



## Lignin and other sustainable carbon sources as metallurgical coal substitutes

**Samane Maroufi** - Samane is part of the SMaRT@UNSW team that is involved in a range of activities one of which is developing alternative sources of carbon for steel making.



**Geoff Bell** - Geoff is the Australian representative for the IEA Bioenergy task 42 and is the CEO of Microbiogen – an industrial biotechnology company that develops superior yeast biocatalysts for biofuels and other industrial applications.





## Lignin and other sustainable carbon sources as metallurgical coal substitutes



Geoff Bell

## Introduction to SMaRT@UNSW's work on metallurgical coal replacement

## The project

### A collaboration between SMaRT@UNSW and Microbiogen

#### SMaRT@UNSW

- The lead technical group in the collaboration headed by Professor Veena Sahajwalla
- Has already successfully commercialised Polymer Injection Technology
- EAF's can now inject blends of coke and rubber that results in improved slag foaming and efficiency
- The technology has so far been used in over 84,000 heats and utilised 2.4 million recycled tyres

#### Microbiogen

- Has been working in the area of 2G bioethanol for over 15 years – organism and process development
- Utilised NREL pre-treatment technology to produce lignin for trials in the SMaRT@UNSW labs
- Successfully developed superior ethanol yeast biocatalysts – Australian Export Award winner



**Lignin and other sustainable carbon sources as  
metallurgical coal substitutes**



Samane Maroufi

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## Background

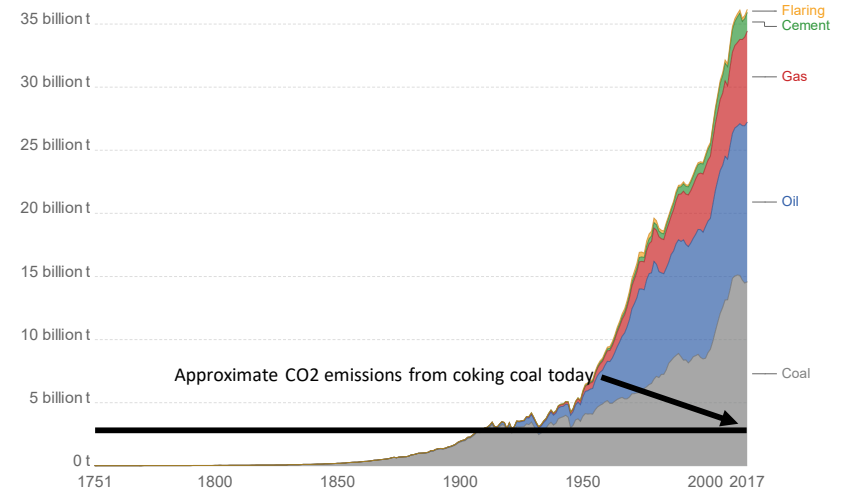
### Coal represents the largest single source of fossil fuel CO<sub>2</sub> emissions

#### Most coal is used for producing power, however...

- Approximately 1.1 billion tonnes of met coal (15% of total coal production) is consumed annually. This means that around 3 billion tonnes of CO<sub>2</sub> comes from the steel making process.
- Due to the energy requirements to produce iron and steel, about 27% of CO<sub>2</sub> emissions of the global manufacturing sector come from iron and steel production.

CO<sub>2</sub> emissions by fuel type, World

Annual carbon dioxide (CO<sub>2</sub>) emissions from different fuel types, measured in tonnes per year.



Source: Global Carbon Project (GCP); CDIAC

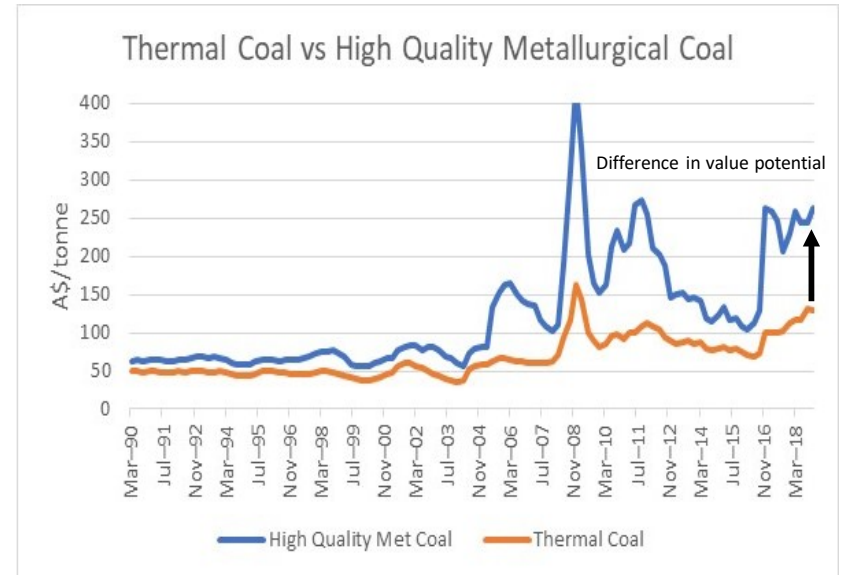
OurWorldInData.org/co2-and-other-greenhouse-gas-emissions/ • CC BY

## Background cont.

### Metallurgical coal is higher value but must satisfy more requirements

#### Coking coal sells around double the price of thermal coal

- Thermal coal's value simply comes from the value of the energy potential utilised in a power plant
- Met coal must also be a reductant and is also used for physical support (structure in a blast furnace)
- There are 4 main types of steel-making process:
  - Blast furnace-basic oxygen (BF-BOF)
  - Smelting reduction iron in BOF (SRI-BOF)
  - Direct reduction iron – electric arc furnace (DRI-EAF)
  - Direct smelting of scrap (Mini-mill)



Source Data: Resources and Energy Quarterly – March 2019

## The opportunity

### Substitutes could present an economic and environmental opportunity

#### Steel industry is looking for opportunities to diversify away from coal

- Cost of coking coal has been rising
- Depletion of high-quality coking coal worldwide
- Tightening environmental regulations regarding CO<sub>2</sub> generation
  
- However, more sustainable alternatives must be able to deliver a substitute:
  - Without large associated capital costs
  - Reduce the carbon footprint without seriously affecting process efficiency

# Steel making “101” – Background to steel making

Used in a wide range of areas

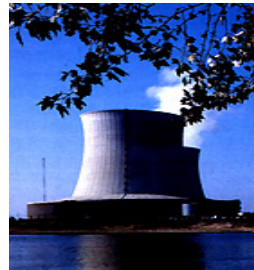
*For everyday uses: cans, pots, containers, etc...*



*At the heart of food preservation...*



*In energy...*



*In communications...*



*In health...*





## Steel making “101” – Background to steel making

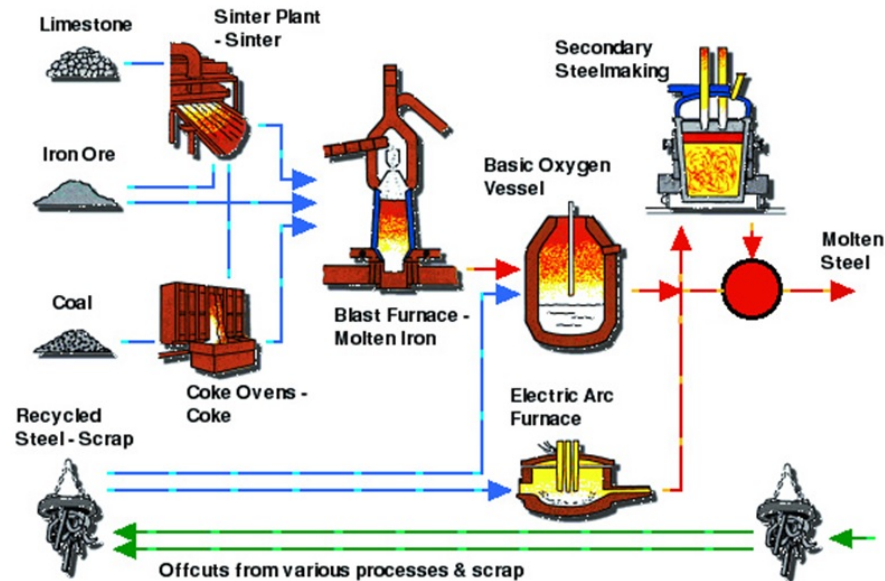
There are a wide range of steel types – each with their own elements

*Iron and carbon are the main ingredient in various forms steels, but the various types of steels contain other elements as well. Sometimes these elements are unwanted; other times they're intentionally added.*

	Carbon	Manganese	Phosphorous	Sulfur	Silicon	Nickel	Chromium
<b>Cast Iron</b>	3.5%	0.5%	0.13%	0.13%	1.2%	0	0
<b>Wrought Iron</b>	0.035%	0.075%	0.075%	0.1%	0.1%	0	0
<b>High strength steel</b>	0.25%	1.65%	0.04%	0.05%	0.12%	2.5%	0.8%
<b>Stainless Steel</b>	0.08%	2%	0.04%	0.03%	0.75%	8%	18%

# Steel making “101” – Background to steel making

## Typical iron and steelmaking process



# Steel making “101” – Background to steel making

## Coke production for ironmaking

*Metallurgical coke is produced by the destructive distillation of coal in coke ovens. Prepared coal is heated in an oxygen-free environment until most volatile components in the coal are removed. The material remaining is a carbon mass called coke.*



# Steel making “101” – Background to steel making

## Coke properties - Physical

- *The ability of coke to withstand breakage at room temperature which reflects coke behaviour outside the blast furnace and in the upper part of the blast furnace.*
- *The potential of the coke to break into smaller size under a high temperature CO/CO<sub>2</sub> environment that exists throughout the lower two-thirds of the blast furnace.*

*Coke is the most important raw material in steelmaking in terms of its effect on operation and product quality.*

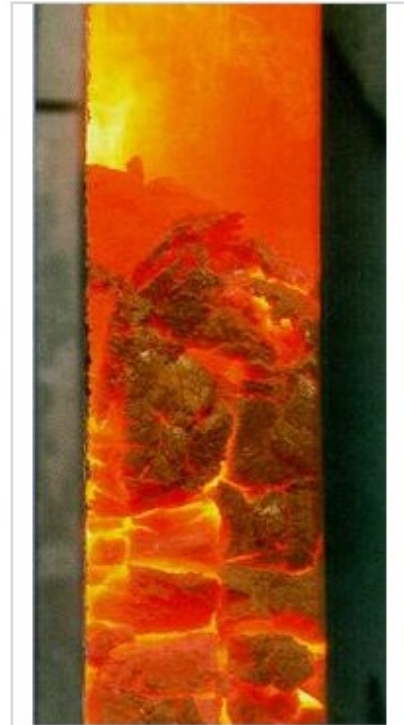


# Steel making “101” – Background to steel making

## Coke properties - Chemical

- *The most important chemical properties are moisture, fixed carbon, ash, sulfur, phosphorus, and alkalies.*
- *Fixed carbon is the fuel portion of the coke; the higher the fixed carbon, the higher the thermal value of coke. The other components such as moisture, ash, sulfur, phosphorus, and alkalies are undesirable as they have adverse effects on energy requirements, operation, hot metal quality, and/or refractory lining*

*Coke is the most important raw material in steelmaking in terms of its effect on operation and product quality.*



# Steel making “101” – Background to steel making

## Coke roles...

- **Physical role:** *In blast furnaces, coke influences the gas distribution in the shaft, provides mechanical support to the charge column and permeable bed below the cohesive zone.*
- **Chemical role:** *Coke produces and regenerates the reducing gases to reduce iron and other oxides and provides carbon to carburise the molten iron.*
- **Thermal role:** *Carbon as a source of fuel providing the heat and energy required for endothermic reaction and melting of iron and slag.*

## Three met coal substitutes tested

### ➤ Waste CDs

CD production and use has been declining since 2000

Potential to utilise in steel making rather than going to landfill

Total potential estimated at about 800,000 tonnes of CDs (0.01%)

### ➤ Macadamia Nut Shells

A growing industry with about 375,000 tonne potential per year

Potential to upgrade the value of a low value side stream from agriculture

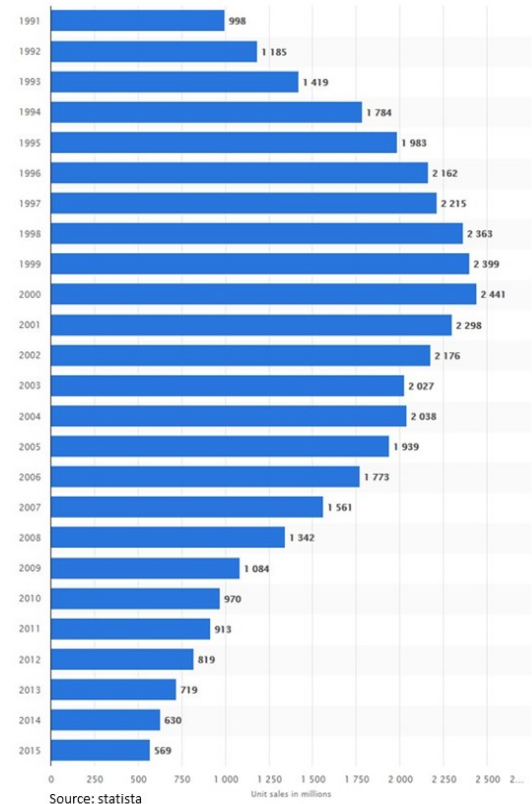
### ➤ Lignin from 2G bioethanol

Massive potential but little short-term potential due to early industry stage

Potential to upgrade a major carbon stream and enhance economics

10% gasoline replacement = 230 million tonnes of met coal lignin/year

Unit sales of DC's worldwide from 1991 to 2015  
(in millions)



## Composition of the substrates – significant differences

### Four substrates = 4 different chemical compositions

- Elemental composition of the substrates was determined by combustion/XRF analysis.
- Lignin has a relatively high lime content of 0.5% which is a positive for steel making as it can be used as a fluxing agent.
- The highest ash content was found in Met Coal of which 60% is silica.

	Met Coal	Waste CD	Macadamia Shells	Lignin (average)
Solid Carbon (wt%)	85.5	19.8	20.8	20.0
Ash (wt%)	11.5	2.0	0.2	6.1
Total Carbon (wt%)	85.5	77.0	48.0	40.7



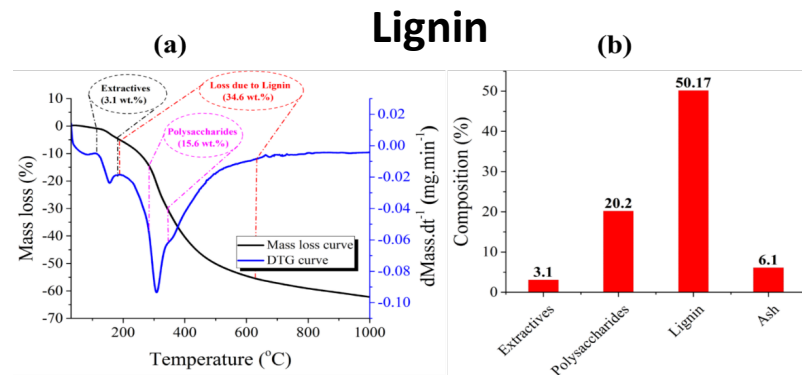
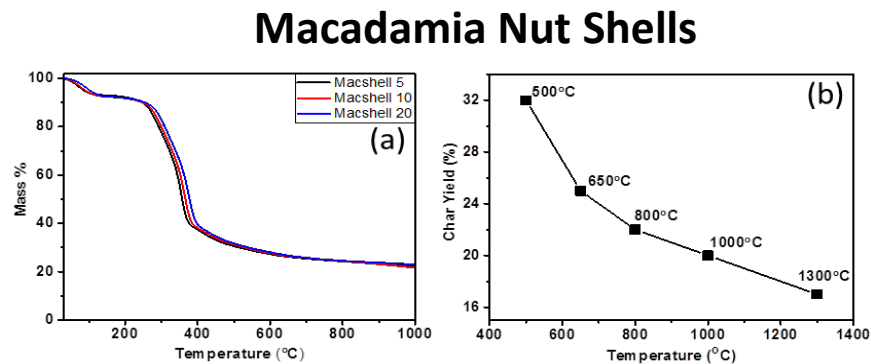
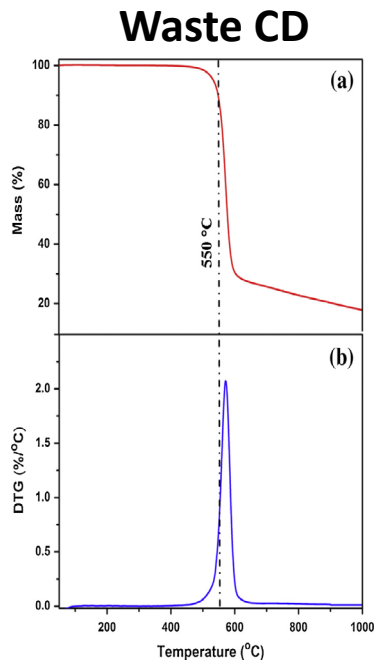
## Selected results from trials

### Two sets of trials were carried out using the various reductants

- The team at the SMaRT@UNSW centre carried out two sets of trials on the various sustainable reductants. A full review of the results can be read in the report entitled “Alternative sustainable carbon sources as substitutes for metallurgical coal”
- Two tests carried out were:
  - Thermal degradation of C-bearing materials. This test was designed to investigate the material’s behavior at various temperatures
  - Iron oxide reduction using C-bearing materials. This test was to determine the effectiveness of the reduction of iron oxide to metallic iron using the various carbon bearing materials

## Thermal degradation

- Each material was tested via a thermogravimetric analysis to determine the thermal degradation of each material
- Waste CDs were tested in a nitrogen atmosphere at a heating rate of 10 degrees C per minute.
- Most of the degradation was observed at around 550 degrees C.
- Lignin had flatter sloped mass loss curve.

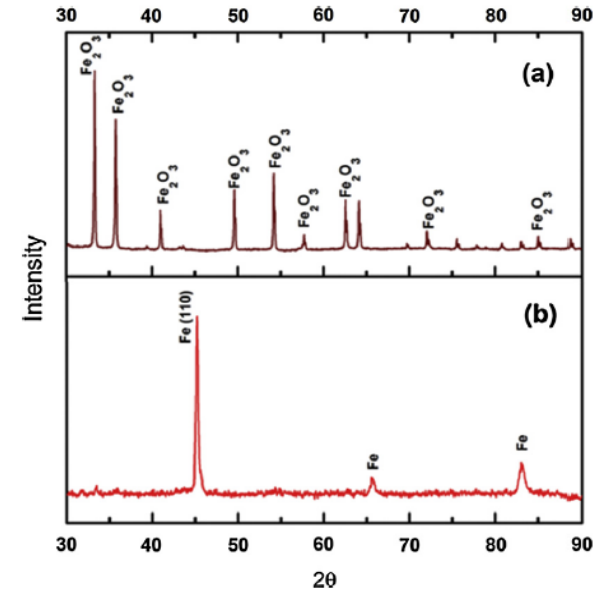


# Iron oxide reduction performance – Waste CD

## Waste CD – complete reduction at 1400 degrees C

- Utilising the pyrolyzed CD char as the reductant resulted in what appears to be a 100% conversion of iron oxide into Fe metal.

XRD spectra of a) hematite and b) reduced sample at 1400oC temperature

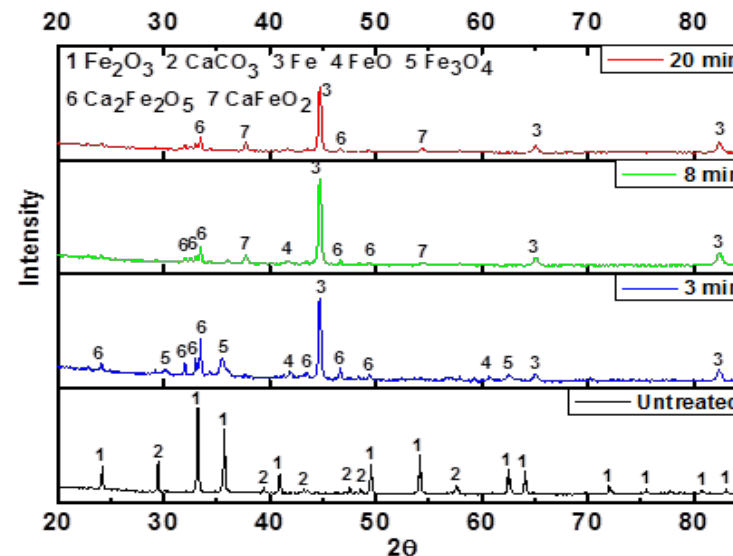


## Iron oxide reduction performance – Macadamia Nut Shells

### Macadamia nut shells – complete reduction after 20 minutes – all temps

- Testing was carried out at 4 different temperatures – 1000, 1100, 1200 and 1300 degrees C.
- Testing was also carried out over 3 different reduction times – 3, 8 and 20 minutes.
- The higher the temperature the lower the time taken to reduce the iron oxide.
- At all temperatures, after 20 minutes, metallic iron was the major phase present.

XRD spectra for untreated pellets and pellets reduced at 1200 oC showing the transformation of iron oxide in composite pellets into metallic iron

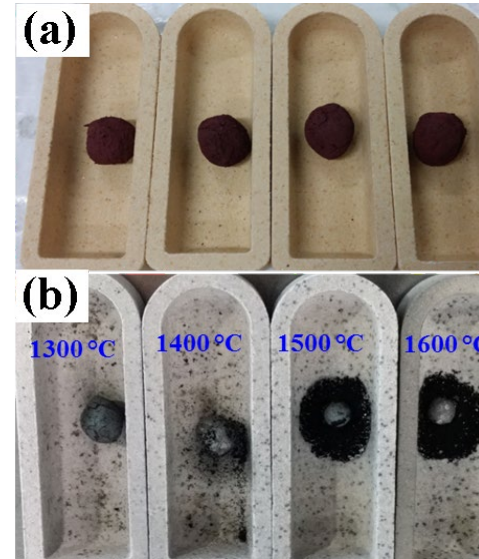


## Iron oxide reduction performance – Lignin

### Lignin – Sponge Iron at lower temps, complete reduction at higher temps

- At the lowest temperature (1300), the largest volume of metal was produced with no carbon around it. This is known as “sponge iron” where the lignin is still trapped as free carbon inside the sinter. This type of material is an important feedstock into many Electronic Arc Furnace (EAF) and Blast Furnaces (BF) around the world.

a) densified pellets of iron (III) oxide/LRC (ratio of 3 g-atoms of carbon to 1 g-mole of iron(III) oxide), b) reduced pellets at different temperatures

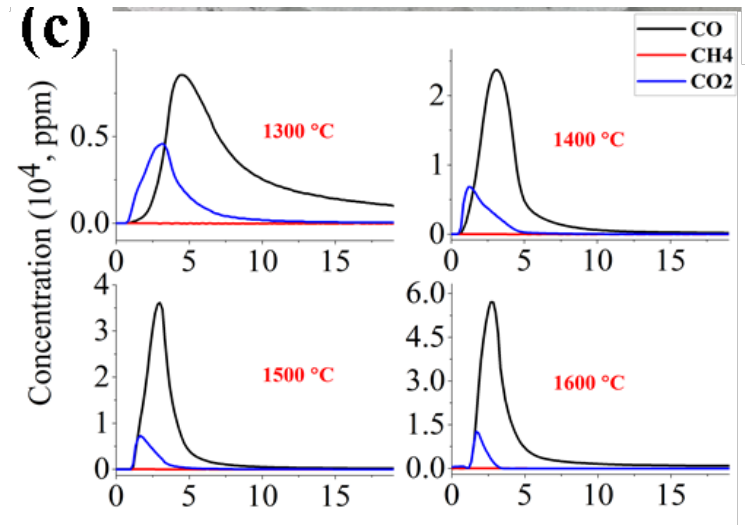


## Iron oxide reduction performance – Lignin cont.

### Lignin – Sponge Iron at lower temps, complete reduction at higher temps

- Gas products from the reduction process was measured for each of the 4 different temperatures
- The amount of carbon monoxide produced can be used as an indicator of the completion of the reduction process. In the case of lignin, at temperatures above 1500 degrees C the reduction reached equilibrium. This is a typical duration for most types of carbon

c) gas product analysis of iron(III) oxide reduction



# Lignin could be a met coal substitute

## Conclusions so far...

- There are several potential alternative sustainable alternatives to metallurgical coal
- To really make a difference, lignin presents the greatest opportunity due to potential future volumes
- Testing of lignin by the SMaRT@UNSW centre has shown that:
  - The thermal transformation of lignin resulted in a reasonable yield of solid carbon
  - Although composition varied, most detected impurities in the lignin would be tolerated or be advantageous in making steel
  - That the reduction of pure iron oxide required a relatively low value of activation energy
  - At high temps, reduction is complete and even at low temps, a typical sponge product is produced



Geoff Bell

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**Opportunities for metallurgical coal  
replacements and benefits for 2G biofuels  
in Australia**



# Lignin as a met coal replacement could be “win-win”

## Benefits to the environment and economics

- One of the keys to accelerating the deployment of 2G bioethanol is to improve project economics
- Assuming that lignin produced from a 2G ethanol plant could be sold as a met coal replacement then...
- ... a 2G ethanol plant could increase its revenues over 10% due to the lignin value doubling
- ... at essentially little or no additional production cost
- Using lignin for steel making would lower the long-term risk of needing met coal substitutes
- As met coal becomes more difficult to access lignin as a met coal replacement could result in lower steel costs

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Questions?

Presentations will be circulated to attendees after the webinar.



THANK YOU!