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

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14th April 2011
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
Thermo-Chemical Conversion
- Torrefaction
- Carbonization
- Pyrolysis
- Combustion
- Gasification
- UCG

Materials
- Corrosion
- Nanofibers
- Metallurgy

Thermal Energy
- Geothermal
- Heat Transfer

Systems & Impacts
- Energyscape
- Carbon Economics

Other Energy
- CSG

CRL Energy Ltd
Thermo-chemical Conversion Methods

- Drying
- Torrefaction
- Carbonisation
- Pyrolysis
- Gasification
- Combustion

Oxygen

Temperature
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
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
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
Sawdust → Lock Hopper → Injection Auger → Pyrolyser → Inlet Plenum → Cyclones → Bio-char → Condensers → Bio-oil → Gas

Nitrogen → Nitrogen Heater

Faster reaction rate with higher temperature
Solid Fuel Combustion

- Fuel Performance Evaluation
- Emissions Testing
- On-Site Boiler Optimisation
- Plant Design
The CRL Energy Research Programme

- Stage 1: Understanding gasification of NZ coals (1996-2002)
- Stage 3: Introducing Biomass and electrolysis into the Mix (2008-2012)

Hydrogen in NZ’s Energy Future
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
An Energy System With Hydrogen

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

Cool Beer → Fridge → Electricity

Electrolyser or Fuel Cell → Electricity

Drive → Car → Hydrogen

Hydraulic Generator, Wind Turbine, Photovoltaics, Gasification → Electricity

Reformation, Natural Gas → Hydrogen

Hydro, Wind, Solar, Coal, Biomass → Energy Carrier
Alignment of CRL Energy’s Research Programmes

- **Services**
  - Cool Beer
  - Drive

- **Service Technologies**
  - Fridge
  - Car

- **Energy Carrier**
  - Electricity
    - Electrolyser or Fuel Cell
  - Hydrogen
    - Electrolyser or Fuel Cell

- **Transformer Technologies**
  - Hydroelectric Generator
  - Wind Turbine
  - Photovoltaics
  - Gasification
    - Coal
    - Biomass
  - Reformation
    - Natural Gas

- **Sources**
  - Hydro
  - Wind
  - Solar
  - Coal
  - Biomass
  - Natural Gas
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
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
Feasibility of Biomass

Cost of Carbon (per t CO2)
Feedstock Cost (per GJ)
Potentially Feasible Range
Future Cost of Carbon
Coal
Pine
Eucalypt
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 $\text{O}_2$ blown coal/biomass gasifier + electrolyser
Hydrogen and Syngas – Flexible, Valuable Products

**Feedstocks**

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

**Products**

- Chemicals
  - Oxo-alcohols
  - Methanol
  - Ammonia
  - Urea
- Hydrogen
- Electricity
- Clean Fuels (FT)
  - (WGS) (CO₂) (CCS)

**Advanced Co-Gasification Plant**

- Oxygen (O₂)
- Hydrogen (H₂)

**Electrolyser**
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
### Testing hydrogen separation membrane technologies

### Bench scale coal biomass char reactivities

### Effect of Ca on reactivities

### Modelling

<table>
<thead>
<tr>
<th>Year</th>
<th>2008</th>
<th>2009</th>
<th>2010</th>
<th>2011</th>
<th>2012</th>
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<tbody>
<tr>
<td>Air 50 kw gasifier lignite</td>
<td>Air 50 kw gasifier lignite, sub-bit woody biomass</td>
<td>30%O\textsubscript{2} 50 kw gasifier lignite, sub-bit woody biomass</td>
<td>+/- 30% O\textsubscript{2} from small electrolyser</td>
<td>100% O\textsubscript{2} from big electrolyser</td>
<td>New 100%O\textsubscript{2} or air 200 kw gasifier designed and built Running on lignite, sub-bit woody biomass</td>
</tr>
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</table>
Questions around Co-gasification

- Feedstock quality vs product quality
- Carbon balance
- Market incentives
- Economic implications
- Constraints
- Supply chain
- Sustainability
- Scale
- Optimum % of various blends
- Geographic implications
  - Landscape
  - Climate
  - Soil
  - Biodiversity
Coal:Biomass Co-gasification: Issues

- Dissimilar fuels
  - size
  - strength
  - compressibility
  - moisture %
- Variable syngas composition
- Variable reaction rates
  - density
  - expansion
- plant feed requirements
  - transportation
  - feed preparation
  - storage
- Handling
  - size
  - density
  - expansion
  - moisture %
  - strength
  - compressibility
  - moisture %
  - strength
  - Compressibility
  - Moisture %
  - Strength
  - size
  - density
  - expansion
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
Things did not always go quite to plan !!!
## Analysis of Feed Stocks

<table>
<thead>
<tr>
<th>CRL Ref</th>
<th>Description</th>
<th>Ash</th>
<th>Vols</th>
<th>Fixed Carbon</th>
<th>Total Carbon</th>
<th>Total Carbon</th>
<th>Total Carbon</th>
<th>Total Carbon</th>
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<tr>
<td>93/000</td>
<td>Pine</td>
<td>0.37</td>
<td>84.6</td>
<td>15.0</td>
<td>51.2</td>
<td>5.87</td>
<td>&lt;0.03</td>
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<tr>
<td>93/001</td>
<td>e niten</td>
<td>0.40</td>
<td>86.2</td>
<td>13.4</td>
<td>50.2</td>
<td>5.89</td>
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<tr>
<td>93/002</td>
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<td>51.8</td>
<td>42.2</td>
<td>62.6</td>
<td>4.50</td>
<td>0.68</td>
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<tr>
<td>93/003</td>
<td>Sub-bit</td>
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<td>44.7</td>
<td>49.1</td>
<td>68.8</td>
<td>4.75</td>
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<td>L-P 20/80 Char</td>
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<td>91.8</td>
<td>90.4</td>
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<td>93/006</td>
<td>L-P 80/20 Char</td>
<td>10.7</td>
<td>7.0</td>
<td>82.3</td>
<td>83.9</td>
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<td></td>
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<tr>
<td>93/007</td>
<td>S-P 20/80 Char</td>
<td>5.2</td>
<td>4.8</td>
<td>90.1</td>
<td>88.8</td>
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<tr>
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<tr>
<td>93/009</td>
<td>S-P 80/20 Char</td>
<td>10.1</td>
<td>3.3</td>
<td>86.6</td>
<td>86.1</td>
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<tr>
<td>93/010</td>
<td>100% Pine Char</td>
<td>1.9</td>
<td>2.1</td>
<td>95.9</td>
<td>94.7</td>
<td></td>
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</tbody>
</table>
• 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
Lignite

P. radiata

Sub-bituminous

E. nitens
Lignite increases reactivity

Lignite / P. radiata

Sub-bituminous / P. radiata

Lignite / E. nitens

Sub-bituminous / E. nitens

Sub-bituminous decreases reactivity
Effect of Gasification Temperature on Reactivity

![Graph showing the effect of gasification temperature on reactivity. The graph plots 1/T (°C⁻¹) on the x-axis and reactivity dX/dt (X=0.5) [s⁻¹] on the y-axis. Different symbols represent different conditions or samples, such as L, L/E, L/P, S, S/E, S/P, E, and P. The graph illustrates the relationship between temperature and reactivity.]
Effect of Gasification Temperature on H$_2$/CO Ratio
Calcium Effect

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

<table>
<thead>
<tr>
<th></th>
<th>$T_{50}$ (min)</th>
<th>$H_2/CO$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lignite</td>
<td>22.8</td>
<td>17</td>
</tr>
<tr>
<td>Acid Washed</td>
<td>99.5</td>
<td>2.8</td>
</tr>
<tr>
<td>Calcium Reloaded</td>
<td>22.5</td>
<td>17</td>
</tr>
<tr>
<td>NZ Lignite</td>
<td>22.8</td>
<td></td>
</tr>
<tr>
<td>German Brown Coal</td>
<td>33.5</td>
<td></td>
</tr>
<tr>
<td>Australian Brown Coal</td>
<td>33.4</td>
<td></td>
</tr>
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</table>
Effect of Calcium on Lignite Reactivity and Syngas Composition
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
- *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*
The CRL Energy Gasifier
Gasifier Detail

Bed: depth of 300 mm
Air flow in: 60 m³/h
Gas flow gasifier exit: 130 m³/h
Coal size: 3 – 10 mm
Coal feed: 18 kg/h
Steam feed: 5 kg/h
Temperature: 950 – 980 °C
Control system: Delta V
The Fluidised Bed Gasifier

Operation

- Time to steady gasification ~ 2 h
- Reliable optimal operation conditions
- Advanced control system
- Regular quality syngas
  \[15\% \text{H}_2, 15\% \text{CO}_2, 12\% \text{CO}, <1\% \text{CH}_4 \text{ plus N}_2.\]
- 2000 h + operation
- Continuous (1 week) operation
Delta V
Particulate Removal

2 stage particulate removal system
  – High efficiency cyclone (95%)
  – Venturi scrubber (5%)

Low yields of tars and condensables recovered
Syngas Clean-up Line
Sulfur Gases

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

Amine scrubber (MDEA)  
Proprietary scavenger  
Packed column, counter flow caustic wash
Syngas Clean-up Line

Gas flow direction through venturi

pH v time

Conductivity v time

Suspended solids v time
Effect of Biomass Addition on Gasifier Control

100% lignite

100% sub-bituminous
## Effect of Biomass Addition on Syngas Composition

<table>
<thead>
<tr>
<th>Fuel</th>
<th>% Gas</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H₂</td>
<td>CO</td>
<td>CO₂</td>
<td>CH₄</td>
</tr>
<tr>
<td>100% lignite</td>
<td>15</td>
<td>12</td>
<td>15</td>
<td>&lt;1</td>
</tr>
<tr>
<td>80% lignite – 20% <em>P. radiata</em></td>
<td>9</td>
<td>11</td>
<td>15</td>
<td>1.5</td>
</tr>
<tr>
<td>80% lignite – 20% <em>E. nitens</em></td>
<td>8</td>
<td>10</td>
<td>14</td>
<td>1.5</td>
</tr>
<tr>
<td>100% sub-bituminous coal</td>
<td>11</td>
<td>15</td>
<td>12</td>
<td>1</td>
</tr>
<tr>
<td>80% sub-bituminous coal – 20% <em>P. radiata</em></td>
<td>14</td>
<td>16</td>
<td>13</td>
<td>2</td>
</tr>
<tr>
<td>80% sub-bituminous coal – 20% <em>E. nitens</em></td>
<td>11</td>
<td>13</td>
<td>14</td>
<td>1.5</td>
</tr>
</tbody>
</table>
- Coal/Biomass + O₂ = CO₂ + heat
- Coal/Biomass + heat = C (char) + volatiles

- C + H₂O = CO + H₂

- CO₂ + C = 2CO (boudouard)
- CO + 3H₂ = CH₄ + H₂O (methanation)
- CO + H₂O = CO₂ + H₂ (WGS)
- CH₄ + H₂O = CO + 3H₂ (steam reforming)
Syngas Clean-up Line
Water Gas Shift Reactor

- CO + H₂O ⇌ H₂ + CO₂ ~40 kJ/kg-mol
- Single high temperature catalyst bed (340 to 360°C)
- Iron Oxide Catalyst
- Gas flow rate 5.0 - 2.4 m³/h
- Regular quality syngas
  - 22% H₂, 20% CO₂, 5% CO, <1% CH₄
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 \( \text{H}_2 \) buffer storage system feed
- Overall electrical conversion efficiencies 50% HHV

- Fuel \((\text{H}_2)\) is fed into the anode
- Oxidant \((\text{O}_2 \text{ air})\) is fed into cathode
- React in presence of KOH
- \( \text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^- \)
- \( 2\text{H}^+ + 2\text{e}^- + \text{O}_2 \rightarrow \text{H}_2\text{O} \)
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 O₂ Blown Gasifier

- Counter flow caustic wash
- WGS reactor
- H₂ separation membrane systems
Specifications

50kw unit
Fluidized bed
O_2 or air blown
Biomass capability (up to 45%)
**Modular design**
Max working temperature 1000°C
Ambient pressure system
Regular quality syngas (>20% H_2)
WHY?

- ASU 15-20% electrical output
- Roaring 40s
- Use of green H\textsubscript{2} and O\textsubscript{2} with biomass and coal interesting
- Green input - reduce process emissions
- If CCS high - minimise CO to CO\textsubscript{2} shift and produce as much H\textsubscript{2} for optimum FT
Benefits and Barriers

- Electrolysis provides a relatively simple means of producing high purity $\text{O}_2$ and $\text{H}_2$ 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.
Product Costs vs Allocation of Electrolysis Cost

NZ$/kWh

% Allocated to Hydrogen Production

- Syngas
- Hydrogen
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
Integrated Electrolyser

- Operates at nominal 50Vdc
- Fully self contained
- Wide operating range
- Fast turn-up and turn-down
- O₂ and H₂ at required quality
- Produces 0.4 Nm³/hr O₂ (0.8 Nm³ H₂)
- Very low peripheral power demand
- Efficiency of 70% HHV without any special electrode surface preparation
- Target module level efficiency of > 80% HHV
2009 - To Date

- PhD student
- Masters Student
- 2 Journal papers
- 4 Conference papers and presentations
- 3 Workshops
- Developed several international collaborations
Future Work

- Prove concept - complete gasifier-electrolyser integration
- Complete test run schedule with 100% O₂ and 45% biomass
- Develop new test programme
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
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
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.