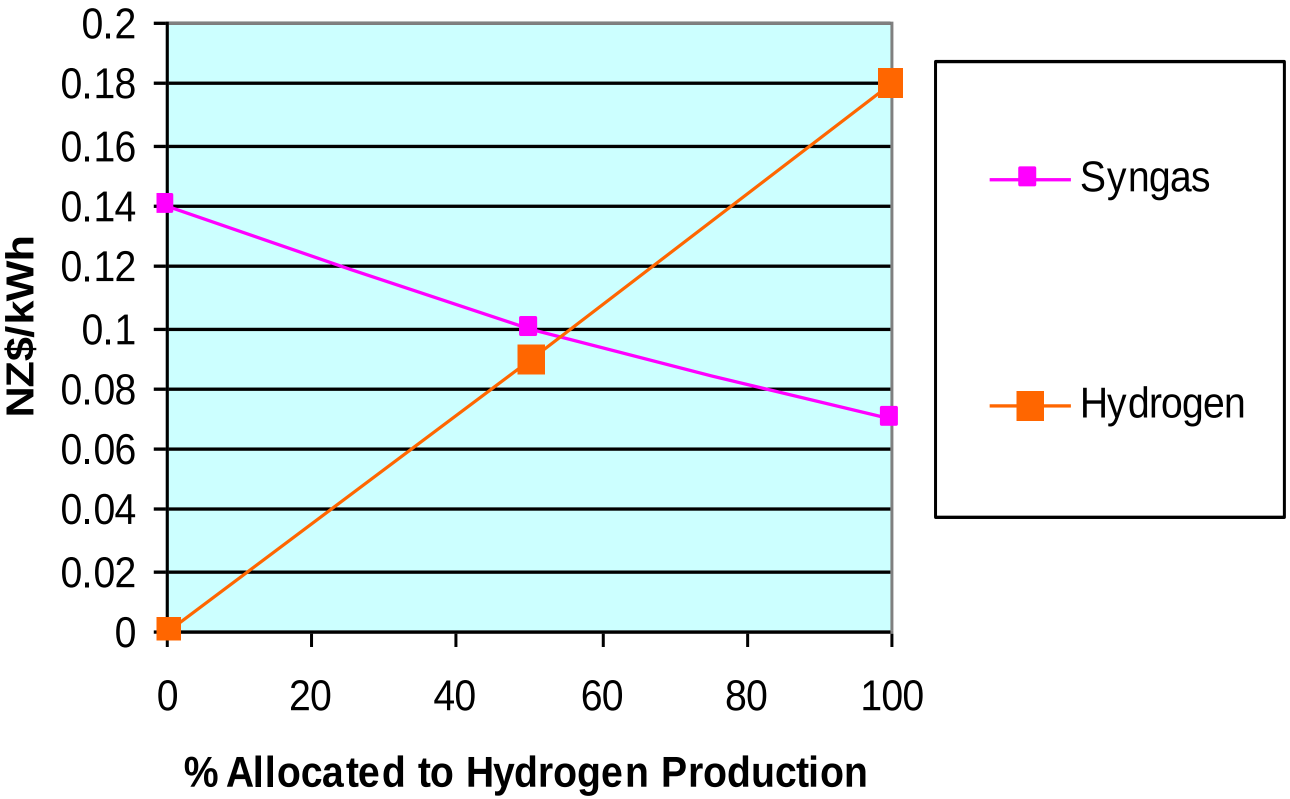
Product Costs vs Allocation of Electrolysis Cost



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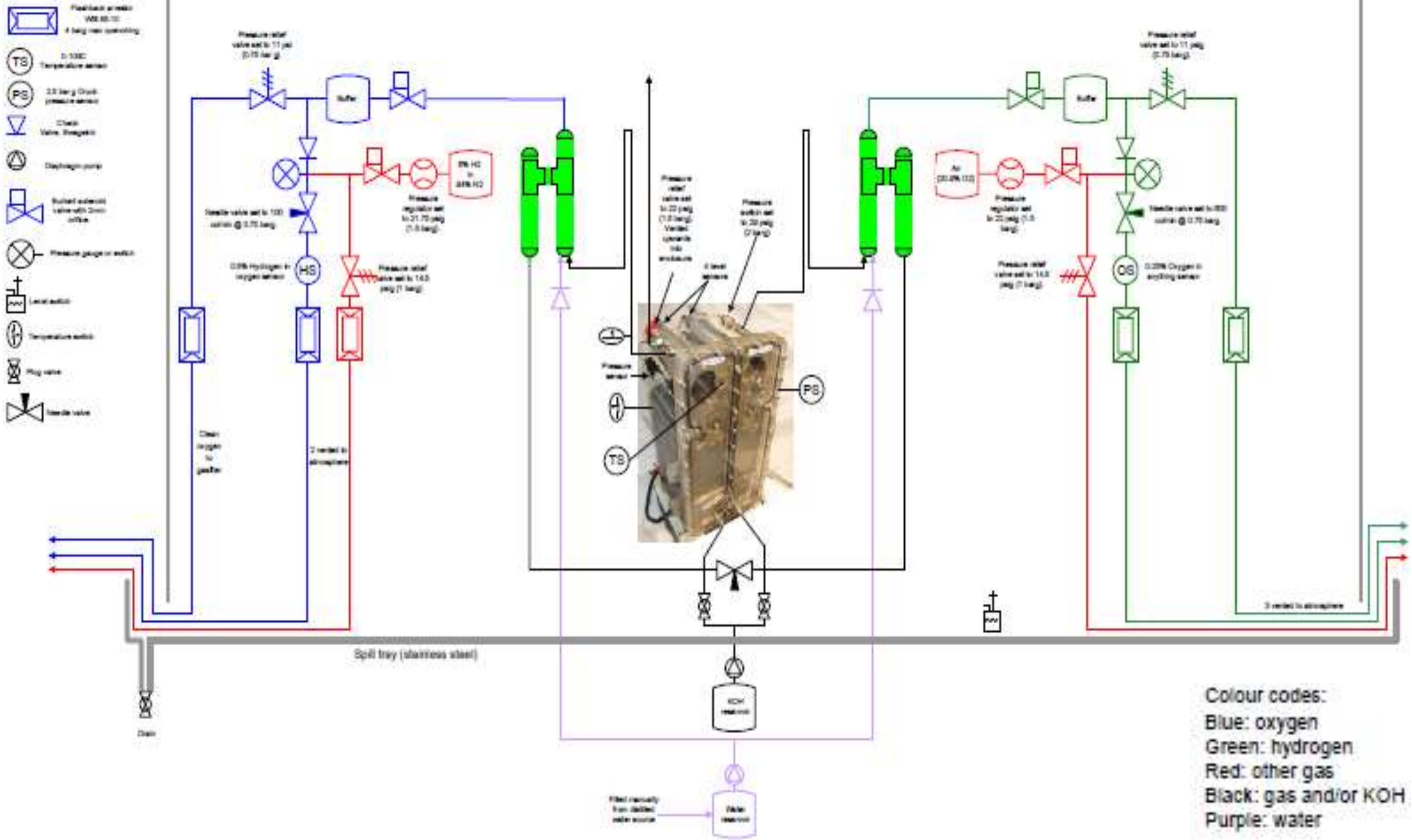
Benefits and Barriers

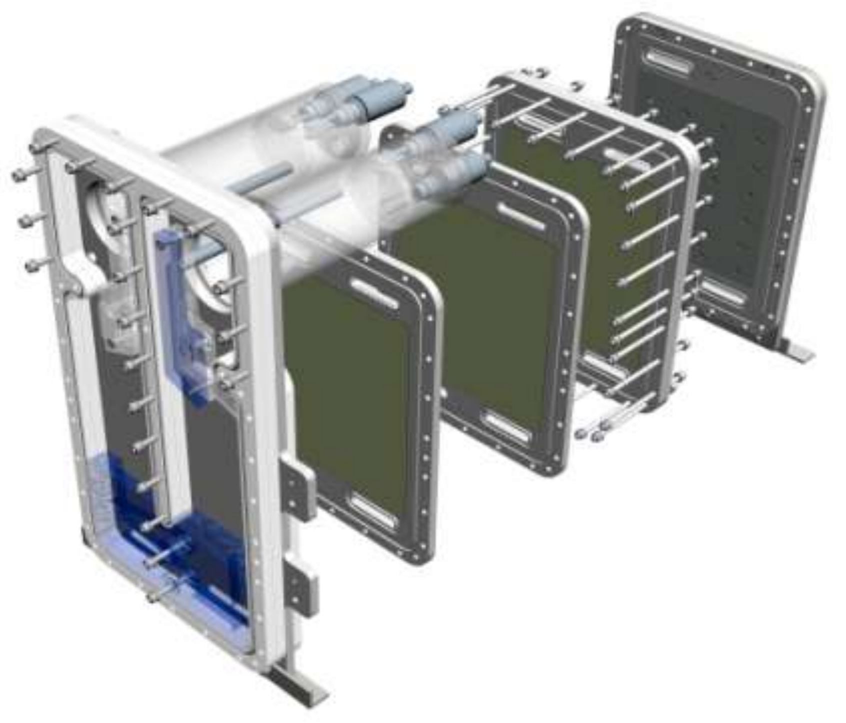
- Recent advances in materials technology can potentially reduce these barriers
- Changing environment of electricity supply + improvements could alter economics in high value O_2 and H_2 applications

Integrated Electrolyser



Colour codes:
Blue: oxygen
Green: hydrogen
Red: other gas
Black: gas and/or KOH
Purple: water

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
- Prof. Shusheng Pang, University of Canterbury, New Zealand
- 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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