

Article

Carbon Dissolution Using Waste Biomass—A Sustainable Approach for Iron-Carbon Alloy Production

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Abstract: This paper details the characterisation of char obtained by high-temperature pyrolysis of waste macadamia shell biomass and its application as carbon source in iron-carbon alloy production. The obtained char was characterised by ultimate and proximate analysis, X-ray diffraction (XRD), Raman spectroscopy, Fourier-transform infrared spectroscopy (FTIR), X-ray photon spectroscopy (XPS), Brunauer-Emmett-Teller (BET) surface area via N₂ isothermal adsorption and scanning electron microscopy (SEM). The results indicated that obtained char is less porous, low in ash content, and high in carbon content. Investigation of iron-carbon alloy formation through carbon dissolution at 1550 °C was carried out using sessile drop method by using obtained char as a carbon source. Rapid carbon pickup by iron was observed during first two minutes of contact and reached a saturation value of ~5.18 wt % of carbon after 30 min. The carbon dissolution rate using macadamia char as a source of carbon was comparatively higher using than other carbonaceous materials such as metallurgical coke, coal chars, and waste compact discs, due to its high percentage of carbon and low ash content. This research shows that macadamia shell waste, which has a low content of ash, is a valuable supplementary carbon source for iron-carbon alloy industries.

Keywords: biomass; waste; carbon dissolution; iron carbon alloy

1. Introduction

Iron-carbon alloy is also known as steel when the dissolved carbon into liquid iron is below 2.1%, and is referred to as cast iron when the percentage of dissolved carbon is even greater. From last few decades, demand for steel has been increasing day by day due to a worldwide population increase. Steel is used in wide range of applications due to its unique combination of strength, formability, and versatility. Global crude steel production reached 1691 Mt in the year 2017, and by 2050 will increase 1.5 times [1]. Overall, 70% of the total global iron-carbon alloy production depends directly on coal. Worldwide, the consumption of coal was over 7800 Mt in 2016, of which 15% was coking coal (~1.2 billion tonnes) used in steel production. Around 70% of global iron-carbon alloy is produced in basic oxygen furnaces (BOFs), which consume 770 kg of coking coal to produce 1 tonne of steel. Furthermore, 28% of iron-carbon alloy/steel is produced in electric arc furnaces (EAF), and significant quantities of electricity used for the EAF process are generated from coal-fired power stations [2,3]. There is a need to reduce the carbon footprint in iron-carbon alloy industries all over the world, and hence it is crucial to explore environment friendly carbon resources as a replacement of coal or coke.

Biomass is a major renewable, sustainable, and environmentally friendly source of energy, and is constituted by a broad range of organic materials derived from plants. Biomass, as an alternative

to carbon, is also cheap and abundantly available, and therefore has gained considerable interest over last few years for various applications [4–6]. In recent years, biomasses including coffee ground, fruit peels, vegetables, have attracted attention for biocompatible packaging, filtration and energy production applications [7–11]. Biomass is composed of high quantity of fixed carbon and less content of inorganic materials, sulphur and nitrogen compare to coal and hence biomass looks as promising materials in steelmaking application [12–14]. Australia is a leading commercial producer of macadamia nuts, producing around 40,000 tonnes a year, out of a total global production of 100,000 tonnes. Waste produced during nut processing which is around 65% of total nut is also expected to increase significantly and currently industry in Australia generates 28,000 tonnes of empty shells each year. Macadamia shell waste is under-utilized, often used for garden mulching and as animal filler, or else incinerated [15]. Limited research has been carried out using waste macadamia shell for producing activated carbons [16]. Macadamia shell contains less inorganic content and high fixed carbon compared to other biomasses. Therefore, macadamia shell has the potential to be used as carbon material for replacement of coal and coke.

In our previous studies, we have utilised various types of waste plastics as an alternative carbon source for steelmaking applications [17–20]. Present study investigates the use of waste biomass i.e., macadamia shell as a replacement of coal and coke in steelmaking industries to produce iron-carbon alloy. Iron-Carbon alloy was produced by using char of macadamia shell waste into iron at 1550 °C. Macadamia shell waste char was characterised in detail, by using various analytical techniques. Our result shows that high temperature pyrolysis of macadamia shell waste produced ~22 wt % of solid char residue containing ~98% C. The kinetics of carbon dissolution and wettability studies was also investigated. Carbon dissolution rate in iron-carbon alloy using macadamia char as source was higher than other carbonaceous materials such as metallurgical coke, coal chars, etc. This novel approach of using macadamia shell waste could be an alternative promising carbon resource for synthesis of iron-carbon alloy.

2. Experimental

2.1. Materials

The macadamia shell waste powder was obtained from the Macadamia Processing Co., Limited, New South Wales, Australia. Prior to experiments, the powder was dried in a hot air oven at 100 °C for 3 h. X-ray florescence (XRF) spectroscopy (PANalytical AXIOS-Advanced WDXRF spectrometer), proximate and ultimate analysis was performed to determine fixed carbon and various elements in macadamia waste and results are represented in Table 1.

Table 1. Ultimate, Proximate and Elemental analysis of macadamia shell waste.

Proximate Analysis (wt % as Received)	
Moisture	5.5
Ash	0.2
Volatile Matter	73.5
Fixed carbon	20.8
Ultimate Analysis (wt % as Received)	
C	48.39
O	40.31
N	0.333

Table 1. Cont.

Elemental Analysis (X-ray Fluorescence Studies)	
Analyte	Concentration (%)
Na	0.0298
Mg	0.0450
Al	0.0620
Si	0.0770
P	0.0140
S	0.0400
Cl	0.0008
K	0.1550
Ca	0.0350
Cr	0.0008
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

2.2. Pyrolysis of Macadamia Shell Waste

The pyrolysis of macadamia shell waste was carried out in horizontal tubular furnace (Ceramic Oxide Fabricators Pty. Ltd., California Gully, Australia) in argon atmosphere under isothermal conditions. The furnace was preheated to 1550 °C and weighed amount of sample was placed on crucible and inserted into hot zone region of furnace. After 15 min of pyrolysis time, the crucible along with the sample was removed from hot zone to cold zone region for cooling. After cooling, the sample was collected, weighed and carefully characterised using carbon and sulphur analyser. Further characterisation of char was also performed by XRD (Cu-K α radiation on a Philips Multipurpose X-ray Diffraction system with step size of 0.026; PANalytical, Sydney, Australia), FTIR (PerkinElmer Spotlight 100; PerkinElmer, Waltham, MA, USA), Raman analysis (Renishaw inVia Raman spectrometer coupled to a microscope with a 514 nm argon ion laser; Renishaw, Wotton-under-Edge, UK), X-ray photon spectroscopy (XPS; Thermo ESCALAB250i; Thermo Scientific, Loughborough, UK), BET surface analysis (TriStar 3000, V6.08 A, N₂ adsorption at liquid nitrogen temperature of –196 °C; Micromeritics, USA), SEM (Hitachi 3400i; Hitachi, Chiyoda, Japan) coupled with energy-dispersive X-ray spectroscopy (EDS, Bruker X flash 5010; Bruker, Preston, Australia) techniques. The collected char after characterisation was used for carbon dissolution for synthesis of iron-carbon alloy. Thermogravimetric analysis (TGA) of waste macadamia shell, at a heating rate of 10 °C/min in nitrogen atmosphere from room temperature to 1000 °C was conducted using Simultaneous Thermal Analyser (STA 8000, PerkinElmer; PerkinElmer, USA).

2.3. Formation of Iron-Carbon Alloy

Investigation of iron-carbon alloy formation between macadamia shell char and molten iron at 1550 °C was carried out using sessile drop method [21] in horizontal tubular furnace (Figure 1). Char collected at 1550 °C was ground and sieved by 100–125 μ m size. Approximately 1 g of char was placed in a die and compacted with a load of 50 kN using a hydraulic press. The compacted char substrate was placed on a graphite sample holder and around 0.5 g of pure electrolytic iron was placed on top of the substrate as shown in Figure 2A.

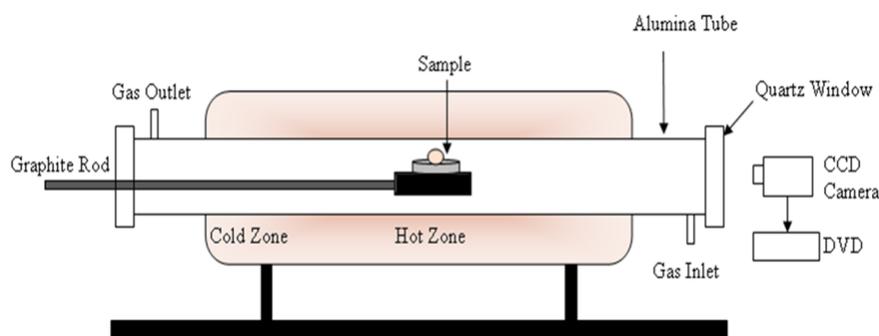


Figure 1. Schematic diagram of horizontal tubular furnace.

Sample holder was initially placed in cold zone for 5 min and slowly pushed into the hot zone region where the temperature was 1550 °C. Experiments were carried out in argon atmosphere and were repeated at different time period to investigate the carburization behaviour. Charge-coupled device (CCD) camera along with video recorder was used to observe the reaction behaviour between iron and carbon. The samples were quenched by withdrawing the sample holder into the cold zone after predefined reaction time. Iron-carbon alloy droplet as shown in Figure 2B was collected and the surface was cleaned with ethanol to remove any attached carbonaceous particles. The percentage of carbon in iron-carbon alloy was measured using LECO carbon analyser (LECO-CS-230).

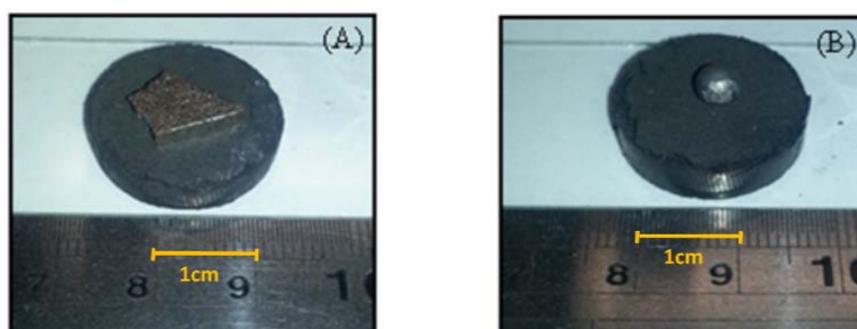


Figure 2. (A) Macadamia char shell substrate and iron—before heat treatment; (B) Macadamia shell char substrate and iron-carbon alloy—after heat treatment.

The interfacial region between molten iron and char substrate was also examined at underside of the droplet which effectively represents the iron/carbon interface. Interfacial investigation was performed for iron-carbon alloy droplet after 30 min of carburisation time in which saturation level of carbon into molten iron was achieved. SEM coupled with EDS was used to examine the interface layer of iron-carbon alloy.

3. Results and Discussion

In depth characterization of macadamia shell char, carbon pick up from char by molten iron and associated kinetics are detailed and discussed below. The obtained results have also been compared with various carbonaceous materials such as synthetic graphite, natural graphite, coke, coal chars and waste Compact Disk (CD) char.

3.1. Elemental Analysis and TGA

A material with high carbon, less volatile contents and low in ash content is desirable to get high carbonaceous residue. The nature of biomass waste and pyrolysis conditions will determine the char yield and quality. Proximate, ultimate analysis and XRF spectroscopy results were performed to

determine fixed carbon and various elements in macadamia waste and obtained results are represented in Table 1. The results show that the moisture content is 5.5%, fixed carbon 20.8%, volatility content 73.5% and ash around 0.2% in macadamia shell waste. The ash content is generally lower than other nut shells such as coconut shell (2.78%) and kukui nut shell (3.27%). The volatile content is around 73%, which is lower compared to other biomasses (like pistachio shell) as they contain around 80–85% [22–24]. Low volatile content compared to other biomasses, less ash, high fixed carbon and low cost biomass makes the macadamia biomass as potential and good precursor of carbon for various applications.

TGA was performed to gain knowledge of pyrolysis of macadamia shell waste. Figure 3 represents the TG curve for pyrolysis of macadamia shell waste at a heating rate of 10 °C/min in nitrogen atmosphere from room temperature to 1000 °C. Initial mass loss occurred between 25 to 150 °C can be attributed to the moisture loss. The main degradation of macadamia shell waste during pyrolysis was observed between 280 to 400 °C which was evident from the maximum peak of the differential thermogravimetric (DTG) curve. The progressive decrease in char yield with pyrolysis temperature is due to increase in primary or secondary decomposition in char. The residue obtained was around 20% of the sample, which consist of carbon and ash.

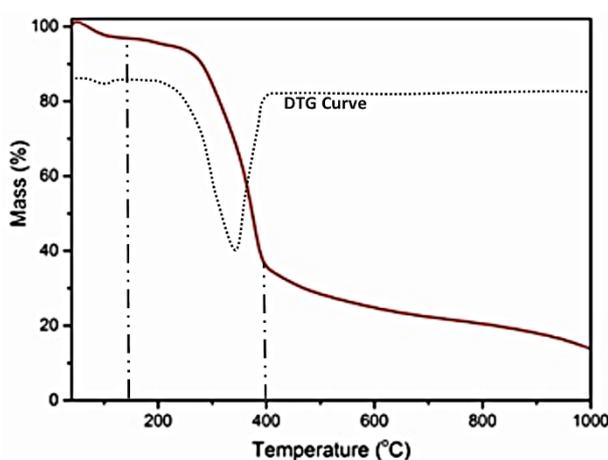


Figure 3. TGA curve of macadamia shell waste.

3.2. Characterisation of Char

This research was an attempt to simulate the direct dissolution of carbon from macadamia shell into molten iron at 1550 °C. Hence char was prepared at 1550 °C; a time of 15 min was found adequate for the completion of macadamia shell degradation as no further weight loss was observed after this time. The aim of this section is to describe the structure and morphological characteristics of macadamia shell char obtained at 1550 °C.

SEM analysis was carried out on char, obtained by pyrolysis of macadamia shell waste at 1550 °C to understand the textural and morphology features. The micrograph of exterior of char obtained by SEM image is shown in Figure 4. It was clearly observed that there were less pores but more solidified areas in appearance. The micrograph indicates that the char was ordered, rich with carbonaceous matter and less ash content. The presence of small vesicles indicates that volatile components were formed and carbon deposits which are observed due to cracking effect caused during the release of volatile matter from the sample. The SEM results are in good agreement with the adsorption-desorption isotherm analysis carried out for BET surface area. Macadamia shell char residue showed BET surface area 5.2 m²/g of with average cumulative adsorption volume of 0.006037 cm³/g; the average pore size was determined to be 10.28 nm. The less surface area of char indicates that the char is composed of ordered carbon structure and with fewer pores.

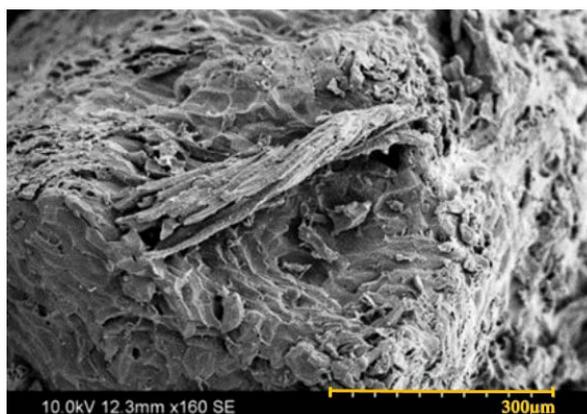


Figure 4. SEM image of macadamia char obtained at 1550 °C temperature.

Graphite crystalline size and structural ordering of macadamia char was investigated by XRD technique. As shown in Figure 5, the XRD of char had two broad peaks at about 24° and 43°, which were assigned to the graphitic (002) and (100) plane, respectively. The (002) peak which is attributed due to parallel packing of carbon layers should be symmetrical theoretically. But (002) peak exhibits asymmetry due to presence of γ -band which is associated with amorphous and aliphatic structures [25]. The peak at 2θ angle of $\sim 43^\circ$ can be assigned to (100) diffraction of hexagonal graphene carbons, which characterise the aromatic part of char. However, it was difficult to differentiate the contents of the graphitic and amorphous phase in pyrolyzed product by XRD. The crystallite size in the char of the carbon structure was determined from the width of the (002) peak. Crystallite height (L_c) of macadamia shell char at 1550 °C was determined to be 1.4 nm. Coals and cokes generally have L_c value of around 0.3–0.5 nm [26], which is lower than the L_c value of macadamia shell char.

Raman spectroscopy is very sensitive and potential technique to characterise carbon materials to study molecular and crystalline structure. As shown in Figure 5, Raman spectra of the macadamia shell char sample was deconvoluted into two peaks around 1590 and 1340 cm^{-1} , known respectively as the G and D bands. For hexagonal graphite, “G band” is assigned to E_{2g} vibrational mode, which is attributed to the in-plane stretching motion pairs of carbon sp^2 atoms. “D band” is due to existence of disorder in graphitic structure which is assigned to A_{1g} symmetry. The intensity ratio (I_V/I_G) of the valley between D and G band (I_V) to the G band (I_G); is related to amorphous carbon structure [27]. In this study, I_V/I_G ratio is found to be 0.45. The macadamia char sample pyrolyzed at 1550 °C exhibited a spectral pattern similar to that of waste CDs. The I_V/I_G ratio results of the Raman spectroscopy tests were almost identical to waste CD char prepared at 1300 °C, which indicates that macadamia shell char is composed of both aromatic and aliphatic structures.

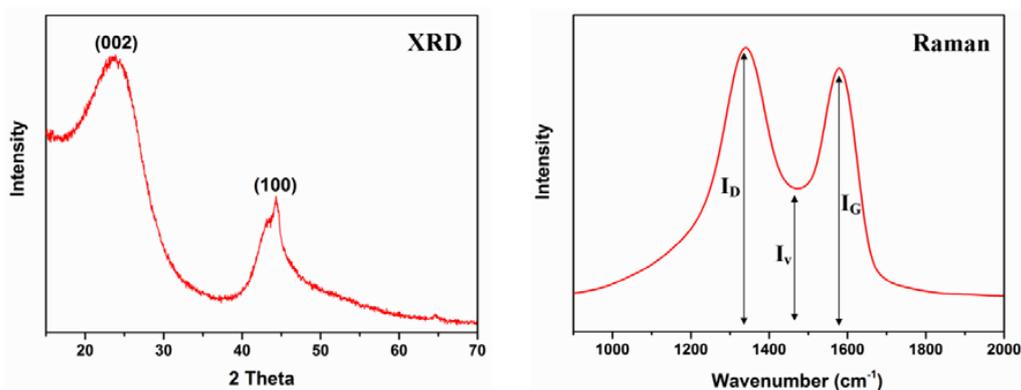


Figure 5. XRD and Raman spectra of macadamia shell char obtained at 1550 °C.

Results from the FTIR analysis of both waste macadamia shell and char obtained by pyrolysis are shown in Figure 6. The waste macadamia shell showed peaks at 3700–3000 cm^{-1} and was related to O–H stretching vibration of phenolic, alcoholic and carboxylic functional groups; sharp peak between 2800–3000 cm^{-1} is attributed to $-\text{CH}_2$ and $-\text{CH}_3$ stretching vibration; peak at 1700 cm^{-1} is stretching vibration of free carbonyl group; peaks at 1650–1510 cm^{-1} is due to C=C stretching vibrations in aromatics; peak at 1400 cm^{-1} is linked to O–H bending; strong peak at 900–1100 cm^{-1} attributed to C–O–C, C–O and C–OH groups stretching. All the peaks clearly signify the presence of cellulose, hemicellulose and lignin components in waste macadamia shell [28]. The FTIR of char doesn't show any major peaks which clearly indicates that the macadamia shell has been decomposed completely with removal of functional groups associated with cellulose and lignin chemical structures. The presence of upward drift (corrected in spectra) clearly confirms the presence of aromatic content in char.

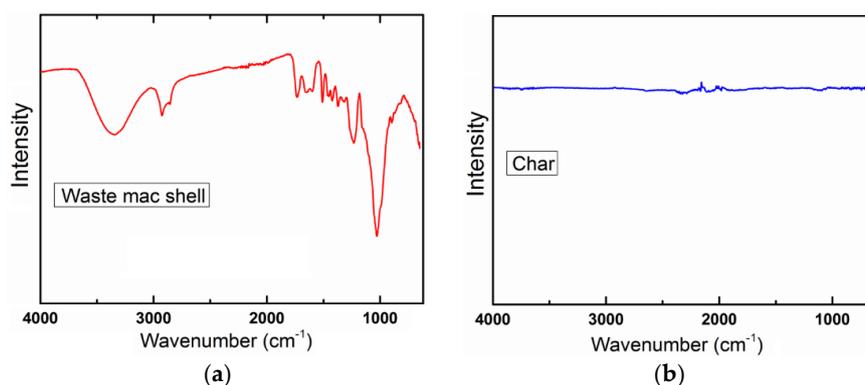


Figure 6. FTIR spectra of (a) waste macadamia shell and (b) char produced at 1550 °C.

XPS analysis was conducted for the waste macadamia shell char to determine the atomic concentration and functionality of carbon in char. Figure 7 shows the convoluted C1s spectra fitted using linear background for waste macadamia shell char obtained at pyrolysis temperature 1550 °C. The calculated results for C1s peak such as start binding energy (BE), peak BE, end BE, full width half maximum (FWHM) and atomic compositions (at %) is shown in Table 2. The core peak, C1s was separated into six components (C1s, A–F) using Lorentzian curve fitting method. The major component observed at 284.49 eV binding energy value (C1s, A) corresponds to highly ordered pyrolytic graphitic (HOPG, $-\text{C}=\text{C}-$ bonds). The appearance of HOPG peak with atomic concentration 40.23% confirms the transformation of carbon to HOPG structure at pyrolysis temperature 1550 °C. The B component generally belongs to C–C and C–H bonds and other components belong to various C=O, C–O, O=C–O groups. The XPS spectrum confirms the presence of both aromatic (40%) and aliphatic carbons in macadamia shell char. The features such as less ash, high char yield, high fixed carbon and aromatic contents specifies that the macadamia shell biomass char can be good precursor of carbon for Iron–Carbon alloy synthesis.

Table 2. XPS peak position of fitted C1s of macadamia shell char at 1550 °C.

Name	Start BE	Peak BE	End BE	FWHM (eV)	Area (CPS eV)	At %
C1s A	298.48	284.49	281.38	0.76	20,714.98	40.23
C1s B	298.48	284.99	281.38	1.73	13,978.33	27.15
C1s C	298.48	286.59	281.38	1.73	3051.44	5.93
C1s D	298.48	287.99	281.38	1.73	1671.52	3.25
C1s E	298.48	289.19	281.38	1.73	147.05	0.29
C1s F	298.48	290.16	281.38	3.2	4575.57	8.89

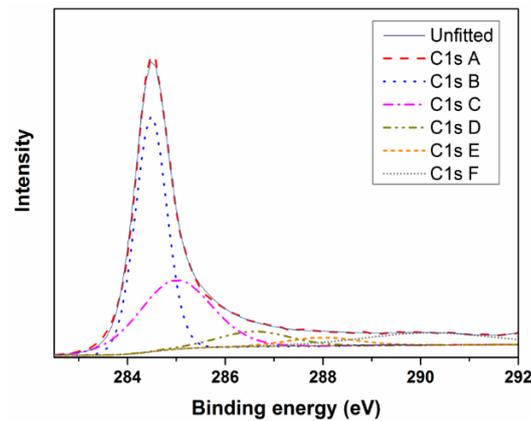


Figure 7. XPS spectra of convoluted C1s fitted using linear background for macadamia shell char.

3.3. Iron-Carbon Alloy

Macadamia shell char obtained at 1550 °C was employed for iron-carbon alloy studies to simulate the direct dissolution of carbon from macadamia shell waste into molten iron. Dissolution of carbon from macadamia Shell chars at 1550 °C as function of time is shown in Figure 8. Rapid carbon pickup by molten iron was observed during first two minutes of contact and it had reached to ~4.78 wt % Carbon. The dissolution rate of carbon slowed down after that and the total carbon level in molten iron reached to a saturation value of ~5.18 wt % after 30 min of contact.

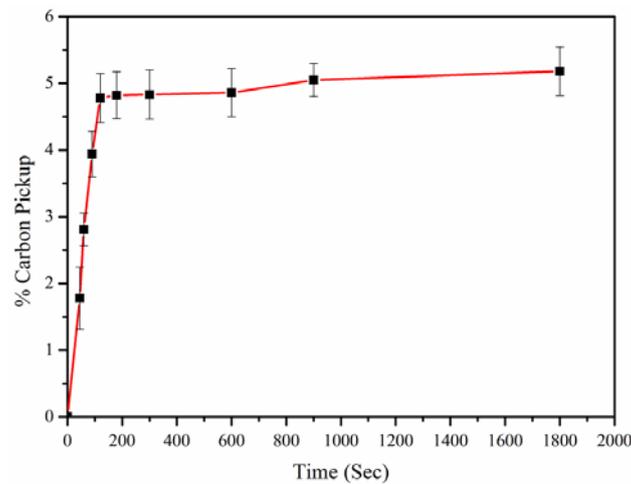


Figure 8. Variations in Carbon Pickup from macadamia shell char by iron at 1550 °C with time.

The overall carbon dissolution rate constant (K) was obtained using following equations [19].

$$\frac{dCt}{dt} = \frac{Ak}{V} * (Cs - Ct) \quad (1)$$

$$\ln \frac{Cs - Ct}{Cs - Co} = -K * t \quad (2)$$

where, C_s and C_t respectively represent the saturation solubility and carbon concentration (wt %) in liquid iron as a function of time t , and k is the first order rate constant ($m \cdot s^{-1}$). A , V are respectively the interfacial area of contact and the liquid iron bath volume. C_o is the initial carbon concentration in liquid metal (wt %), as we have used 99.98% electrolytic pure iron for all experiments, hence the value of C_o is set to zero. Overall carbon dissolution rate constant, $K = Ak/V$ was measured from

the negative slope of $\ln((C_s - C_t)/(C_s - C_0))$ vs. time plot. It was assumed that there was not much change in the contact area during this short initial period of contact.

The respective plot for $\ln((C_s - C_t)/(C_s - C_0))$ vs. time was plotted as shown in Figure 9. The slope to determine the overall carbon dissolution rate constant for initial two minutes of reaction was calculated by using best fitted points without fixed intercept option and found to be $21.1 \times 10^{-3} \text{ s}^{-1}$. Carbon dissolution using macadamia char was compared with other carbonaceous materials such as metallurgical coke, coal chars, synthetic graphite and waste CD char as shown in Table 3. This has proved that carbon dissolution is much faster than traditional carbonaceous material such as coke and coal chars. The value of overall carbon dissolution rate constant using macadamia shell char is very close to that previously observed with synthetic graphite by Wu et al. [21].

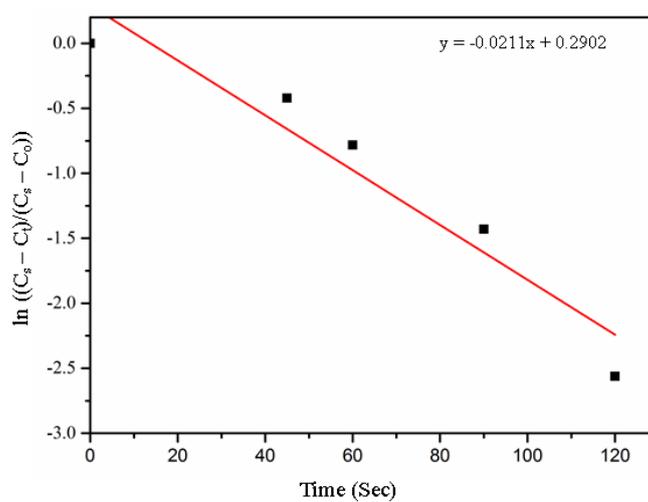


Figure 9. Plot of $\ln((C_s - C_t)/(C_s - C_0))$ vs. time for first 2 min to show carbon dissolution rate constant using waste macadamia char.

Table 3. Comparison chart of overall carbon dissolution rate constant (K).

Material	Overall Rate Constant $K \times 10^{+3} \text{ s}^{-1}$	References
Macadamia Char	21.1	This research
Synthetic Graphite	24	Wu et al. [21]
Waste CD char	19.2	Mansuri et al. [19]
Coal char 1	0.1	McCarthy et al. [29]
Coal char 4	0.3	McCarthy et al. [29]
Coke	0.003	Kongkarat et al. [30]

Ash is a significant factor in the carbon dissolution reaction and its role has been extensively explained by many of researchers. Explaining the role of ash impurities on carbon dissolution, McCarthy et al. [29] observed that the ash in different types of carbonaceous materials can directly influence the composition of the liquid iron during reaction. The formation of semifused ash layer at the interface which acts as a physical barrier and reduced the interfacial contact area between molten iron and carbon source was observed. Reduction of silica from the ash consumes carbon and retard the carbon pickup in the liquid metal and lowered the carbon dissolution rate was also observed and clearly signifies the role of ash content on carbon dissolution. 98 wt % of carbon content in macadamia shell char was measured with a LECO-CS-444-DR carbon analyser (Laboratory Equipment Corporation, USA) and negligible amount of ash content in char was apparently dominant factor for higher rate of carbon dissolution into molten iron. Hence macadamia shell char showed higher carbon dissolution rate compared to other carbonaceous materials (Table 3).

Interface of Iron-Carbon alloy between molten iron and char substrate underside of the iron droplet was examined by SEM/EDS analysis. SEM images coupled with EDS for interfacial layer at iron side is shown in Figure 10. The SEM/EDS analysis confirms the complete absence of ash layer at the interface between molten iron and char substrate. EDS spectra showed only carbon and iron peak, no other elements or phase was identified at interfacial layer.

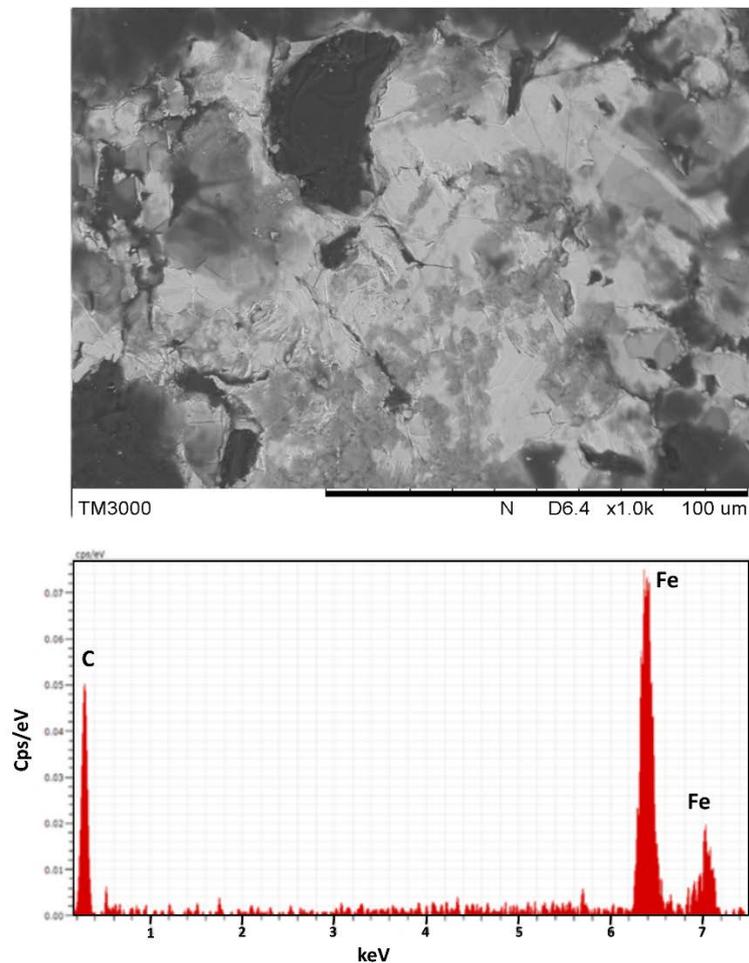


Figure 10. SEM images coupled with EDS of metal/carbon interface of macadamia shell char substrate and iron.

In the absence of interface blockage between molten iron and carbon source, more contact area of iron was available for carbon to transfer. Hence a very high dissolution rate and high carbon pickup was observed for waste macadamia shell char. This study evidently confirms that waste macadamia shell can be used as a promising supplementary carbon source in Iron-Carbon alloy making.

4. Conclusions

In this study, the use of waste macadamia shell biomass as a carbon source for Iron-Carbon alloy making was investigated. The main conclusions are summarised below.

1. High temperature pyrolysis of waste macadamia shell yield 22 wt % char residue with rich in carbon content of ~98 wt % C and negligible amount of ash impurities.
2. Less ash, high char yield, high fixed carbon and aromatic contents makes char as ideal carbon precursor for Iron-carbon alloy synthesis.

3. The high rate of carbon dissolution into molten iron was observed using macadamia shell char as a carbon source reaching to 5.2 wt % of C in Iron-carbon alloy.
4. Carbon dissolution rate using macadamia char was comparatively higher than other carbonaceous materials such as metallurgical coke, coal chars and waste CD char due to high % of carbon and low ash content.

This research shows the sustainable way of recycling low ash content waste macadamia shell through their transformation into higher carbon Iron-Carbon alloy.

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Conflicts of Interest: The authors declare no conflict of interest.

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