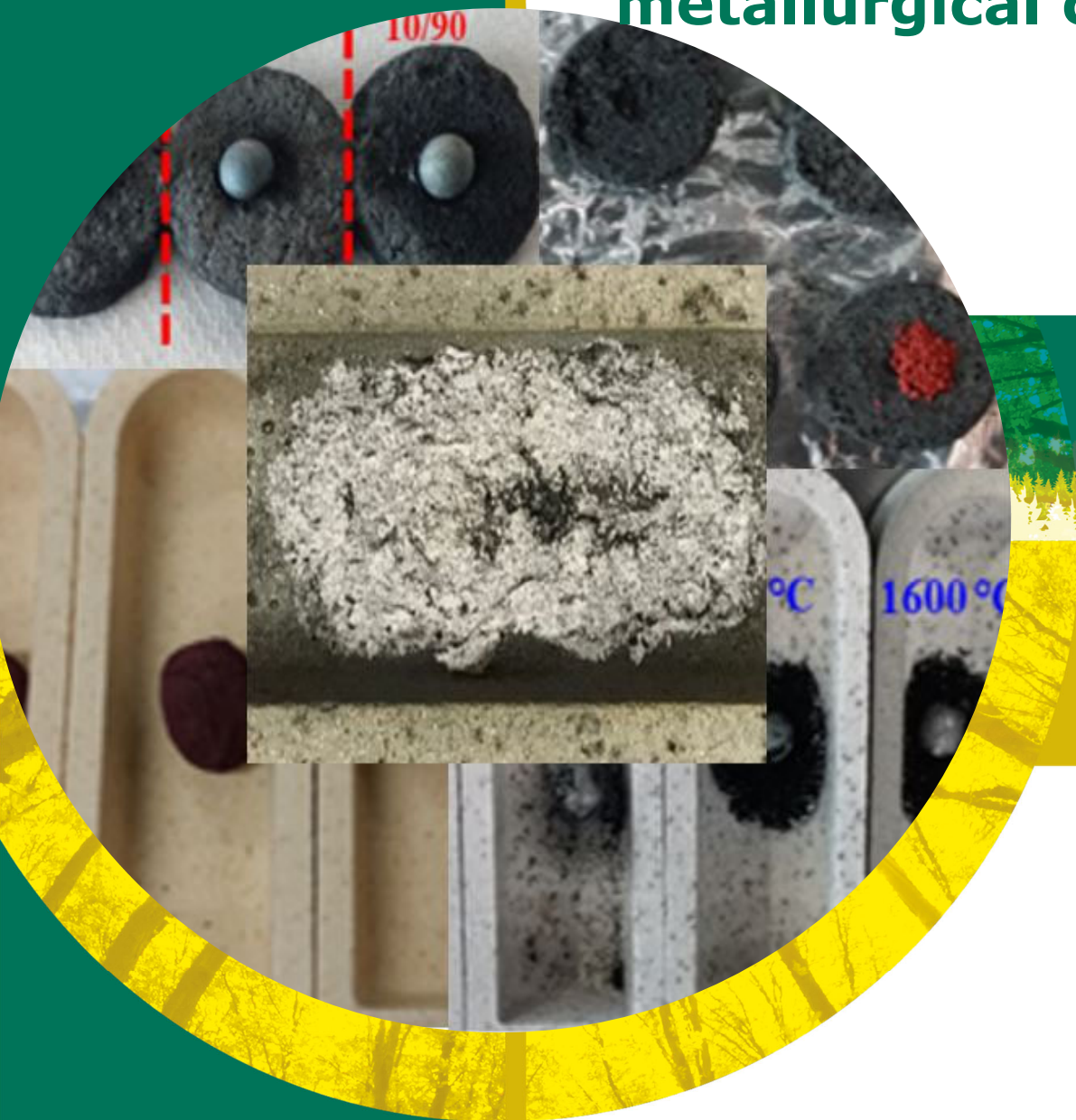


# Alternative sustainable carbon sources as substitutes for metallurgical coal



Images of testing of various renewable coking coal substitutes carried out at the SMaRT@UNSW laboratories in Sydney

**IEA Bioenergy**

IEA Bioenergy: Task 42

Biorefining in a Circular Economy

# Alternative sustainable carbon sources as substitutes for metallurgical coal

Based on original collaboration work between the SMaRT@UNSW Centre and Microbiogen Pty Ltd

Authors

Scientia Professor Veena Sahajwalla (FAA FTSE HonFIEAust CPEng)

Samane Maroufi

Geoffrey Bell: CEO Microbiogen Pty Ltd (B.Sc, B.Ec, MAppFin)

Dr Philip Bell – Head of research at Microbiogen Pty Ltd

Dr Isabella De Bari – Biorefineries and Green Chemistry

Copyright © 2019 IEA Bioenergy. All rights Reserved

ISBN, 978-1-910154-67-0

Published by IEA Bioenergy

# Executive Summary

## Steel production is a major contributor to CO2 emissions

Each year over 1 billion tonnes of metallurgical coal (coking coal) is utilised to produce most of the 1.7 billion tonnes of steel produced worldwide. Renewable alternatives need to be developed so that current fossil derived coking coal can be substituted by renewables at reasonable cost. This would be a significant step forward in addressing the underlying cause of climate change

## A collaboration lead by UNSW SMaRT@UNSW Centre has tested alternatives

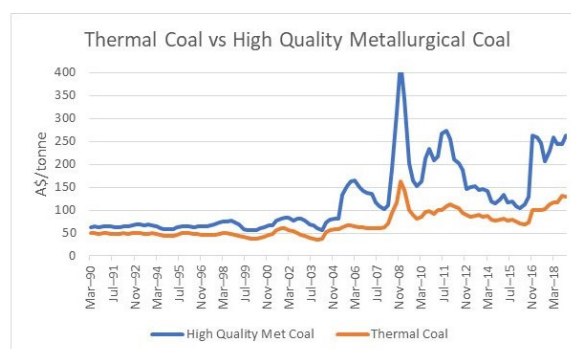
The SMaRT@UNSW Centre based at the University of New South Wales is a leading developer of renewable solutions in the field of material sciences. Lead by Professor Veena Sahajwalla and in collaboration with Microbiogen, a series of experiments were carried out to test the potential of utilising waste compact disks, macadamia nut husks and lignin derived from a lignocellulosic bioethanol process. The SMaRT@UNSW team have a high level of expertise in the area of coke substitutes with the successful development, trialling and commercialisation of Polymer Injection Technology where waste tyre rubber effectively replaces fossil coke. This technology is now used in many parts of the world with over 2.4 million tyres used so far.

## Tests show lignin can be a suitable substitute for metallurgical coal

The results from tests of the lignin showed that the impurities contained can be advantageous or at least tolerated by steel manufacturers. It was found that the lignin was also a suitable substitute at a range of temperatures with typical sponge iron product being produced.

## Lignin has the greatest potential of products trialled

Of the three products trialled in the program, lignin has the greatest potential to reduce non-renewable coke consumption. CDs and macadamia nuts have potential to contribute to reduced fossil coke utilisation. However, due to limited supply potential they are unlikely to make a significant difference into the future. On the other hand, calculations suggest that if 10% of the world's gasoline demand were replaced with ethanol produced from lignocellulosic sources approximately 20% of fossil coke consumption could be replaced by renewable lignin.



Source Data: Resources and Energy Quarterly – March 2019

## Lignocellulosic biorefinery revenues could rise over 10%

Not only would the use of lignin derived from lignocellulosic sources reduce the need for fossil coke, it could significantly enhance the economics of lignocellulosic bioethanol production. Metallurgical coal typically trades at a premium to that of thermal coal. In replacing the relatively low value option of burning lignin in the lignocellulosic bioethanol refinery, the effective value of the lignin could be doubled if sold as a metallurgical coal replacement (ignoring any potential carbon credits). In total, lignocellulosic biorefinery revenues could be lifted by between 5.8% and 11.2% depending upon whether higher or lower met coal price assumptions are utilised

## About this report

This report has been prepared as a collaboration between the SMaRT@UNSW Centre at the University of New South Wales that is headed by Professor Veena Sahajwalla and supported by her team and Microbiogen Pty Ltd with the technical work headed by Dr Philip Bell (Head of Research), and the economic analysis headed by the CEO Mr Geoffrey Bell.

The authors would like to thank the members of Task 42 for their input and review of the commercial and technical analysis.

## Introduction – steel making a major source of CO2

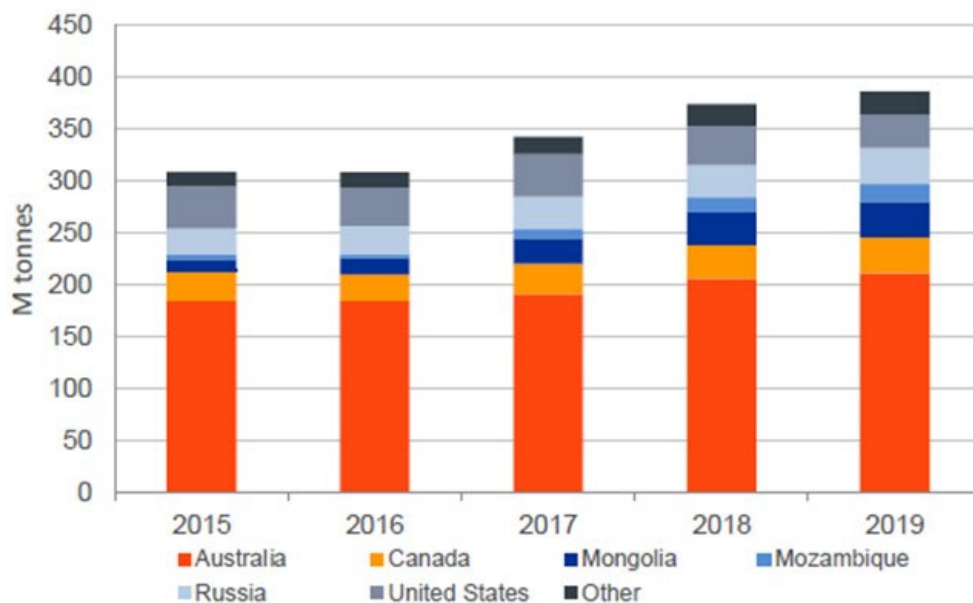
### Global Steel Production: Over 1 billion tonnes of coking coal required

The world currently produces approximately 1.7 billion tonnes of steel per year. Most of this steel production requires coking coal to reduce the iron ore and generate a steel product. Typically, 1 tonne of steel requires 770kg of metallurgical coal to make the conversion possible.

In total approximately 1.1 billion tonnes of coking coal are consumed annually adding significant quantities of CO2 to the atmosphere from fossil carbon sources. The steel industry today is a significant contributor to CO2 emissions and alternative sources of coking coal could help mitigate the industry's reliance on non-renewable sources of carbon.

China is the world's largest producer of steel and consumer of coking coal. In terms of trade, Australia is the largest exporter of coking coal by a considerable margin. Other significant exporters include Canada, Mongolia and the US.

### Estimated Global Metallurgical Coal Production 2016–2018 by Country



Source: AME

Figure (1)

## Steel production is a major source of CO<sub>2</sub> emissions

Steel manufacturing is one of the most energy-intensive industries worldwide [1]. The average energy consumption in the iron and steel industry is about 10% of the national gross energy consumption in countries such as China [2]. Nearly 70% of total energy required in steelmaking industry is covered by coal-based thermal power stations [3]. In 2013, around 7.8 billion tonnes of coal was produced globally of which almost 15% was utilized only by iron and steelmaking industry (World Coal Association, 2014). With increasing annual demand for steel worldwide, steel production is expected to reach ~2.2 billion tonnes of crude steel in 2050. With ever increasing demand for steel, leading to use of more and more coking coal for its production, there is a risk of complete depletion of suitable coal reserves.

Owing to its reliance on carbon-based fuel and reductant, iron and the steelmaking industry is one of the largest industrial sources of CO<sub>2</sub> emission, accounting for ~27% of global CO<sub>2</sub> emissions from the manufacturing sector [4]. The rapid depletion of natural resources and highly rising costs, as well as the tightening of environmental regulations regarding CO<sub>2</sub> generation, are driving steelmaking industries to seek new ways to reduce their dependence on coal and replace raw material fuels with alternative carbon sources while lowering CO<sub>2</sub> emissions and reducing carbon footprint without seriously affecting the process efficiency. In recent years, there has been considerable effort towards developing alternative steelmaking routes to pass the rigorous environmental regulations and to avoid large capital costs by using alternative carbon sources which are capable of performing some of the functions of coke.

Moreover, with depleting natural resources and rapidly increasing demand for steel worldwide, beneficiation and utilization [4, 5] of low-grade materials becomes more important for the steelmaking industries. Currently, the direct use of waste materials is considered a more appropriate approach compared to the conventional natural resources in terms of environmental protection and cost effectiveness. An opportunity exists to utilize waste plastic (polymer) and other products that would normally have limited or no recycling options, and that currently go to landfill, to manufacture a replacement for coke.

## Background - understanding steel making

### Four main methods to make steel

The steel making processes are classified into four main technologies; namely, blast furnace-basic oxygen furnace (BF-BOF), smelting reduction iron in BOF (SRI-BOF), direct reduction iron in electric arc furnace (DRI-EAF), and direct smelting of scrap in EAF (also known as mini mill) [7-9]. For each technology, the carbon source performs a particular task. For instance, in the blast furnace, the carbon source is primarily used as fuel and reducing agent but also provides physical support in a packed bed structure. The main source of carbon is a well-graphitizing carbon (i.e., coke); some coal is also used in the main furnace and in some other auxiliary operations. In the EAF mini-mill, the carbon is mainly used to reduce iron oxide and to make a foamy slag.

In the blast furnace, the fuel (i.e., coke) should have specific physical and chemical characteristics and must fulfil strict operational requirements. Since biochar and coke have different characteristics, the transition toward biochar in the blast furnace represents a significant challenge. One of those challenges is the high reactivity of biochar which leads to specific reactions of low exothermic energy that reduces the furnace temperature [10]. As such, investigations in this regard have been restricted to study the partial replacement of coal with biochar.

While the use of biochar in the blast furnace is still under debate, their use in the EAF mini mill constitutes a great opportunity. The EAF mini mill has significant tolerance to adapt with biochar

and plastics. Furthermore, enhanced process efficiency and performance are achieved with such sources of carbon. Due to its high reactivity, biochar shows desirable interactions with slag leading to an increase in the volume of the foamy slag, which is proved to significantly reduce the energy consumption and equipment damage [11, 12].

Carbonaceous materials injected into EAF furnaces have two key roles. Gases produced during carbon/slag reactions lead to slag foaming and provide insulation and energy efficiency; and solid carbons participate in reduction reactions of iron oxide to produce metal. Extensive research has been carried out at the SMaRT@UNSW Centre on the reduction of iron oxide rich slags using coke/polymer blends [4, 5], with coke contributing solid carbon and polymers providing gaseous volatiles and reductants.

## **Three metallurgical coal alternatives tested**

### **Initial substitute to metallurgical coal has already started deployment**

Professor Veena Sahajwalla and the SMaRT@UNSW Centre at the University of New South Wales have already enjoyed some success in exploring and commercialising alternatives to fossil coking coal as a source of carbon in the production of steel.

In the SM@RT@UNSW group, in-depth investigations have been carried out on slag foaming and carbon dissolution from waste plastics into liquid steel at 1550°C. Experiments compared the behavior of polymer/coke blends containing up to 50% plastics with 100% metallurgical coke. Slag foaming performance of waste blends was found to be better than metallurgical coke [5]. This research has established fundamental pathways for recycling polymers as resources in EAF steelmaking which resulted in developing and commercializing Polymer Injection Technology (PIT), which enables EAFs to inject blends of coke and rubber in place of coke, resulting in improved slag foaming and hence furnace efficiency. PIT has been used as a standard practice in Australia steelmaking industry in more than 84,000 heats, consuming over 2.4 million recycled tyres in the process. PIT has been granted patent protection in most major industrial countries and it has been commercially implemented at UMC Metals, Thailand since May 2011, at SeAH Besteel, Korea since April 2014, at Celsa Group's plant in Cardiff, UK since October 2014 and at Celsa Nordic in Norway since December 2015.

The benefits of using PIT, were statistically proven during the commercial implementation trials on each site. This innovation offered an excellent opportunity to improve furnace efficiency with a positive impact on the environment through energy savings and the transformation of waste streams into value added products.

However, waste polymers cannot completely replace coke as these produce very small amounts of solid residues, an essential requirement for iron oxide reduction. Agricultural waste and by-products from agricultural resources can be considered as a source of solid carbon, to replace coke as a reductant for iron oxide.

### **Three alternative carbon sources that could replace met coal tested**

In this report, three potential alternative sources of carbon have been considered. That is:

- (1) Waste compact disks (DC)
- (2) Macadamia nut shells
- (3) Lignin from an ethanol biorefinery (LR)



### (1) Waste compact disks (CD)

One potential source of carbon for the production of steel could be from old and used compact disks (CD). Significant production of CD's commenced in the 1990's, with peak production occurring in the year 2000.

With the advent of on-line streaming services, the need for compact disks has declined rapidly with production in 2015 having declined by over 75% from the peak in 2000.

### Unit sales of DC's worldwide from 1991 to 2015

(in millions)

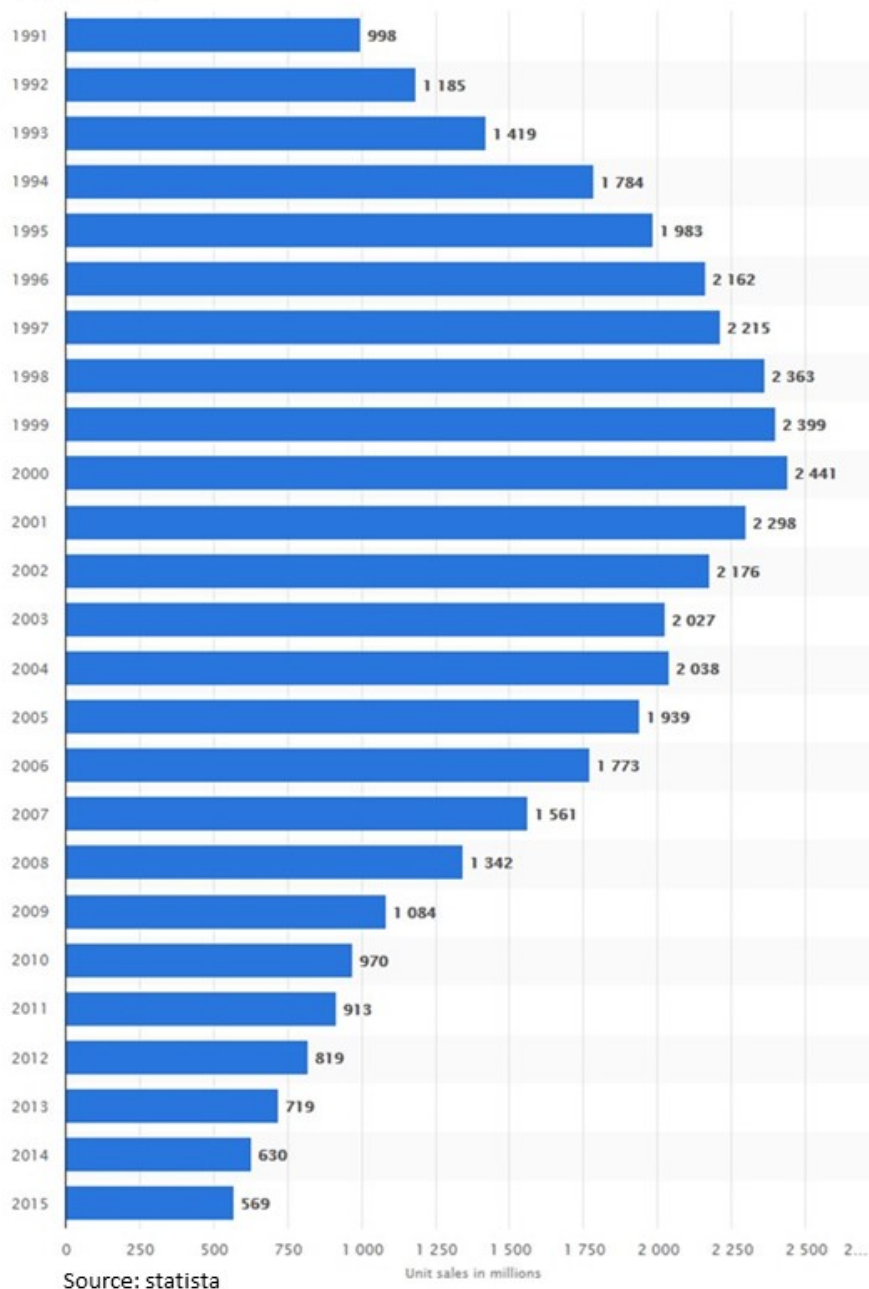


Figure (2)

A simple calculation can determine the potential of CD's to replace metallurgical coal. A typical CD weighs between 15 and 20 grams. Assuming that all CD's weighed 20 grams and all CDs produced between 1991 and 2015 were collected and were available to be utilised as a metallurgical coal replacement, the total mass of CDs would be approximately 800,000 tonnes. This represents less than 0.01% of annual coking coal demand.

While the potential of CDs to replace metallurgical coal may be limited, the ability to re-purpose the CDs into a useful product and reduce land fill waste would be of clear benefit and thus its technical potential is considered in this report.

## **(2) Macadamia nut shells**

Macadamia nut production is a growing industry and at this stage there are a limited number of high-value uses of the waste shells. Total macadamia nut production is estimated by Fresh Plaza at approximately 160,000 tonnes per year. The flesh only accounts for about 30% of the mass of the unhusked nut. This means that close to 375,000 tonnes of macadamia shells are produced on an annual basis.

Given that macadamia nut production is growing, is a sustainable business and there are only a limited number of higher value options to utilise the shells, the use of macadamia nut shells as a metallurgical coal replacement is a reasonable notion. It is arguably a more interesting option compared to CDs due to the ongoing production of the nuts and the larger volumes that would be available into the future.

## **(3) Lignin from an ethanol biorefinery**

Millions of tonnes of agricultural waste are thrown away worldwide. This waste comprises three main types of carbon-based polymers: cellulose, hemi-cellulose, lignin collectively called lignocellulosic materials.

Many researchers have studied the use of biomass in the production of different value-added materials and showed that biomass could be utilized to produce chemicals, fertilizers, starch plastics, cellulosic polymers, carbon fiber, resins, olefins, bio-oil, biochar, biodiesel etc. Several studies have reported the use of three lignocellulosic biomasses (bagasse, rice straw and wood fiber) as feedstocks to produce bioethanol. The use of lignin-rich biomass to produce pyrolytic lignins by fast pyrolysis has also been investigated, and results suggest that lignin could serve as a potential feedstock for the environmentally sound production of chemicals and materials. Biomass waste is under-utilized, often used for garden mulching, and as animal filler, or else incinerated. Limited research is carried out in using biomass to enhance resource availability and environmental sustainability of ferrous processing.

In the last few decades, substantial growth was seen in the use of lignocellulosic agricultural biomass waste as an alternative source of energy and biomaterials production in order to reduce the depletion of non-renewable resources and to decrease the emissions of greenhouse gases.

With ~220 billion dry tonnes of global annual availability, biomass is the world's largest, most sustainable and carbon-neutral energy resource [6]. Such waste material consists mainly of carbon and hydrogen; elements vital in the metallurgical industries due to their role as reductants/carburizers. As a valuable source of both carbon and hydrogen; these could potentially be used for the reduction of iron oxide and could play an important role as a fuel/carbon resource for iron and steelmaking.

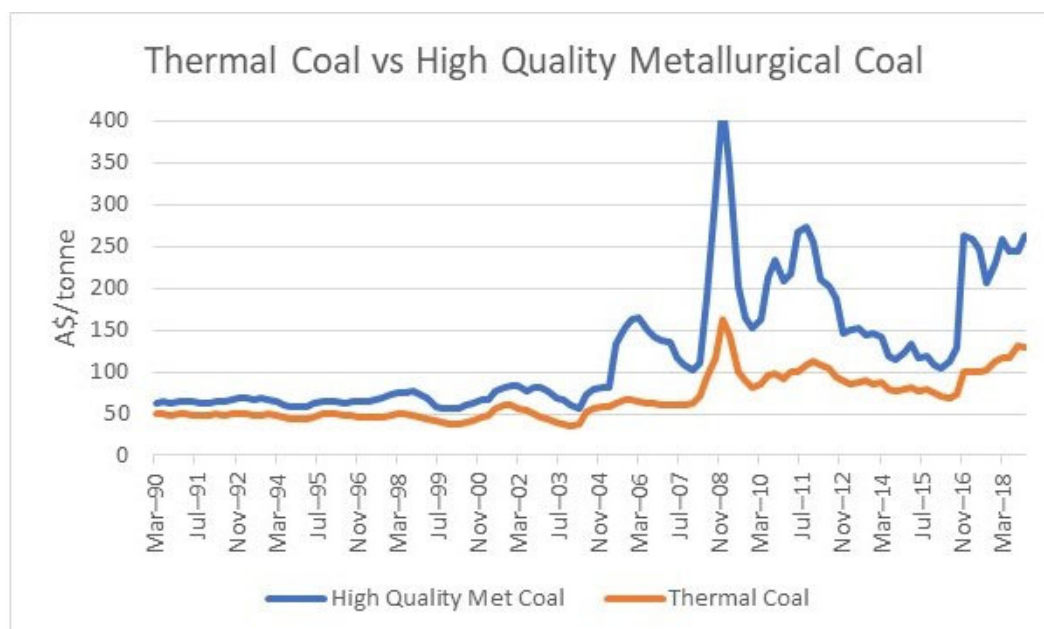
A simple analysis can determine the global potential of lignin produced from lignocellulosic ethanol production facilities that could be developed over the coming decades.



- An operating facility today (POET/DSM Project Liberty) currently produces about 290 litres of ethanol from every bone-dry tonne of biomass. (Source: Ethanol Producer Magazine: June 2018)
- Lignin makes up to 30% of lignocellulosic biomass. (Source: Lignin – a natural resource with huge potential: Bioeconomy BW: 20 March 2017)
- World gasoline consumption in 2018 is 2,700 billion litres. (Source: EIA 2018)
- To replace 10% of gasoline would require 270 billion liters of ethanol
- A full-scale lignocellulosic bioethanol facility producing 250 million liters of ethanol could produce 215,000 tonnes of lignin assuming 25% of biomass is lignin and recovered. This requires 1080 lignocellulosic facilities each with a production capacity of 250 million liters of ethanol to replace 10% of global gasoline consumption.
- If all the lignocellulosic bioethanol facilities utilised their lignin as a metallurgical coal replacement, then 232 million tonnes of lignin would be produced annually. This equates to 21% of current global metallurgical coal supply

### Lignin shows the greatest macro potential to replace met coal

Due to the scale potential of lignin derived from lignocellulosic ethanol biorefineries, it is lignin that shows the greatest potential from a macro perspective as a metallurgical coal replacement. Under a scenario where enough lignocellulosic ethanol facilities are developed to replace 10% of gasoline consumption with high octane, clean burning ethanol, over 20% of global metallurgical coal could potentially be replaced.



Source Data: Resources and Energy Quarterly – March 2019

Figure (3)

Not only does it make the most sense from a macro perspective, it appears to make sense from a financial perspective as well. Metallurgical coal typically sells at a premium to thermal coal. In lignocellulosic ethanol facilities today, the lignin is generally utilised as a source of energy for

running the plant and any excess energy sold to the grid as electricity.

This means that currently lignin in a typical lignocellulosic bioethanol production facility is utilised in much the same way as thermal coal – as an energy source. If a lignocellulosic ethanol facility were able to secure energy from a competitive alternative source such as bio or fossil gas or even thermal coal, then the sale of the lignin as a met coal replacement could effectively double its unit value from the current implied value of A\$130/tonne to met-coal replacement price of A\$260/tonne.

### **Lignin as a metallurgical coal replacement could lift revenues over 11%**

Utilising a number of simple assumptions it is possible to determine the potential impact on revenues of a lignocellulosic bioethanol facility. Key assumptions are as follows:

- An ethanol sale price of US\$0.60/litre and the lignocellulosic ethanol facility sells 250 million litres of ethanol/year
- A A\$/US\$ exchange rate of 0.70
- Value of lignin as a metallurgical coal replacement generates either:
  - a 50% increase in lignin value relative to thermal energy
  - A 100% increase in lignin value relative to thermal energy
- Lignin represents 25% of the biomass
- Lignin credit as a thermal coal equivalent at A\$130/tonne generates either:
  - lignin as a metallurgical coal replacement at A\$195/t
  - lignin as a metallurgical coal replacement at A\$260/t
- The potential impact of carbon credits has not been incorporated.

Under the above assumptions, a lignocellulosic bioethanol facility that sells its ethanol and burns its lignin would achieve the following:

Ethanol revenues of US\$150M/year with a lignin thermal credit of  $(215,000 \times 130 \times 0.70) =$  US\$19.5M. In total, effective revenues for the entire lignocellulosic ethanol facility of US\$169.5M/year.

### **A 50% increase in lignin unit value:**

If the lignin were sold as a metallurgical coal replacement, then under a conservative met coal replacement scenario (relatively low met coal price - +50%), the revenue calculation is US\$150M of ethanol sales plus  $(215,000 \times 195 \times 0.70) =$  US\$29.3M. In total, revenues would rise to US\$179.3 million for the entire lignocellulosic ethanol facility. This calculation assumes the lignin that would otherwise be used to power the biorefinery is replaced with an equivalent source of power at the same cost. In total, the increase in revenues under the conservative case is calculated at 5.8%

**A 100% increase in lignin unit value:**

If the lignin were sold as a metallurgical coal replacement, then under a less conservative met coal replacement scenario (higher met coal price - +100%) the revenue calculation is US\$150M of ethanol sales plus  $(215,000 \times 260 \times 0.7) = \text{US\$}39\text{M}$ . In total, revenues would rise to US\$189.0 million for the entire lignocellulosic ethanol facility. This calculation assumes the lignin that would otherwise be used to power the biorefinery is replaced with an equivalent source of power at the same cost. In total, the increase in revenues under the less conservative case is 11.2%

**Between 5.8% and 11.2% revenues increase – 2 met coal price assumptions**

Overall, if a lignocellulosic ethanol facility were able to sell its lignin as a metallurgical coal replacement at prices ranging from a 50% to 100% increase in lignin unit value, then this has the potential to lift revenues for the project by between 5.8% and 11.2%.

The following section considers the experimental program and results

## Experimental procedure

### Carbon production and pellets/briquettes making

All heat treatment experiments discussed in this report were carried out in an alumina crucible covered in a pre-heated tubular furnace (100 cm length × 5 cm diameter) under Ar purge (1 L min<sup>-1</sup>) for a given period of time. The furnace was coupled with an infrared gas analyser (Advanced Optima AO2020, ABB Measurement and Analytics, Australia) for continuous measurement of non-condensable Syngas, e.g., CO, CO<sub>2</sub> and CH<sub>4</sub>.

Carbon bearing materials were ground by a ring mill to make a powder which was then used to make pellets for reduction experiments. For reduction experiments, iron oxide and carbon bearing material powders were mix-agglomerated (in stoichiometric ratio) using a wet-densifier. The resulting pellets were oven-dried at 105 °C overnight. The powder mix was hot-pressed into briquettes (2 cm diameter × 5 mm thickness) using a uniaxial hydraulic press by applying 3 bar of pressure at 200 °C for 20 min, the briquettes here were denoted as LRC-PC briquettes.

## Characterisation of C bearing materials

### Chemical composition

The elemental composition of C-bearing materials (i.e., coke, waste CD, macadamia shell and LR) was examined by combustion/ XRF analysis and results are shown in [Tables 1 to 4](#). As can be seen in [Table 1](#), metallurgical coke contains around 85 wt. % solid carbon ([Table 1](#)) while waste CD, macadamia shell and LR have carbon content of around 20% ([Tables 2-4](#)). However, total carbon content of these waste resources is high with waste CD being 77wt. %, macadamia shell and LR being around 48wt. % and 40 wt. %, respectively.

The nitrogen and sulphur of LR were respectively 1.7 and 0.74%. The content of these elements is almost similar to a typical plant residue [\[19-21\]](#). Metallurgical coke contains around 11.5 wt. % ash, while waste CD, macadamia shell and LR contain much less ash (waste CD: 2 wt%, macadamia shell: 0.2 wt. % and LR: 6 wt. %). The ash analysis of carbon bearing materials was performed, and results are summarized in [Table 1-4](#). As can be seen the ash content of LR is around 6% of which 66% is silica. Other oxides such as lime, SO<sub>3</sub>, Na<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub> and K<sub>2</sub>O are also present in the ash. The ash content of metallurgical coke is around 11.5 w% of which 60% is silica. The high percentage of lime in LR is an advantage for steel making process since it can be used as fluxing agent. The other impurities can be either removed by water-wash or using slag during the steel making process.

**Table 1** Chemical composition of metallurgical coke [22]

Solid carbon (wt.%)	85.54
Ash (wt.%)	11.52
<i>Trial No.</i>	<i>1</i>
<i>Compound</i>	<i>(wt.%)</i>
Na <sub>2</sub> O	0.38
MgO	0.4
Al <sub>2</sub> O <sub>3</sub>	31.0
SiO <sub>2</sub>	55.8
P <sub>2</sub> O <sub>5</sub>	1.25
SO <sub>3</sub>	0.18
K <sub>2</sub> O	0.76
CaO	1.95
TiO <sub>2</sub>	1.51
Mn <sub>3</sub> O <sub>4</sub>	0.02
Fe <sub>2</sub> O <sub>3</sub>	3.46
BaO	0.08
<b>Ash%</b>	<b>11.52 wt.%</b>

**Table 2** Chemical composition of waste CD [23]

Proximate analysis	(wt% as received)
Moisture	0.22
Ash	2.02
Volatile matter	77.99
solid carbon	19.77
Ultimate analysis	(wt% as received)
C	76.03
O	20.62
N	0.21
Elemental analysis	Concentration (wt%)
F	0.914
Na	0.036
Mg	0.44
Al	0.070
Si	2.160
P	0.007
S	0.028
Cl	0.074
Ca	0.750
Fe	0.058
Ni	0.004
Br	0.005
Ag	0.142
Bi	0.004

**Table 3** Chemical composition of macadamia shell [24]

Moisture	5.5
Ash	0.2
Volatile Matter	73.5
Solid carbon	20.8
C	48.39
O	40.31
N	0.333
Na	0.0298
Mg	0.045
Al	0.062
Si	0.077
P	0.014
S	0.04
Cl	0.0008
K	0.1550
Ca	0.0350
Cr	0.008
Mn	0.0047
Fe	0.0113
Co	0.0001
Cu	0.0015
Zn	0.0005
Se	0.0004
Br	0.0004
Rb	0.0001
Cd	0.0001
Pb	0.0002



**Table 4.** Elemental and mineral composition of lignin.

<b>a) Combustion/oxidation analysis</b>				
<i>Trial No.</i>	<i>Nitrogen (wt.%)</i>	<i>Total Carbon (wt.%)</i>	<i>Sulphur (wt.%)</i>	
1	1.703	39.88	0.7296	
2	1.837	42.10	0.7365	
3	1.731	39.95	0.7592	
4	1.776	40.78	0.7358	
<b>b) Ash analysis</b>				
<i>Trial No.</i> / <i>Compound</i>	<i>1</i> <i>(wt.%)</i>	<i>2</i> <i>(wt.%)</i>	<i>3</i> <i>(wt.%)</i>	<i>4</i> <i>(wt.%)</i>
<i>Na<sub>2</sub>O</i>	1.219	1.333	1.204	1.245
<i>MgO</i>	1.468	1.491	1.490	1.488
<i>Al<sub>2</sub>O<sub>3</sub></i>	2.500	2.709	2.568	2.579
<i>SiO<sub>2</sub></i>	65.109	67.421	66.318	66.226
<i>P<sub>2</sub>O<sub>5</sub></i>	1.345	1.339	1.338	1.335
<i>SO<sub>3</sub></i>	11.203	8.834	10.438	10.329
<i>K<sub>2</sub>O</i>	3.722	3.572	3.715	3.623
<i>CaO</i>	8.151	8.264	8.204	8.217
<i>TiO<sub>2</sub></i>	0.188	0.200	0.186	0.189
<i>PbO</i>	0.004	0.004	0.005	0.004
<i>Cr<sub>2</sub>O<sub>3</sub></i>	0.227	0.196	0.201	0.211
<i>Mn<sub>3</sub>O<sub>4</sub></i>	0.059	0.057	0.057	0.058
<i>Fe<sub>2</sub>O<sub>3</sub></i>	2.546	2.443	2.435	2.435
<i>NiO</i>	0.085	0.072	0.071	0.075
<i>CuO</i>	0.135	0.138	0.137	0.136
<i>ZnO</i>	0.059	0.065	0.042	0.057
<i>SrO</i>	0.037	0.039	0.005	0.015
<i>ZrO<sub>2</sub></i>	0.040	0.040	0.007	0.009
<b>Ash%</b>	<b>6.17 wt.%</b>	<b>5.95 wt.%</b>	<b>6.07 wt.%</b>	<b>6.01 wt.%</b>

# Thermal degradation of C-bearing materials

Thermal degradation of C-bearing materials (i.e. waste CD, macadamia shell and LR) was carried out to investigate their behaviour at different temperatures

## (1) Waste compact disks (CD)

Thermogravimetric analysis (TGA) was performed to gain knowledge of thermal degradation of waste CDs. Figure 4 exhibits the TG curve for thermal degradation of waste CD at a heating rate of 10 °C/min in nitrogen atmosphere from room temperature to 1550 °C. The degradation of waste CD started around 550 °C which can be observed from TGA curve, and hence the rapid pyrolysis studies were carried out from 550 °C to 1550 °C.

Figure 5 shows the effect of temperature on char yield during rapid heat treatment. It can be observed that the char yield decreases from 26% to 19% when the pyrolysis temperature increased from 550 to 1550 °C. The decrease in the yield is due to increase in primary or secondary decomposition in char residue at higher temperatures. The progressive increase in carbon content and decrease in oxygen content with pyrolysis temperature was observed in chars. The increase in carbon/oxygen ratio (Figure 5); clearly indicates the increase of aromatic and carbonaceous nature in chars.

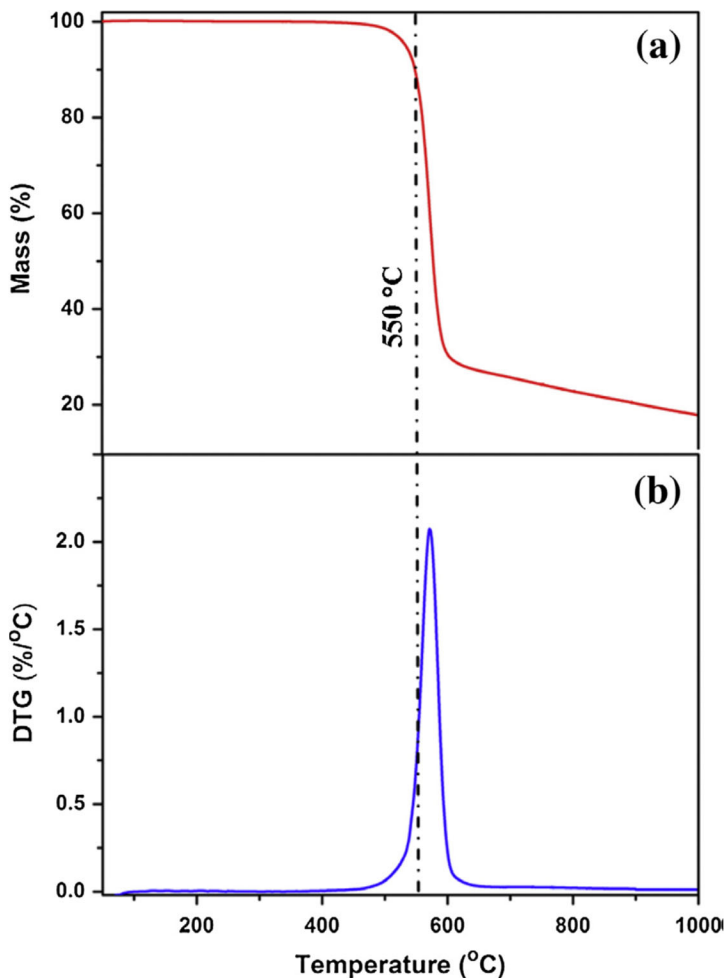
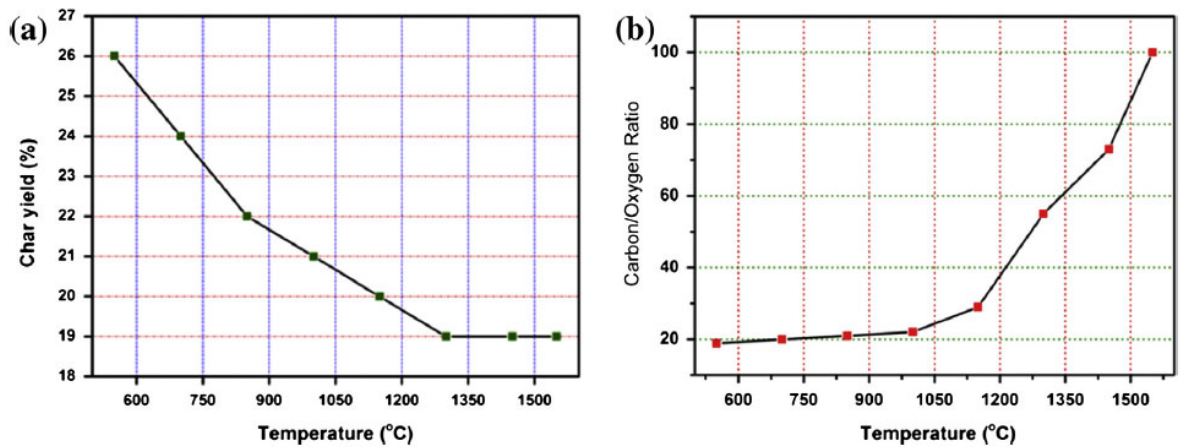


Figure 4 (a) TGA and (b) DTG curve of waste CD [23]

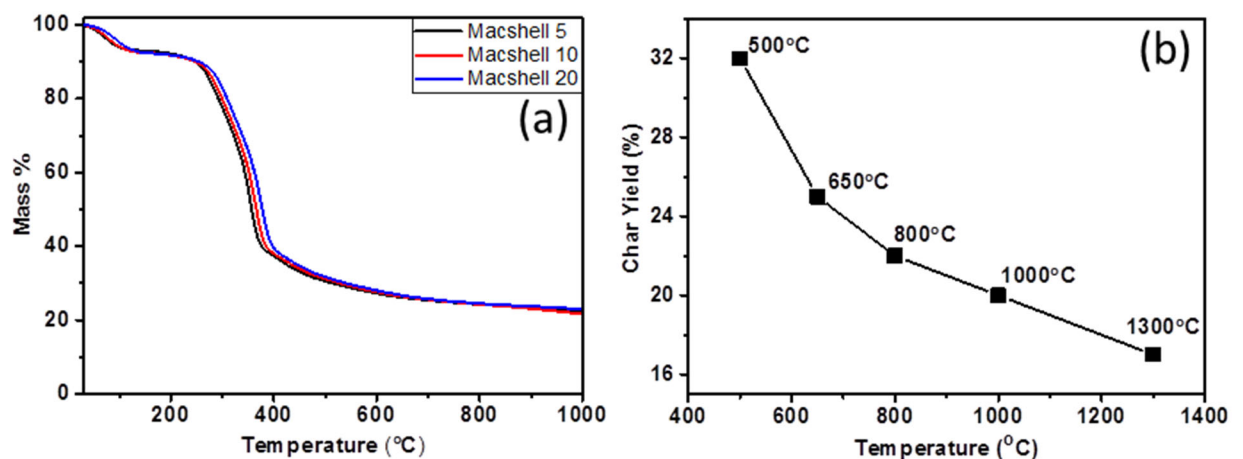


**Figure 5** Change of (a) char yield and (b) carbon/oxygen ratio during rapid pyrolysis of waste CDs at different temperatures [23]

## (2) Macadamia nut shells

Raw macadamia shell powder was heated from room temperature to 1300 °C under nitrogen atmosphere at heating rates of 5, 10 and 20 °C/min. The results obtained from TGA at three different heating rates are illustrated in **Figure 5 (a)**. Decomposition started at temperature around 260 °C; with increasing temperature up to 400 °C the mass loss reached around 65% indicating that majority of mass loss occurred between 260 to 400 °C.

Initial degradation might involve the emission of low molecular weight compounds resulting in the formation of more crosslinked structure. Thermal degradation might also involve breakage of C-C and C-H bonds and formation of CO<sub>2</sub> and H<sub>2</sub>O leading to further weight loss. **Figure 5 (b)** shows that char yield decreased from 32% at 500 °C to 17% at 1300 °C.



**Figure 5. (a)** TGA thermogram of macadamia shell showing the degradation behavior at three heating profiles (5, 10 and 20 °C/min) and (b) Char yield at different pyrolysis temperatures in the range 500-1300 °C [25].

### (3) Lignin from an ethanol biorefinery

The process to generate the lignin was as follows:

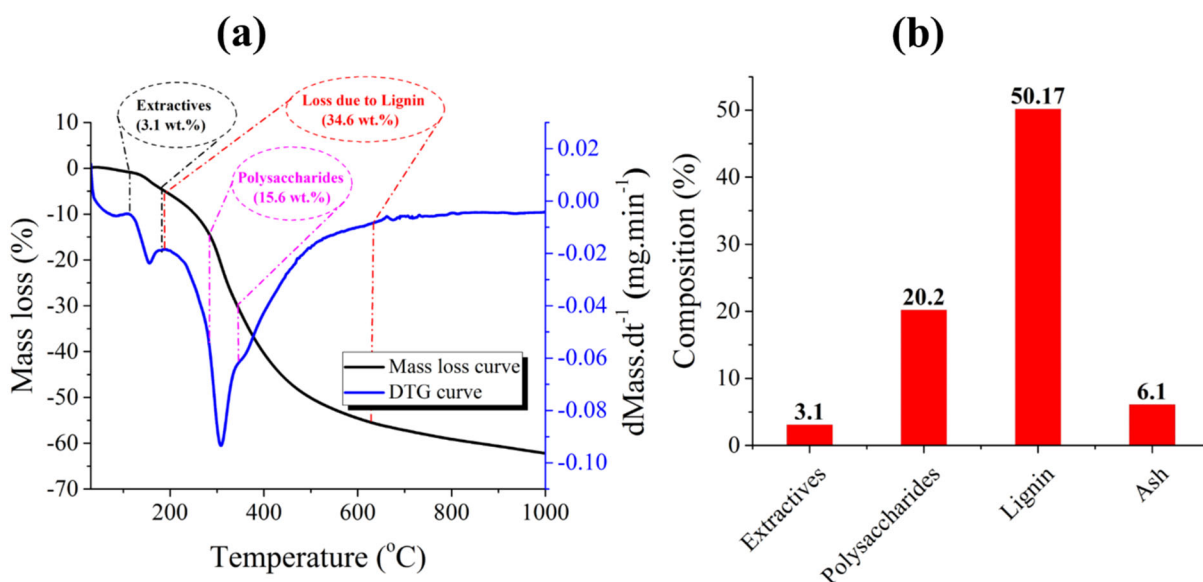
- Sugar cane bagasse from Florida was pre-treated in the NREL laboratories in the US utilizing a standard NREL dilute acid pre-treatment process. In the process, the bagasse is passed through a screw press where it is subject to high temperature and pressure in the presence of dilute sulphuric acid which breaks down the hemicellulose into monomers of xylose, mannose, galactose and acetic acid.
- The pre-treated bagasse was sent to Australia. The semi-solid slurry containing fibre is neutralized using aqueous  $\text{NH}_4$ , and the cellulosic component approximately 90% digested using cellulases.
- After the digest is complete the fibre slurry is washed and pressed where the sugar rich syrup is separated and sent for fermentation. The fibre is stored until it is oven dried and ground to produce the dried lignin product.

Thermogravimetric analysis (TGA) of LR was also performed at the UNSW. The initial observation from the mass loss curve of LR, [Figure 6 \(a\)](#), shows a gradual decrease in weight which starts at 130 °C. The thermal-induced mass loss increases with temperature and around 37.8% of the sample remains at 1000 °C. The DTG curve provides a visual evidence of the different degradation events, which can be assigned to specific components of biomass. Biomass is mainly composed of several constituents which can be collectively classified into extractives, lignin and polysaccharides; each of which exhibits a distinct degradation characteristic. "Extractives" is a term used to describe a very complex class of organic compounds, e.g., aromatics, phenols, terpenes, aliphatic acids and alcohols, which have low molecular weight and low thermal stability [\[26\]](#). The DTG curve of LR shows the mass loss event due to this class of compounds in the temperature range between 130 and 180 °C. The polysaccharides, i.e., cellulose and hemicellulose, typically exhibit a rapid degradation resulting in a sharp DTG event as can be observed in the temperature range of 280 to 345 °C [\[27, 28\]](#). Lignin, which decomposes slowly [\[29, 30\]](#), shows a wide DTG event overlapping with that of polysaccharides in the temperature range of 190 to 630 °C. By assigning the DTG events to the LR components, the mass loss contribution from each component is estimated. Given that each component yields a known amount of solid residue, an approximate estimation of LR composition is obtained as shown in [Figure 6 \(b\)](#). If normalized for the ash content then the percentages would rise.

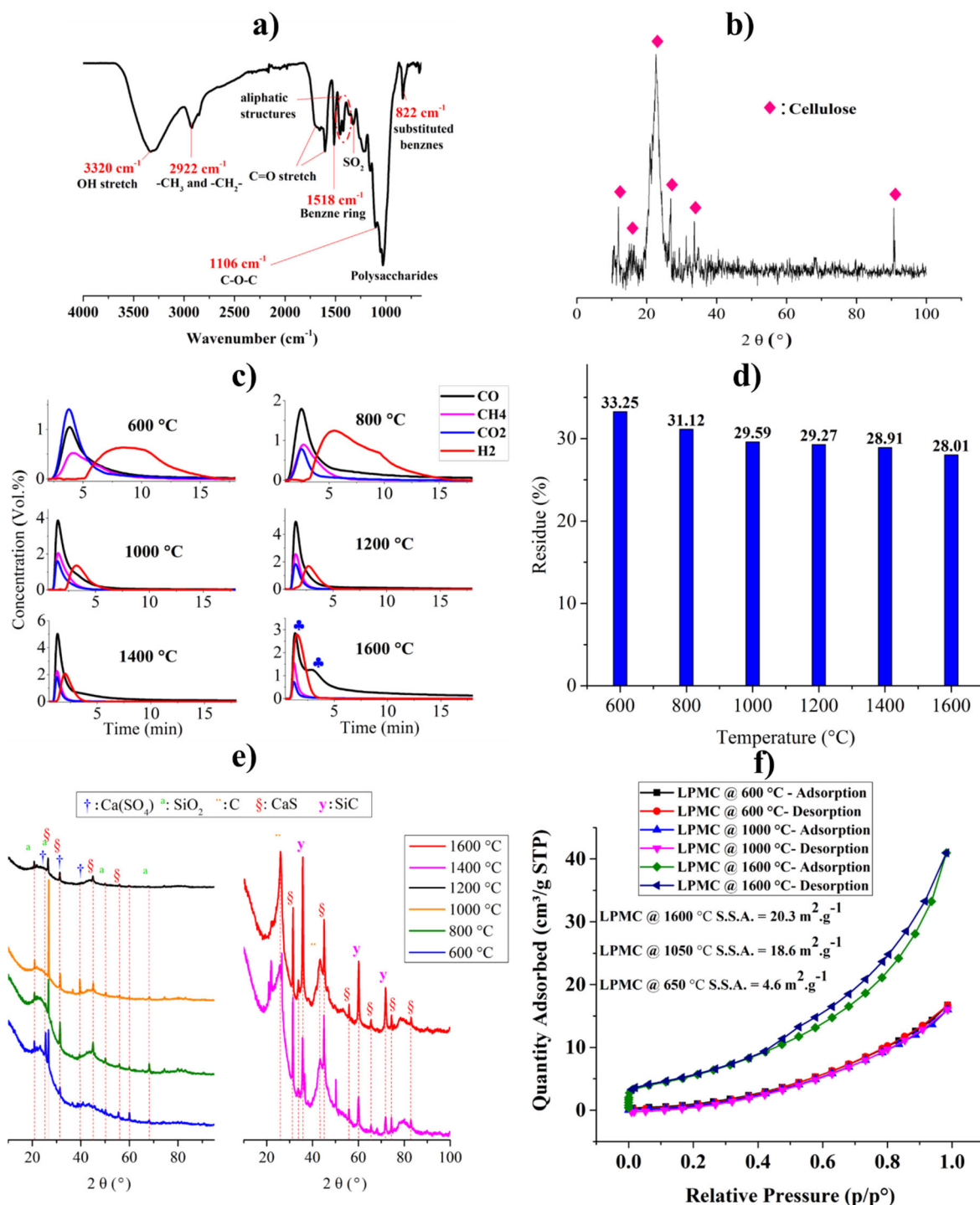
The FTIR spectrum of LR sample, [Figure 7 \(a\)](#), shows a large band at  $3320\text{ cm}^{-1}$  which is a distinct feature of the OH stretch in the phenolic moiety of lignin and hydroxylic moieties in polysaccharides. Lignin and polysaccharides (e.g., cellulose and hemicellulose) are major biopolymer component of plant matter. The other band at  $2922\text{ cm}^{-1}$  corresponds to the symmetric and antisymmetric stretching of  $-\text{CH}_3$  and  $-\text{CH}_2-$ ; which can be present in all biopolymers. The doublet between  $1600$  and  $1700\text{ cm}^{-1}$  is assigned to the stretching mode of carbonyl groups in alkoxy cross-linkers and substituted benzene rings of lignin. The band at  $1618\text{ cm}^{-1}$  is assigned to the stretching mode of lignin benzene ring. The doublet between  $1400$  and  $1460\text{ cm}^{-1}$  corresponds to the antisymmetrical deformation and scissors vibration of aliphatic structures. The  $\text{SO}_2$  antisymmetrical stretch in sulphones is indicated by the band at  $1325\text{ cm}^{-1}$ . The band at  $1000\text{ cm}^{-1}$  is a typical feature of carbon ring in cyclic compounds of polysaccharides. The XRD pattern of the sample, [Figure 7 \(b\)](#), shows a crystalline phase corresponding to cellulose. The LR sample contains non or less-crystalline mineral-impurities which, upon heat-treatment, can generate other minerals with a well-defined crystal structure.

Heat-treatments of LR were performed at isothermal conditions in a high-temperature tubular furnace. The off-gas was monitored to give an insight into the different reactions taking place at those temperatures and to indicate the completion of the carbonization process. In [Figure 7 \(c\)](#),

the charring of LR at low temperature (600 °C) results in several gases (CO<sub>2</sub>, CO, CH<sub>4</sub> and H<sub>2</sub>) with CO<sub>2</sub> being the most dominant gas. The H<sub>2</sub> release, which seems to be slow at this temperature, is an indication of the aromatic polycondensation reactions leading to the formation of graphitic carbon structure. In other words, at 600 °C, the LR needs around 17 min (i.e., the time required to release all H<sub>2</sub>) to complete the conversion into graphitic carbon. At temperatures 800 to 1400 °C, the CO becomes the dominant gas and CO<sub>2</sub> concentration decreases. This increase of CO concentration and along with the subsequent decrease of CO<sub>2</sub> is related to the Boudouard reaction, where CO<sub>2</sub> reacts with C and generates CO. This reaction becomes possible at temperature above 750 °C.



**Figure 6.** Thermogravimetric analysis of LR. a) Mass loss and DTG curves of LR, and b) proximate composition of LR as calculated from the thermogravimetric analysis, assuming that polysaccharides and lignin respectively yield 30 and 45% carbon residues.



**Figure 7.** Composition analysis of LR; a) FTIR spectrum and XRD pattern of LR b) Isothermal degradation characteristics and product distribution; c) Syngas analysis from 500 mg sample charge, d) carbonization yield at different temperatures, e) XRD patterns of LRC obtained at different temperatures, and f) N<sub>2</sub> physisorption analysis of LRCs<sup>[31]</sup>.

As expected, the XRD patterns of the LR carbonized at high temperatures (1400 and 1600 °C), Figure 7 (e), show new phases of graphitic carbon and β-SiC. The LR samples heated at low, moderate and high temperatures show low surface area ranging between 4.6 and 20.3 m<sup>2</sup>.g<sup>-1</sup> as shown in Figure 7 (f).

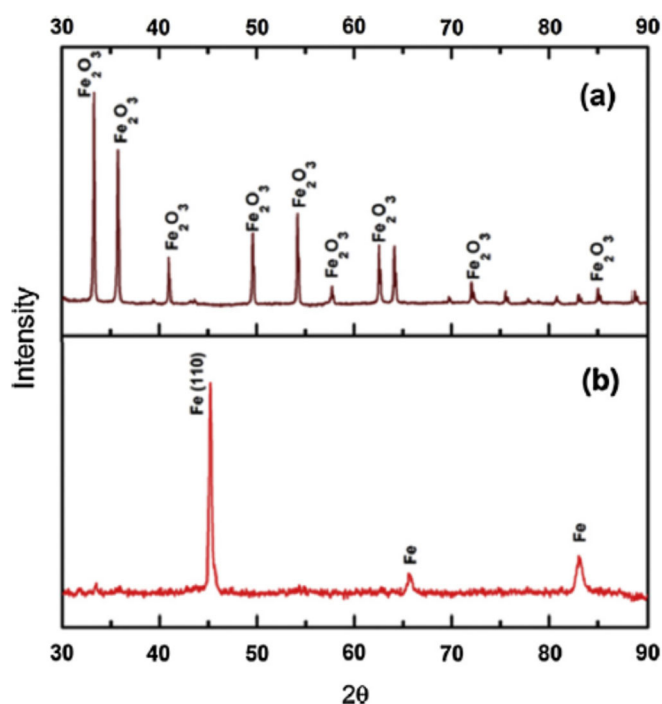
## Iron oxide reduction using waste resources

It has been proved that the reduction of iron oxide to metallic iron is significantly enhanced when graphite is used as a reductant; this increase is attributed to the catalytic activity of metallic iron on the gasification of carbon. The graphitic structure of carbon plays an important role in enhancing the reduction and further enhancing the carburization of iron.

The results of reduction of iron oxide to metallic iron using different carbon bearing materials have been investigated.

### (1) Waste compact disks (CD) – as a source of carbon for reduction of iron oxide

Characterisation results of pyrolyzed CD char has shown the transformation of carbon structure from disordered to highly order pyrolytic graphitic (HOPG) nature at high temperature. Fig. 8a shows the XRD pattern of hematite used for reduction studies. XRD pattern of reduced iron oxide at 1400 °C using waste CD char as reductant is shown in Fig. 8b. The appearances of peaks corresponding to Iron (Fe) phases can be observed in XRD pattern. The Fe phase peak (110) appeared to be dominant and absence of hematite phase clearly indicates complete reduction.



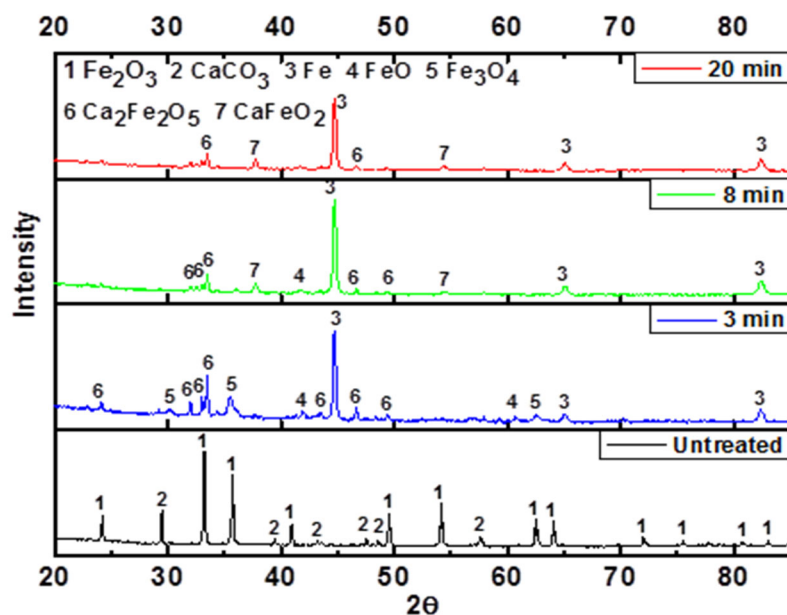
**Figure 8** XRD spectra of a) hematite and b) reduced sample at 1400°C temperature [23]

### (2) Macadamia nut shells as a carbon source for reduction of iron oxide

The performance of the carbon derived from macadamia shell as an iron oxide reductant was investigated using densified pellets of hematite and macadamia shell. The pellets were reduced at four different temperatures (1000 °C, 1100 °C, 1200 °C and 1300 °C) and three different reduction times (3, 8 and 20 minutes). After 3 minutes  $\text{Fe}_2\text{O}_3$  transformed into iron as indicated by a sharp iron peak at  $2\theta = 44.67^\circ$ . At 1000 °C, metallic iron phase was observed only after 20 minutes of reduction and at 1100 °C, it could be observed even after 8 minutes of reduction indicating faster



reduction rate at higher temperature. Similar to 1200 °C, for 1300 °C the metallic iron phase was present after 3 minutes of reduction time. At all the temperature, presence of sharp iron peaks suggested that metallic iron phase was the major phase present after 20 minutes of reduction time indicating very high degree of reduction. Magnetite and wustite phase were also detected at different stages of the reaction confirming the fact that magnetite and wustite were the intermediate products. **Figure 9** shows the XRD spectra for untreated pellets and pellets reduced at 1200 °C for different reaction times.



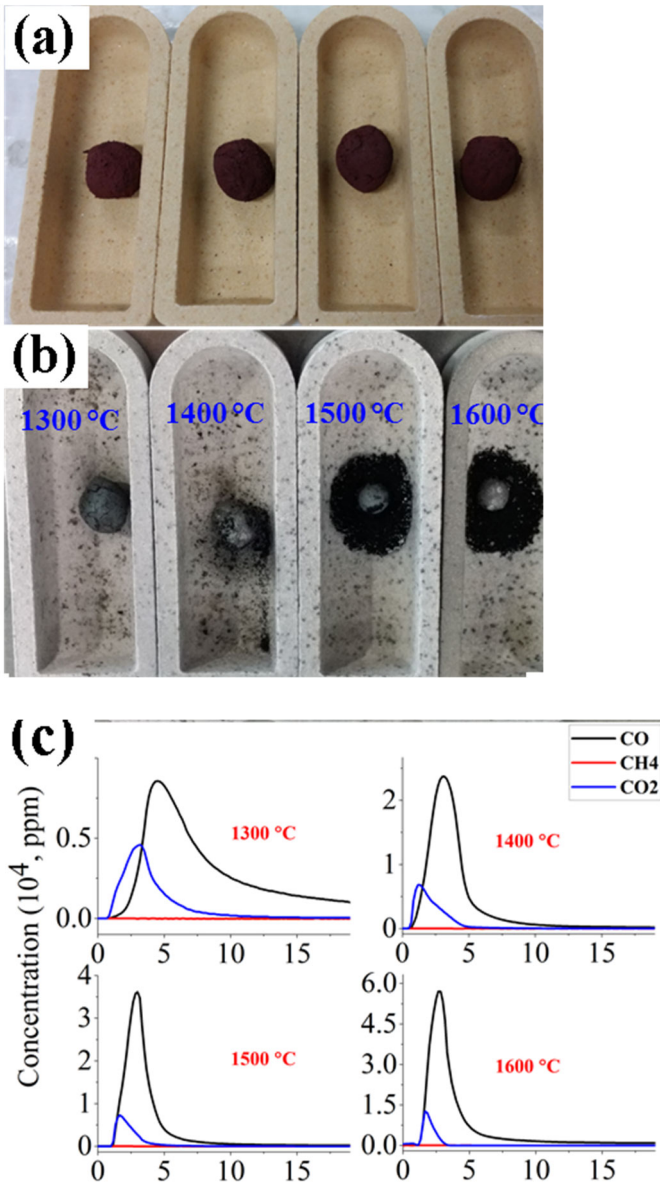
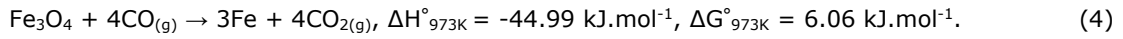
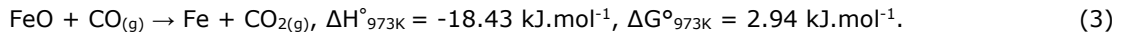
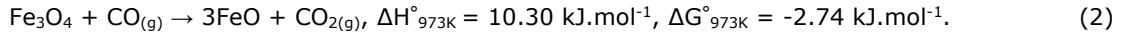
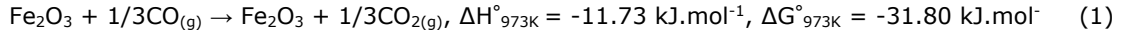
**Figure 9.** XRD spectra for untreated pellet and pellets reduced at 1200 °C showing the transformation of iron oxide in composite pellets to metallic iron [25].

### (3) Lignin from an ethanol biorefinery as a source for carbon reduction of iron oxide

To evaluate the performance of the carbon derived from RL (LRC) as an iron oxide reductant, densified pellets of hematite and LRC were produced and heat-treated at several temperatures ranging between 1300 and 1600 °C. **Figure 10 (a and b)** provides a visual evidence on the complete reduction of iron oxide into iron metal. The pellet heated at 1300 °C shows the largest volume with no expelled carbon around it. This type of iron is widely known as a "sponge iron" where solid phase reduced iron is in an intimate contact (i.e., sinter) with the LRC which is trapped as a free carbon inside the sinter.

This type of iron is an important material feedstock of many EAF and BF operations around the world [29]. As temperature increases and iron starts to melt, the carbon is expelled from the sinter leaving behind a reduced iron melt droplet. The reduction of iron oxides at temperature above the melting point of the eutectic system of iron and carbon is known as smelting reduction iron (SRI) [1]. The gas product from the heat-treatment of those pellets was monitored using IR analyser and plotted against time as shown in **Figure 10 (c)**. According to **Eqs. (1 to 4)**, the CO<sub>2</sub> is a product of iron oxide reduction which transforms into CO based on Boudouard reaction.

The CO evolution can be used as indicator of the reduction completion. At temperature above 1500 °C, the reduction reaches equilibrium within 10 minutes which is a typical duration for most types of carbon.



**Figure 10.** Iron (III) oxide reduction using LRC. 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, c) gas product analysis of iron(III) oxide reduction<sup>[31]</sup>

#### (4) Lignin and waste plastic as carbon sources for reduction of iron oxide from slag

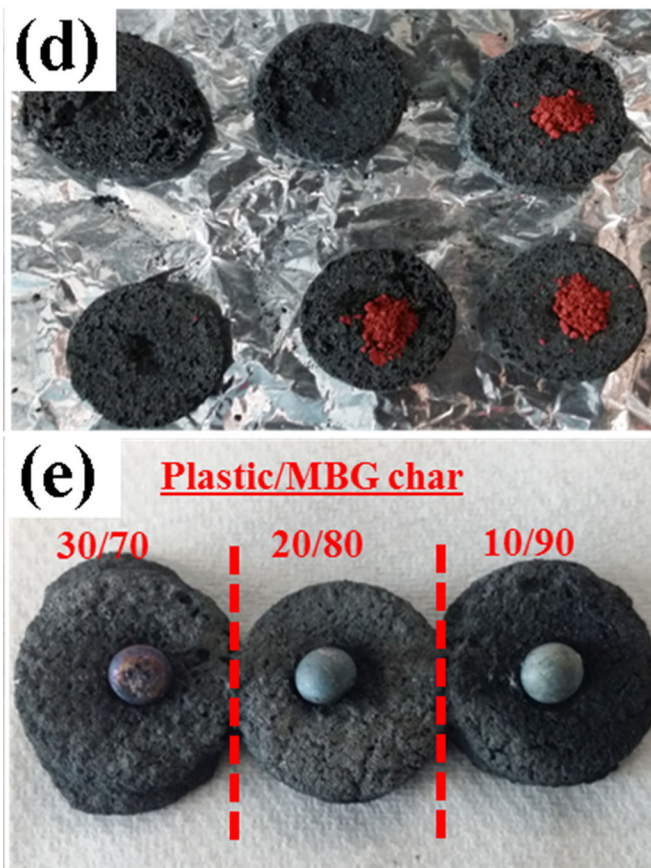
The plastic component is a good source of reducing gases that can contribute to the reduction process such as CO, H<sub>2</sub> and CH<sub>4</sub>.

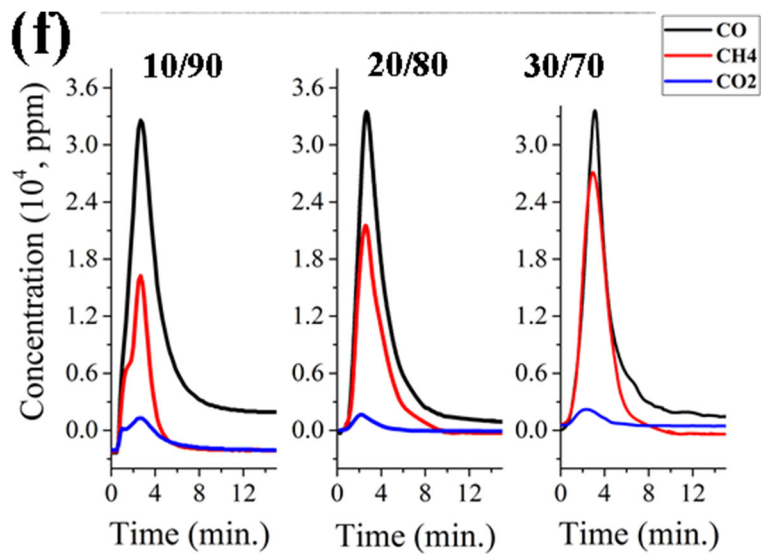
In the steelmaking industry, a considerable amount of iron oxide is lost within slag (a by-product of steelmaking) as a result of utilization of low-quality carbonaceous materials. Coke is the widely used type of carbonaceous material in iron and steelmaking, which is a high-cost additive.

The use of LR and waste plastic (polycarbonate) as alternative carbon sources for the recovery of iron from industrial slag have been compared with coke. Such waste materials consist mainly of carbon and hydrogen; elements vital in the metallurgical industries due to their role as reductants/carburizers. The industrial EAF slag with 29 wt% FeO content was mixed with LR and waste plastic at 1550°C under argon purge at atmospheric pressure, and their reduction behaviors were compared with coke.

Figure 11 (e) shows the product of EAF slag reduction with LRC-PC briquettes. As shown in Figure 11 (f), the increase of plastic in the LRC-PC briquette slightly contributes to the reduction of slag.

In the cases of LR and plastic, carbon is present in the form of both solid and volatile. The reaction between CO and iron oxide is fast which results in completing reaction in a very short time. The Boudouard reaction in coke- EAF slag interaction acts as a driving force which can be the rate controlling stage.





**Figure 11.** EAF slag reduction using LRC and waste plastic .d) LRC-PC briquettes interaction with iron(III) oxide upon reduction, e) EAF slag reduction with LRC-PC briquettes, and f) gas product analysis of EAF slag reduction<sup>[31]</sup>.

According to our experiment, the reaction between RL/plastic samples and EAF slag was complete in less than 15 minutes while reaction between coke and EAF slag took a longer time. **Figure 12** displays the images of industrial EAF slag after reaction with coke.



**Figure 12.** EAF slag reduction using coke

## Summary – lignin is a suitable metallurgical coal substitute

Most of research around the utilization of biomass in the steel making industry has focused on certain types of virgin biomass resources such as hard wood from eucalyptus plantation [13]. The information on other types of inedible biomass waste (e.g., lignin waste) in metal manufacturing are scarce or missing. Lignin is a biopolymer present in plant materials (or biomass) alongside hemicellulose and cellulose. It typically constitutes 15 to 40 wt.% (dry) of the biomass [14, 15]. Biomass is processed to recover cellulose which is used in the fermentation process to make biofuels and in the Kraft-pulping process to make papers. In these processes, lignin-rich biomass residues (LR) are generated as a waste by-product. It has been reported that only 40% of LR is used as fuel in thermal power plants while the rest of that is destined for landfills [14-16]. It is also worth mentioning that depending on the type of plant precursor, carbonization yields carbons with significant variations in their physical and chemical properties (e.g., surface area, crystallinity, chemistry, impurity distribution, reactivity, etc.). These variations may limit the utility of specific types of biomass in steel industry, and therefore, studies addressing each type of plant residues and their utilization in steel industry are necessary.

An article by Kumar et al. [17] reported from our group on the use of macadamia nutshell-derived carbon as an iron oxide reductant, i.e., as a replacement for the traditionally used metallurgical coke in steel making process. In this study, the biomass-derived carbon showed an excellent performance and high degree of reduction which equals that of the traditionally used coke [17]. Other article by Mansuri et al. [18] shows another example of biomass utilization where biochar was used as a carbon source (i.e., carburizer) to increase the carbon content in steel. With such type of waste, high carbon steel/dissolution (~5.18 wt.%) was achieved, which is considered high if compared with other types of coke [18]. Although these studies layout the foundation for the transition from coal/coke to biomass in steel industry, a comprehensive study addressing all possibilities and challenges is needed.

In the SMaRT Centre, we have assessed the suitability of the biomass waste, i.e., lignin-rich press mud (LR), for reduction of iron oxide in steel industry. The thermal transformation of lignin waste resulted in a reasonable yield of solid carbon. Investigations were carried out to assess the possibility of using such type of biomass in the steel making process. Although the chemistry and composition of the resulting carbon vary with temperature, most of the detected impurities can be advantageous or tolerated in the steel industry. The LRC, obtained at moderate temperature, contains appreciable content of oxides, e.g., SiO<sub>2</sub> and CaO. The fundamental studies on the reduction of pure iron oxide suggested a relatively low value of activation energy (~160 kJ.mol<sup>-1</sup>) with a complete reduction at elevated temperatures. Even at temperature below the iron melting point (~1300 °C), a typical product of iron sponge was obtained.

## References

- (1) Hasanbeigi, A.; Arens, M.; Price, L. Alternative emerging ironmaking technologies for energy-efficiency and carbon dioxide emissions reduction: A technical review. *Renew. Sustain. Energy Rev.* **2014**, *33*, 645–658.
- (2) Dhunna, R.; Khanna, R.; Mansuri, I.; Sahajwalla, V. Recycling Waste Bakelite as an Alternative Carbon Resource for Ironmaking Applications. *ISIJ Int.* **2014**, *54* (3), 613–619.
- (3) Power Generation from Coal, International Energy Agency, Paris, (2011).
- (4) Sahajwallam, V.; Zaharia, M.; Mansuri, I.; Rajarao, R.; Dhunna, R.; Nur Yunos, F.; Khanna, R.; Saha-Chaudhury, N.; O'Kane, P.; Fontana, A.; Jin, Z.; Skidmore, C.; Vielhauer P; O'Connell, D.; Knights, D. The power of steelmaking-harnessing high-temperature reactions to transform waste into raw material resources', *Iron and Steel Technology*, 2013, vol. 10, pp. 68 - 83
- (5) Zaharia, M.; Sahajwalla, V.; Saha-Chaudhury, N.; O'Kane, P.; Fontana, A.; Skidmore, C. ; Knights, D. Recycling of rubber tyres in electric arc furnace steelmaking: Carbon/slag reactions of coke/rubber blends', *High Temperature Materials and Processes*, 2012, 'vol. 31, pp. 593 – 602.
- (6) Azargohar, R., Jacobson, K.L., Powell, E.E., Dalai, A.K., 2013. Evaluation of properties of fast pyrolysis products obtained, from Canadian waste biomass. *J. Anal. Appl. Pyrolysis* 104, 330–340. doi:10.1016/j.jaap.2013.06.016
- (7) A. Hasanbeigi, M. Arens, L. Price, Alternative emerging ironmaking technologies for energy-efficiency and carbon dioxide emissions reduction: A technical review, *Renew. Sustain. Energy Rev.* 33 (2014) 645–658. doi:https://doi.org/10.1016/j.rser.2014.02.031.
- (8) J. Morfeldt, W. Nijs, S. Silveira, The impact of climate targets on future steel production – an analysis based on a global energy system model, *J. Clean. Prod.* 103 (2015) 469–482. doi:https://doi.org/10.1016/j.jclepro.2014.04.045.
- (9) H. Suopajärvi, K. Umeki, E. Mousa, A. Hedayati, H. Romar, A. Kemppainen, C. Wang, A. Phounglamcheik, S. Tuomikoski, N. Norberg, A. Andefors, M. Öhman, U. Lassi, T. Fabritius, Use of biomass in integrated steelmaking – Status quo, future needs and comparison to other low-CO2 steel production technologies, *Appl. Energy.* 213 (2018) 384–407. doi:https://doi.org/10.1016/j.apenergy.2018.01.060.
- (10) M. Geerdes, R. Chaigneau, I. Kurunov, O. Linguardi, J. Ricketts, *Modern blast furnace ironmaking : an introduction*, (2015). <http://public.ebib.com/choice/publicfullrecord.aspx?p=2033826>.
- (11) A.P. Luz, A.G. Tomba Martinez, F. López, P. Bonadia, V.C. Pandolfelli, Slag foaming practice in the steelmaking process, *Ceram. Int.* 44 (2018) 8727–8741. doi:https://doi.org/10.1016/j.ceramint.2018.02.186.
- (12) H. Suopajärvi, A. Kemppainen, J. Haapakangas, T. Fabritius, Extensive review of the opportunities to use biomass-based fuels in iron and steelmaking processes, *J. Clean. Prod.* 148 (2017) 709–734. doi:https://doi.org/10.1016/j.jclepro.2017.02.029.

- (13) E. Mousa, C. Wang, J. Riesbeck, M. Larsson, Biomass applications in iron and steel industry: An overview of challenges and opportunities, *Renew. Sustain. Energy Rev.* 65 (2016) 1247–1266. doi:<https://doi.org/10.1016/j.rser.2016.07.061>.
- (14) S.P. Cline, P.M. Smith, Opportunities for lignin valorization: an exploratory process, *Energy. Sustain. Soc.* 7 (2017) 26. doi:[10.1186/s13705-017-0129-9](https://doi.org/10.1186/s13705-017-0129-9).
- (15) M.N. Ragan S, Activated carbon from renewable resources—lignin, *Cellul Chem Technol.* 45 (2011) 527.
- (16) D.J. Horst, Lignin as alternative fuel: an estimate of the thermal energy generation potential from Brazilian crops, *Env. Prog Sustain Energ.* 36 (2017) 717–722.
- (17) U. Kumar, S. Maroufi, R. Rajarao, M. Mayyas, I. Mansuri, R.K. Joshi, V. Sahajwalla, Cleaner production of iron by using waste macadamia biomass as a carbon resource, *J. Clean. Prod.* 158 (2017) 218–224. doi:<https://doi.org/10.1016/j.jclepro.2017.04.115>.
- (18) I. Mansuri, R. Farzana, R. Rajarao, V. Sahajwalla, Carbon Dissolution Using Waste Biomass—A Sustainable Approach for Iron-Carbon Alloy Production, *Met.* 8 (2018). doi:[10.3390/met8040290](https://doi.org/10.3390/met8040290).
- (19) S. Kopriva, A. Calderwood, S.C. Weckopp, A. Koprivova, Plant sulfur and Big Data, *Plant Sci.* 241 (2015) 1–10. doi:<https://doi.org/10.1016/j.plantsci.2015.09.014>.
- (20) J. Verzeaux, B. Hirel, F. Dubois, P.J. Lea, T. Tétu, Agricultural practices to improve nitrogen use efficiency through the use of arbuscular mycorrhizae: Basic and agronomic aspects, *Plant Sci.* 264 (2017) 48–56. doi:<https://doi.org/10.1016/j.plantsci.2017.08.004>.
- (21) J.J. Fischer, P.H. Beatty, A.G. Good, D.G. Muench, Manipulation of microRNA expression to improve nitrogen use efficiency, *Plant Sci.* 210 (2013) 70–81. doi:<https://doi.org/10.1016/j.plantsci.2013.05.009>.
- (22) McCarthy F.; Sahajwalla, V.; Hart, J.; Chaudhury, S. C. Influence of ash on interacial reactions between coke and liquid iron. *Metallurgical and Materials Transaction B.* 34B (2003), 573.
- (23) Rajarao, R.; Mansuri, I.; Dhunna, R.; Khanna, V.; Sahajwalla, V. Study of Structural evolution of chars during rapid pyrolysis of waste CDs at different temperatures. *Fue.* 134 (2014), 17-25.
- (24) Mansuri, I.; Farzana, R.; Rajarao, R and Sahajwalla, V. Carbon dissolution using waste biomass-A sustainable Approach for Iron-Carbon alloy production. *Metals.* 8(2018).
- (25) Kumar, U.; Maroufi, S.; Rajarao, R.; Mayyas, M.; Mansuri, I.; Joshi, R and Sahajwalla, V. Cleaner production of iron by using waste macadamia biomass as a carbon resource. *Journal of Cleaner Production.* 158 (2017), 218-224.
- (26) A. Brandt, J. Grasvik, J.P. Hallett, T. Welton, Deconstruction of lignocellulosic biomass with ionic liquids, *Green Chem.* 15 (2013) 550–583. doi:[10.1039/C2GC36364J](https://doi.org/10.1039/C2GC36364J).
- (27) Y. Le Brech, J. Raya, L. Delmotte, N. Brosse, R. Gadiou, A. Dufour, Characterization of biomass char formation investigated by advanced solid state NMR, *Carbon N. Y.* 108 (2016) 165–177. doi:<https://doi.org/10.1016/j.carbon.2016.06.033>.



- (28) E. Jakab, O. Faix, F. Till, Thermal decomposition of milled wood lignins studied by thermogravimetry/mass spectrometry, *J. Anal. Appl. Pyrolysis*. 40–41 (1997) 171–186. doi:[https://doi.org/10.1016/S0165-2370\(97\)00046-6](https://doi.org/10.1016/S0165-2370(97)00046-6).
- (29) H. Yang, R. Yan, H. Chen, D.H. Lee, C. Zheng, Characteristics of hemicellulose, cellulose and lignin pyrolysis, *Fuel*. 86 (2007) 1781–1788. doi:<https://doi.org/10.1016/j.fuel.2006.12.013>.
- (30) H. Li, Y. Qu, J. Xu, Microwave-Assisted Conversion of Lignin BT - Production of Biofuels and Chemicals with Microwave, in: Z. Fang, J. Smith Richard L., X. Qi (Eds.), Springer Netherlands, Dordrecht, 2015: pp. 61–82. doi:10.1007/978-94-017-9612-5\_4.
- (31) Mayyas M;Nekouei RK;Sahajwalla V, 2019, 'Valorization of lignin biomass as a carbon feedstock in steel industry: Iron oxide reduction, steel carburizing and slag foaming', *Journal of Cleaner Production*, vol. 219, pp. 971 - 980, <http://dx.doi.org/10.1016/j.jclepro.2019.02.114>

**IEA Bioenergy**



**Further Information**

IEA Bioenergy Website  
[www.ieabioenergy.com](http://www.ieabioenergy.com)

Contact us:  
[www.ieabioenergy.com/contact-us/](http://www.ieabioenergy.com/contact-us/)

IEA Bioenergy Task 42 Website  
<http://task42.ieabioenergy.com/>