The Formation of Metallurgical Coke within Minutes through Coal Densification and Microwave Energy

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ABSTRACT

This paper shows how feedstock densification gives rise to a step change in the time required to create a metallurgical grade coke using microwave energy. Five densified coking and non-coking coals were heated in a multi-mode microwave 2450 MHz cavity for varying treatment times (2-20 minutes) with a fixed power input (6 kW). Proximate analysis, intrinsic reactivity, coke reactivity, dielectric properties, and petrographic analysis of the coals and microwave produced lump cokes were compared to a commercial lump coke. Densifying the sample prior to microwave treatment enabled a dramatic acceleration of the coking process when combined with targeted high microwave energy densities. It was possible to form fused coke lump structures with only 2 minutes of microwave heating compared to 16-24 hours via conventional coking. Anisotropic coke morphologies (lenticular and circular) were formed from non-coking coal that are not possible with conventional coking and increasing treatment time improved overall coke reflectance. Three of the coals produced coke with equivalent coke reactivity index values of 20-30, which are in the acceptable range for blast furnaces. The study demonstrated that via this process, non-coking coals could potentially be used to produce high quality cokes, potentially expanding the raw material options for metallurgical coke production.

1. Introduction

Metallurgical coal for coke production has been classified as a critical raw material for the EU economy due to its essential role in steel production and the scarcity of coking coals globally.[1] India has the fifth largest coal reserve in the world,[2] but Indian coals characteristically have high ash, low sulfur content, with a low-to-medium calorific value,[3] and are therefore considered to be poor coking coals. Only 13 Mt of the 57 Mt of coking coals used to make coke in India in 2015-2016 were sourced from indigenous sources.[4] With depleting coking coal reserves and the high cost of metallurgical coking coals,[5] new methods of coke production need to be established which can coke non-coking coals.

Metallurgical coking coals are those coals that soften, swell and then solidify as they are heated through the temperature range 350 to 550 °C.[6] Aromaticity increases as aromatic and non-aromatic hydrocarbons present in the coal are polymerized to form larger, complex aromatic polymers, which are then condensed by eliminating hydrogen and other side chains to form coke.[7] If a coking coal is heated beyond 300–1000 °C, regardless of the heating mechanism, it will devolatilize, plasticize and soften (depending on the coal rank), and with sufficient residence time at 1000 °C, will produce coke.[8] Coke structures can take the form of anisotropic and isotropic structures.[9] Anisotropic cokes are favored over isotropic cokes for several reasons. While isotropic cokes have properties in the same direction, anisotropic cokes properties vary with different orientations. Anisotropic coke is less reactive to carbon dioxide than isotropic coke, and thus minimizes the reactivity.[10]

From a physical perspective, coking coals form a solid residue when heated to 1100 °C in an inert atmosphere, while a non-coking coal will form a powder residue or a solid residue without the physical and chemical properties of coke.[7] Non-coking coals and biomasses have been added to coke blends to reduce costs and environmental concerns.[11–13] The coking of coal blends has been improved by densifying the coal through stamp charging.[14] Densification has

also been shown to improve the coking of coking coal blends,[15] low grade semi-soft coals,[16] non-coking coals,[17] Victorian brown coal[18] and blends of saw-dust and non-coking coal with binder.[19] While densification enhances coke properties in conventional coking, it does not have a significant impact on coking time, which is around 24 hours.[7]

Previous studies have shown the potential of microwave heating of coal to rapidly form coke.[8,20] Several studies have used susceptors to increase the microwave absorbance of coal.[21–24] However, Lester *et al.*[8] and Binner *et al.*[20] showed that it is possible to produce coke with a similar vitrinite reflectance to that of conventional cokes without the use of susceptors, although the cokes formed were only in powdered form. The physical structure of coke is a key feature of blast furnace operation,[25] as it provides the bed support and permeability for the liquid phase drainage and upward flow of blast furnace gases. Microwave material processing needs to exploit the dielectric properties of a material to achieve effects that could not be achieved with conventional heating.[26] Microwaves heat selectively and volumetrically, resulting in instantaneous heating, and thus avoiding the heat transfer limitations of conventional heating and drastically reducing treatment times. The degree of microwave heating depends on the dielectric properties of the coal,[27] and in particular its coal rank and carbon layer stacking in combination with aromatic cabin content.[28] Although coal as a bulk material at room temperature has relatively low dielectric properties, coal constituents such as moisture, bound hydroxyl groups and pyrite have significantly higher dielectric loss than the organic component,[29–31] and can be selectively heated. Water trapped inside porous materials has the potential to superheat to temperatures well above 100 °C.[20]

This paper demonstrates for the first time that densifying coal prior to microwave treatment enables a dramatic acceleration of the coking process when combined with targeted high microwave energy densities. Petrographic and thermal analysis shows that with this process, coke structures can be formed in non-coking coal that cannot be formed with conventional

coking or other microwave heating techniques, and the coke produced is equivalent to the quality of commercially produced coke. Finally, the paper presents the potential the process has to effect a step change in coke making, potentially allowing some non-coking coals to be used to make high quality cokes.

2. Materials and Methods

2.1. Materials

Five coals were supplied by Tata Steel Ltd India (both coking and non-coking). The coals were an indigenous medium coking coal which is used as the base coal for a coke plant blend (Coal A), an imported vitrinite rich prime coking coal (Coal B), an imported Pulverized Coal Injection (PCI) coal (Coal C), a typical coke plant commercial blend coking coal (Coal D), an indigenous Indian non-coking/thermal coal which is a typical high ash non-coking coal (Coal E). All coals were supplied pre-crushed < 3.35 mm. A commercially produced coke from a UK conventional coke plant was used as a comparison (UK Coke).

2.2. Product Analysis

2.2.1. Dielectrics

The dielectric properties of the coals were tested to assess how strongly they interact with electromagnetic energy at certain frequencies. The cavity perturbation technique provides accurate dielectric data at discrete frequencies for low loss granular materials. The measurements were performed at a microwave frequency of 910 MHz and 2470 MHz due to the dimensions of the cavity, which are close as possible to the industrial used microwave frequencies of 896/915 MHz and 2450 MHz,[32] and at temperatures from 20 °C up to 800 °C. The dielectric properties of coal exceeded the measurement abilities of the cavity at temperatures above 650-700 °C due to the graphitization of the coal.[8] The resonant cavity consists of a cylindrical copper cavity connected to a vector network analyzer, which measures

the frequency shift and change in quality factor relative to the empty resonating cavity when a sample is introduced. The powdered coal samples were loaded into a quartz tube with a density equivalent to the coal pellets ($\sim$1100 kg.m^{-3}), and held in a conventionally heated furnace above the cavity until the temperature set-point was reached. The tube was then moved into the cavity, and the properties determined at 2470 MHz. The Q factor of the cavity was calculated and used, in turn, to calculate the dielectric constant, ε', and dielectric loss factor, ε''. A detailed description of the equipment is given elsewhere.[8] ε' is a measure of a material's ability to store electromagnetic energy through polarization, and ε'' is a material's ability to convert this stored energy into heat.[33] ε' and ε'' can be used to assess the general ability of a material to heat in an electromagnetic field, and this quantity is known as the loss tangent, $\tan \delta$:

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'} \tag{1}$$

When a wave of electromagnetic energy propagates in a dielectric material, its amplitude diminishes due to power absorption in the material.[26] The penetration depth of electromagnetic energy into a material (D_p) is defined as the depth at which the power flux falls to 1/exp (0.368) of its surface value (eq. 2). The penetration depth into a material is a good indicator of the potential to achieve heating uniformity within a material where penetration depth is proportional to wavelength, and therefore increases with decreasing microwave frequency.[34]

$$\boldsymbol{D_p} = \frac{\lambda_0}{2\pi\sqrt{2\varepsilon'}} \frac{1}{\sqrt{\left[\left\{1+\left(\frac{\varepsilon''}{\varepsilon'}\right)^2\right\}^{1/2} - 1\right]}} \tag{2}$$

Where D_p is the penetration depth (m) and λ_0 is the free space wavelength of incident radiation (m). All dielectric tests were conducted in duplicate.

2.2.2. *Thermal Characterisation, CO_2 Reactivity, and Surface Area*

Thermogravimetric Analysis (TGA) was used to analyze any changes in composition during the microwave pyrolysis treatment. Thermal profiles were produced using TA Instruments Q500 TGA. TGA tests used 10-15 mg of sample with a particle size range of 75-

300 µm. The method used was based on a slow pyrolysis method.[35] The sample was heated in a furnace at 5 °C.min^{-1} in 100 ml.min^{-1} of nitrogen from ambient to 900 °C, after which the gas was switched to air at 100 ml.min^{-1}. The composition of the samples is given by moisture, dry ash free volatile, fixed carbon, and dry ash contents. The intrinsic reactivity of the coals was assessed via non-isothermal TGA analysis. The heating rate was set 10 °C.min^{-1} in 100 ml.min^{-1} of air from atmospheric temperature to 900 °C.[8] The burnout profile was used to obtain the burnout temperature and peak temperatures.[36] Due to the small sample sizes being produced, it was not possible to conduct the CO_2 reactivity test according to ASTM D-5341.[37] Instead a modified version of the test using a TGA was conducted.[18,38] 10-15 mm long fragments of lump coke and UK commercial coke were heated to 1000 °C in nitrogen at a flow rate of 50 ml.min^{-1} in the TGA at a ramp rate of 20 °C.min^{-1}, then held in CO_2 at a flow rate of 50 ml.min^{-1} for 30 and 120 minutes, and then allowed to cool in nitrogen.[18] The reactivity (RCO_2) is calculated as follows:[17,38]

$$RCO_2 = \left(\frac{m_1 - m_2}{m_1}\right) \times 100 \qquad (3)$$

Where m_1 was the original test sample weight before reaction (g) and m_2 was sample weight after reaction in CO_2 (g). All TGA tests were conducted in triplicate.

Surface area was measured by CO_2 adsorption isotherms which were acquired using a Micromeritics ASAP 2420 instrument at 0 °C. Approximately 1 g of coke sample (1 -7 mm particle size) was weighed into a sample tube and degassed for 15 hours under vacuum (0.01 mbar) at 120 °C. Adsorption data was acquired from 0.00–1.20 bar with surface area and micropore volume determined by the dubinin-Radushkevich model. Samples were run in duplicate.

2.2.3. *Petrographic Analysis*

Petrographic analysis was conducted for morphological analysis and mosaic images of the samples before and after treatment. Oil immersion analysis was carried out using polished

blocks of the samples, prepared with an epoxy liquid resin blend, and examined manually using a polarized-light microscope Leitz Ortholux Pol II BK with ×50 magnification oil-immersion objective and ×10 magnification eyepiece.[20] Random reflectance was measured on each sample with the system calibrated using a silicon carbide light standard (7.51 % reflectance in oil).[39] Color images were captured using a Zeiss Axio.Imager.M2m microscope operating with a light polarizer at 6.5 Amps and a 50x magnification oil immersion objective and a 10x fixed lens (500x total magnification).

2.3. Mineral Liberation Analysis

Characterization of each of the coal samples was performed using a Mineral Liberation Analyzer (MLA) to investigate their compositional and textural characteristics. The MLA investigation was conducted using a FEI Quanta 600Mk1 Scanning Electron Microscope (SEM), operating MLA version 3.1 software, and equipped with a tungsten filament electron source, two Bruker XFlash® 5030 silicon drift detector (SDD) EDX spectrometers, a secondary electron detector and a backscatter electron (BSE) detector. Preliminary EDX characterization of individual mineral phases in the coal samples was performed using Bruker Esprit V1.9 software to allow for the development of the MLA mineral reference list. The MLA characterization performed in this study used the 'Extended backscatter' (XBSE) mode, which segments particles based on their backscatter (greyscale) differences. Subsequently, X-ray spectra are acquired from centroid spots on each different mineral phase delineated by the greyscale differences. These spectra are then matched against the mineral list of known characteristic X-ray spectra, and each grain is classified as the mineral which best matches the library entry. Measurement results can then be processed and extracted to a database where they can be interrogated using the MLA Dataview module. This measurement mode produces mineral abundance, dimensional and liberation data for all particles and grains measured in a sample.

2.4. Microwave Experiments

The microwave coking system consisted of a variable power (2-6 kW) microwave generator (IBF Electronic GmbH, Germany) set to 6 kW power input (maximum power input) at an applied frequency of 2.45 GHz for all tests (Fig. 1). The electromagnetic energy produced by the generator was transmitted through WR340 waveguide to a Sairem multi-mode cavity (model CM 02510) measuring 420 x 420 x 550 mm. An automatic 3-stub tuner (S-Team STHD V1.5) was attached to the waveguide for power analysis and impedance matching purposes in order to maximize the absorbed microwave power and minimize reflected power from the coal. Incident, absorbed, and reflected power were monitored and recorded at a constant incident power (6 kW) during the tests via a PC connected to the tuner.
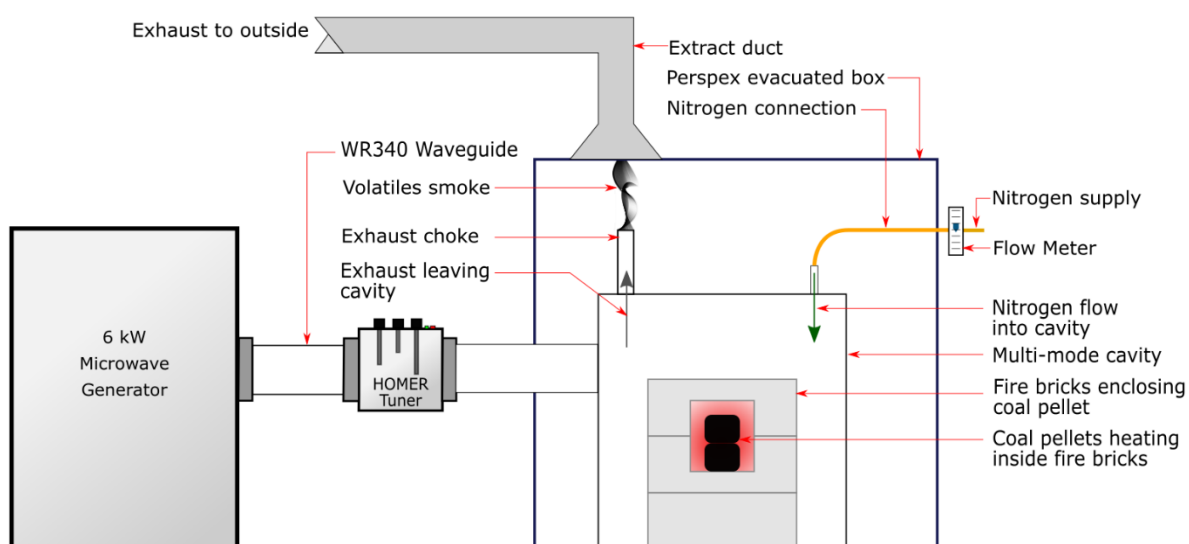
Figure 1. Schematic of microwave coking rig

Each sample was initially densified in a 20 ton Specac automatic pellet press using a 1 ¼" (31.75 mm) pellet die using approximately 30 g (2 pellets) of coal was weighed and dimensioned for initial bulk density. The coal pellets were placed into a base and lid firebrick (Victas, grade 30) with pre-drilled holes coated in thermally resistant grout (Victas), and then situated in the center of the cavity. The firebricks contained the pellet within an inert atmosphere and reduced heat losses from the sample surface during processing. The dielectric

properties of the firebrick were significantly lower than those of the coal (tan δ = 0.0019 at 20 °C, tan δ = 0.0076 at 700 °C), and thus were effectively transparent to microwave energy compared with the coal. It was assumed that all applied energy was absorbed by the coal. The system was purged with nitrogen at a flowrate of 80 l.min^{-1} to provide anoxic conditions prior to treatment (5 minutes), throughout treatment, and after microwave treatment until the sample had cooled, and extraction was used during microwave processing to remove any gases and particulates generated during pyrolysis of the coal. Once the coal sample had cooled to room temperature, the product was removed from the cavity and weighed and measured.

Due to the coking process taking up 10 minutes for all volatiles to leave the microwave cavity, the coking trials treatment durations were initially set to 10, 15 and 20 minutes at 6 kW power input to assess the impact of heating beyond complete devolatilisation. In order to assess the degree of coking achieved over shorter microwave treatment periods, Coal C, a non-coking coal, was tested for additional times of 2, 5, 7.5 minutes. Coal B was only tested for 10 and 15 minutes as treatment times greater than this resulted in plasma formation within the cavity. Due to the inert atmosphere within the cavity and the extremely high temperatures being reached, it was not possible to measure the temperature using a fiber optic thermocouple or thermal imaging camera.

3. Results and Discussion

3.1. Influence of Coal Composition on Coking Potential and Microwave Heating

The suitability of a coal for coking can be explored through proximate analysis and petrographic analysis. The petrographic analysis of the coals provides maceral identification and vitrinite reflectance (R_{ran}) or rank of the coals. All coals are high volatile bituminous coals, apart from coal E which falls between lignite (R_{ran} - 0.303 %) and sub-bituminous (R_{ran} - 0.617%).[40] Coal E is also a blend with some high rank coal, which is likely to give some

coke morphologies that would not normally result from coking of the base Coal E sample. Coal E is the least likely to produce good coke due to its high inertinite macerals (semi-fusinite and fusinite) content, which inevitably form 'filler' morphologies in the coke.[41] Coal B has the lowest percentage of semi-fusinite and Coal C has the lowest percentage of fusinite. The liptinite content is quite high for Coal E, and this will not contribute to any morphology in the coke since it is predominantly volatile matter.[42] No liptinite was observed in Coal A and B, and virtually none in Coal C and D. The vitrinite reflectance of Coal E is very low (< 0.5 %), which will form isotropic coke structures, rather than anisotropic.[42] In comparison, Coal A, B and C have much higher average vitrinite reflectance values, which means that anisotropic morphologies are more likely to result during the coking process. Coal C is similar to Coal B, but with a slightly higher reflectance, making it more suitable for coke production. It is also more likely to produce circular morphologies over incipient or isotropic. Coal D is inertinite rich, mainly with fusinite and semi-fusinite. The high vitrinite reflectance for Coal D means that the small amount of vitrinite that is present is likely to form medium to coarse circular and lenticular morphologies.[42]

Table 1. Proximate and petrographic assessment of the coals

	Coal A	Coal B	Coal C	Coal D	Coal E
Proximate analysis					
Moisture (%)	0.7	0.9	0.9	1.0	3.3
Dry Fixed Carbon (%)	58.8	63.5	66.3	62.2	41.7
Dry Volatiles (%)	24.1	28.4	22.9	26.7	35.5
Dry Ash	17.0	8.1	10.8	11.1	22.8
Maceral analysis					
Vitrinite (%)	49.6	60.8	60.0	35.6	37.6
Liptinite (%)	0.0	0.0	2.4	0.4	9.6
Semi-Fusinite (%)	34.8	19.6	23.2	38.4	32.4
Fusinite (%)	15.6	19.6	14.4	25.6	20.4
Vitrinite reflectance					
Average (%)	0.94	0.79	0.89	0.97	0.46
Minimum (%)	0.81	0.63	0.68	0.80	0.33
Maximum (%)	1.15	1.06	1.58	1.23	1.11
St.Dev.	0.078	0.107	0.132	0.095	0.157

Studies have shown that cokes with good thermal strength can be made from coals with 22-26 % volatile matter and reflectance of 1.1-1.2 %,[43] and the CSR index passes through a maxima in the region of prime coking coals with a reflectance of 1.2-1.3 %.[44] The coals in this study are slightly below the optimal reflectance, but have volatile matter content between 25-28 %, apart from non-coking Coal E (35.5 %), which makes them suitable for coking[7] (Table 1).

3.2. Influence of Coal Composition on Coking Potential and Microwave Heating

The behavior of the coals under the influence of microwave energy can be understood via their dielectric properties. Dielectric properties demonstrate the coals potential to absorb electromagnetic energy and reject it as heat. Fig. 2 illustrates that the dielectric loss tangent (*tan δ*) changes between 20 °C and 700 °C for a frequency of 2450 MHz. The coals have relatively consistent low loss tangent values between 20 and 550 °C, indicating low dielectric absorption. The initial drop in tan δ around 100 °C is due to the removal of free water in the coal.[31] Low temperature dielectric properties are strongly dependent on a coal's moisture content. This is particularly notable for Coal D, which shows a halving in tan δ once moisture has been removed from the sample (0.06 to 0.03). Above 550 °C, the dielectric absorption of all the coals increases as all volatile matter is released, and start to form coke structures. After 650 °C, the dielectric properties were too high for the cavity perturbation system to measure. This indicates that thermal runaway has been achieved and the coal is interacting strongly with the electromagnetic energy. Thereafter, the coals interact strongly with the electromagnetic field, enabling continued heating (without susceptors) at the temperatures required to form coking structures. Hence, the aim of any microwave coking process should be to ensure that thermal runaway of the coal is already underway before the bound water has fully vaporized.[20]
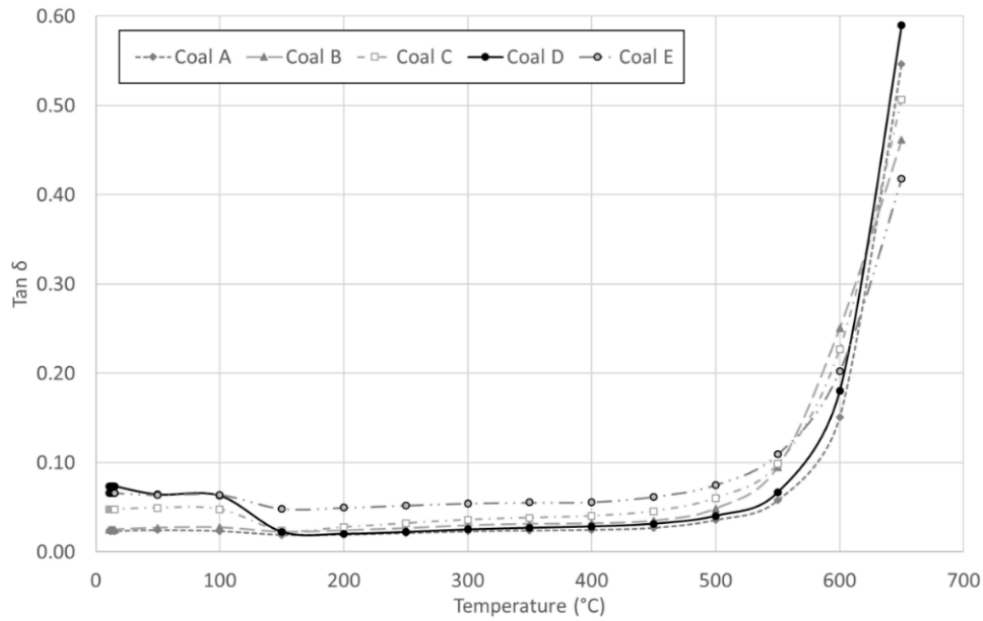
Figure 2. Dielectric loss tangent (tan δ) of the coals at temperatures up to 650 °C at a frequency of 2470 MHz. As temperature increases beyond 500 °C and the coal starts to graphitize, the ability of the coals to heat in an electric field increases exponentially.

The chemical composition of coal affects its dielectric properties. The proximate analysis of the coal varies with rank, while mineral content and composition is influenced by its geological age and origin.[29] The mineral content of coals is located in the ash content, which can include material that can be selectively heated with microwave energy in the coal matrix, such as pyrite.[45] To investigate the potential for minerals to assist in the microwave heating process, MLA characterization was performed to establish the type and abundance of minerals present in the coal matrix, and to determine their textural distribution. Table 2 shows that in addition to coal, two main microwave heaters were identified within the coals. These were hematite, a mineral consisting of ferric oxide, and kaolinite, a clay mineral (Fig. 3). The majority of the coal matrix was composed of coal, with Coal B having the lowest percentage at 72 %, and Coal D the highest percentage at 84 %. Hematite and kaolinite was highest in Coal C (13.9 %) and lowest in Coal B (7.4 %).

**Table 2**. Mineral Abundance (wt. %) for the 5 Coals

Mineral	Coal A	Coal B	Coal C	Coal D	Coal E
Coal	76.3	71.9	80.7	84.0	83.0
Orthoclase	0.8	0.4	0.0	0.3	0.5
Kaolinite	10.2	4.4	13.9	6.3	6.9
Hematite	1.1	3.1	0.0	2.2	1.9
Quartz	4.9	1.7	2.7	2.6	0.9
Apatite	0.0	2.8	0.0	0.9	0.6
Muscovite	6.6	15.8	0.0	3.3	5.6
Calcite	0.0	0.0	1.8	0.1	0.6
Pyrite	0.0	0.0	0.0	0.2	0.0
Rutile	0.0	0.0	1.0	0.0	0.0
Total	100.0	100.0	100.0	100.0	100.0
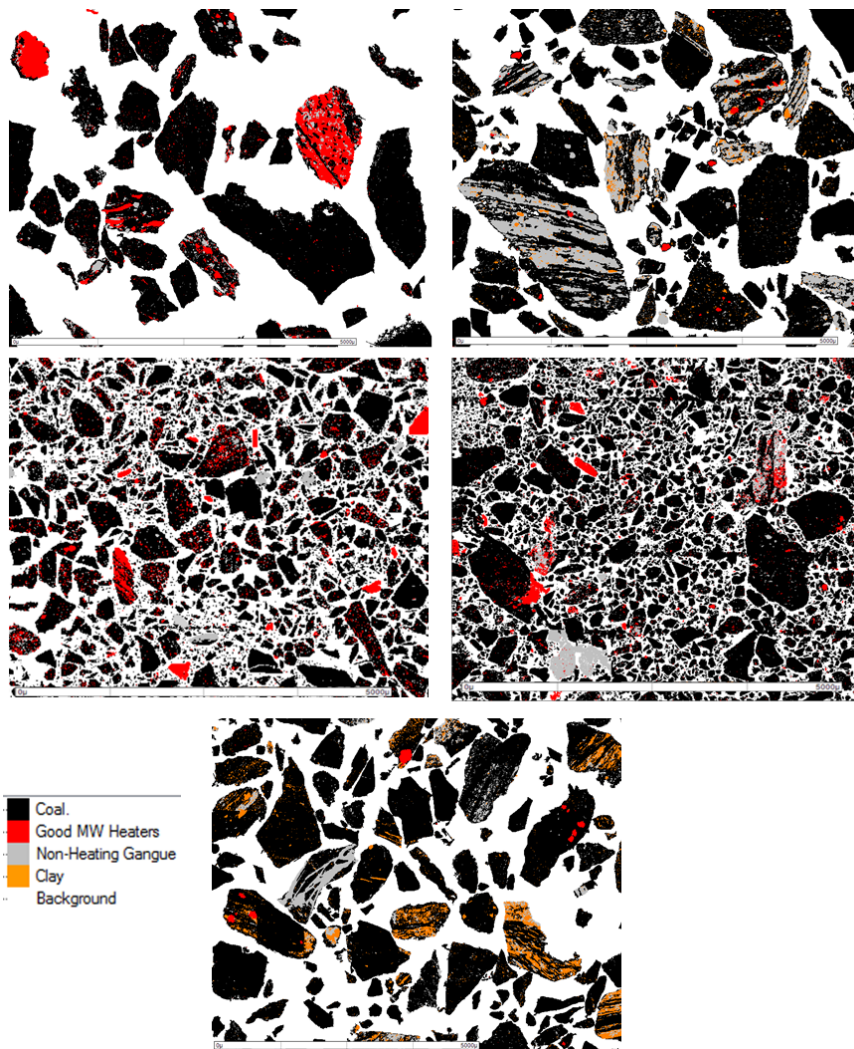
Figure 3. Coarse particle false-color images illustrating observed characteristic mineralogical textures in Coal A–E. Good microwave heaters are kaolinite and hematite. Non-heating gangue minerals are quartz, calcite, muscovite, apatite and orthoclase feldspar.

The textural distribution of the minerals within the coal matrix is illustrated in Fig. 3. The microwave absorbent minerals of kaolinite and hematite (red) are heterogeneously distributed and concentrated within individual particles in Coal A and C, but appear more uniformly distributed as discrete grains or inclusions in particles of the other coal types. These concentrations could lead to microwave hotspots as they will preferentially absorb microwave energy at temperatures below 600 °C, when kaolinite[46] and hematite[47] have greater dielectric properties than coal.[29] Coal C and E have large concentrations of gangue material (grey), which is transparent to microwave energy in comparison to kaolinite, hematite and coal.[48] With an ash content of 22.8 %, the composition of the ash has the potential to have a significant impact on the microwave heating behavior of Coal E.

The intrinsic reactivity of the coals provides an indication of how reactive the coals are (Fig. 4). In principle, if the reactivity of the material decreases, the burnout and peak temperatures also will increase.[8] The intrinsic reactivity of the coals shows that the peak temperature for weight loss is very similar for all the coals (524-547 °C) apart from non-coking Coal E, which is much lower at 449 °C. The burnout temperatures for these coals in air show the same trend, with most coals burning out between 626-690 °C apart from non-coking Coal E, which burns out at a lower temperature (550 °C). Coking coals soften, swell and solidify between 350 and 550 °C.[6] Above this temperature, complete volatile release occurs and the remaining coke shrinks and hardens. Fig. 2 showed that there are only significant changes to the dielectric properties of the coals when they are well above their burnout temperatures, and all volatile matter has been released, which has also been noted for biomass samples.[49]
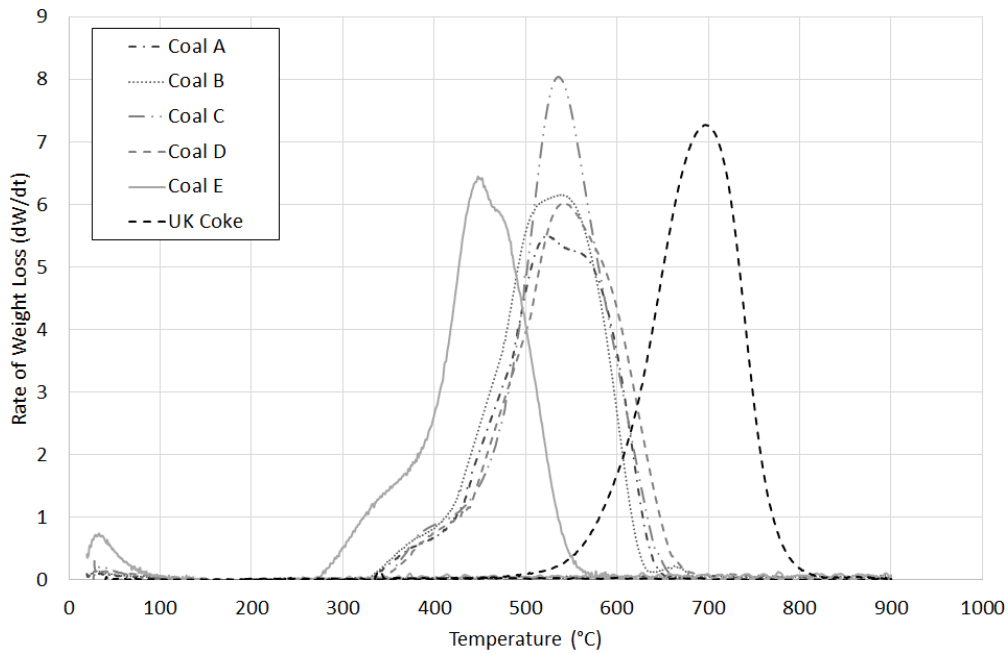
Figure 4. Intrinsic reactivity (in air) of coal samples and reference coke

3.3. Microwave Test Results

The microwave coking experiments resulted in rapid devolatilisation and coking of the all

coals. After testing, all densified coked samples had formed a solid fused lump coke, as shown

in Fig. 5A-D for Coal C and D. Interestingly, all cokes appeared to be similar in terms of

physical structure regardless of whether they were from coking (Fig. 5C and 5D) or non-coking

coals (Fig. 5A and 5B). Furthermore, they formed extremely rapidly, with similar structures

for short (Fig. 5A) and long treatment times (Fig. 5D). 30 g of Coals D and E were treated for

3 kW for 10 minutes in powdered form to assess their potential to form fused lumps of coke.

3 kW of power was used as 6 kW caused arching in the wave guide. The cokes produced from

the powder coals did not have the fused petal structure and did not fuse into one lump. Instead

they formed small lumpy clusters (Fig. 5E) or did not fuse at all (Fig. 5E), which has also been

noted in previous studies.[8,20] The density of the densified coals was 400-576 kg.m^{-3} after

testing, which is less than half that of the pre-treated coal pellets (Table 3). After testing, parts

of the firebrick closest to the coal had melted, indicating that temperatures had exceeded

1650 °C during the experiment. Devolatilisation was evident after 30 seconds, which occurs

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above 400 °C based on the intrinsic reactivity of the coals (Fig. 4) indicating that the temperature rise within the coal was approximately 1000 $^{\circ}$C.min^{-1} range. Similar studies have not demonstrated such rapid coking potential. Coetzer and Rossouw[24] produced lump coke from a semi-soft coking coal with microwave susceptors over a period of 2-3 hours, while Lester *et al.*[8] formed coke structures in powdered coke over 70 minutes with microwave energy.
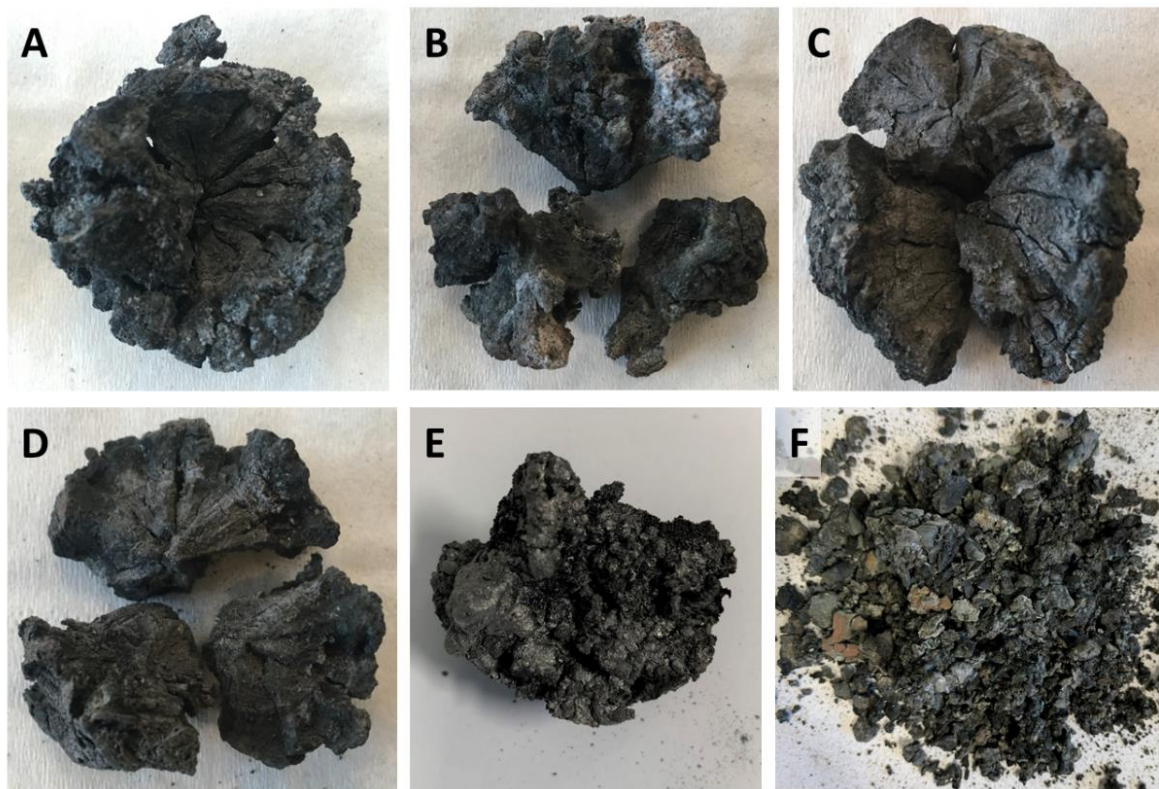

Figure 5. Coke lumps formed after microwave treatment. Densified Coal C for 5 minutes (A), densified Coal C for 15 minutes (B), densified Coal D for 8 minutes (C), densified Coal D for 20 minutes (D), powder Coal D for 10 minutes (E), powder Coal E for 10 minutes (F)

Table 3. Pre and post treatment densities and coke structures for all coals and treatment times

| Sample | Conditions | | Density | | Coke Structures | | | | | | |
	Power (kW)	Time (min)	Before (kg.m^{-3})	After (kg.m^{-3})	Isotropic	Incipient	Circular	Lenticular	Ribbon	Filler	Coal
Coal A	6	10	1258	652	0.0	0.8	14.4	59.6	2.4	22.8	0.0
	6	15	1247	754	0.4	0.0	14.0	56.0	0.4	29.2	0.0
	6	20	1244	787	0.0	0.8	8.0	58.8	1.6	30.8	0.0
Coal B	6	10	1146	634	4.0	3.2	15.6	42.0	0.4	34.0	0.0
	6	15	1187	545	2.0	1.2	11.2	43.6	0.0	42.0	0.0
Coal C	6	2	1223	761	32.0	4.8	53.2	4.4	0.0	5.6	0.0
	6	5	1213	650	20.4	6.4	54.4	10.4	0.0	8.4	0.0
	6	7.5	1211	612	23.6	1.2	53.2	19.2	0.4	2.4	0.0
	6	10	1161	724	16.8	2.8	55.2	20.0	0.0	5.2	0.0
	6	15	1203	765	10.4	7.6	60.0	16.8	0.0	5.2	0.0
	6	20	1168	746	22.4	16.4	48.8	8.0	0.0	4.4	0.0
Coal D	6	10	1197	427	8.0	10.8	69.2	3.6	0.0	8.4	0.0
	6	15	1172	507	8.8	0.4	70.0	10.0	0.4	10.4	0.0
	6	20	1196	521	4.4	3.6	73.6	4.4	0.0	14.0	0.0
Coal E	6	10	1169	399	10.4	0.4	0.4	0.0	0.0	88.8	0.0
	6	15	1174	576	6.2	0.4	2.4	0.0	0.0	90.2	0.0
	6	20	1179	420	7.2	0.4	3.2	0.0	0.0	89.2	0.0

Petrographic analysis was used to identify the coke structures which formed during each treatment. Good cokes were produced from Coals A-D (Table 3), and some coke structures were found in Coal E. No coal or green coke was present in any of the cokes. The filler content of Coal A was between 22 % and 30 %, and virtually no isotropic components were formed, with the other components being anisotropic in nature. Coal B contained 34 % and 42 % filler, with small quantities of isotropic coke with the rest of the coke being anisotropic in nature. The quantity of Coal B's lenticular coke was lower than Coal A, and virtually no ribbon components was observed.

Coal C was tested for shorter additional periods to assess if coke structures were being formed before the completion of the devolatilisation stage, and how these structures developed over time. Coal C, a PCI coal, formed good coke structures after only 2 minutes of treatment time (Fig. 6 and Table 3). The resulting coke structures for Coal C were mainly circular (Fig. 6 and 7), which is an indicator of good coke formation.[41] The filler content was between 2.4 % and 8.4 %, which is the lowest of all the coals tested, however with 10-32 % isotropic coke structures. The isotropic structures reduce and anisotropic structures increase as treatment time increases for Coals B-D (Table 3), which was also noted by Lester *et al.*[8] over longer periods. Isotropic structures from poor to marginal coking high volatile coals with vitrinite reflectance below 0.8 %,[41] which matches the characteristics of some of the coals in this study (Table 1).
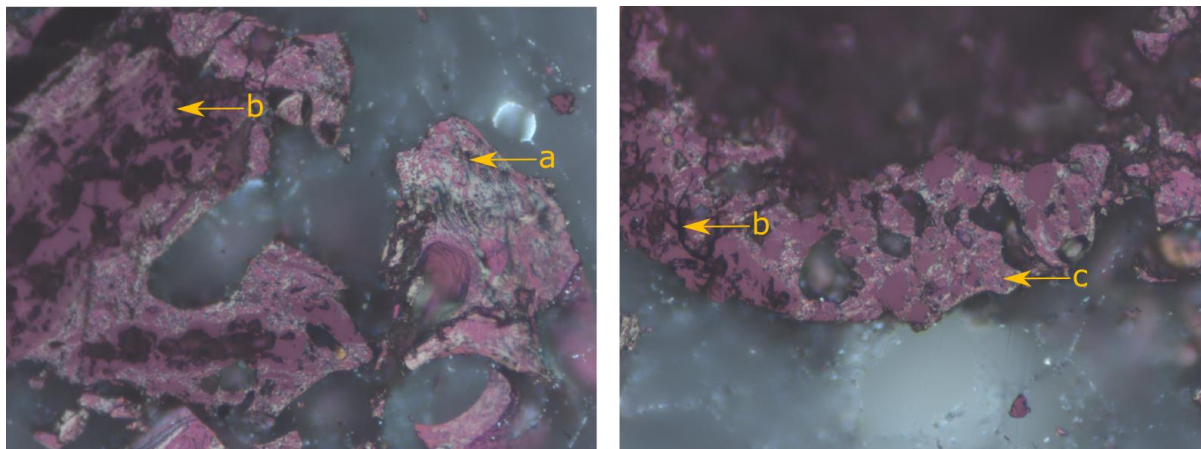
Figure 6. Micrograph of textured coke made from Coal C after 2 minute of microwave treatment. Identified components are: (a) Lenticular, (b) small amount of filler, and (c) circular (scale of 390 microns x 308 microns)
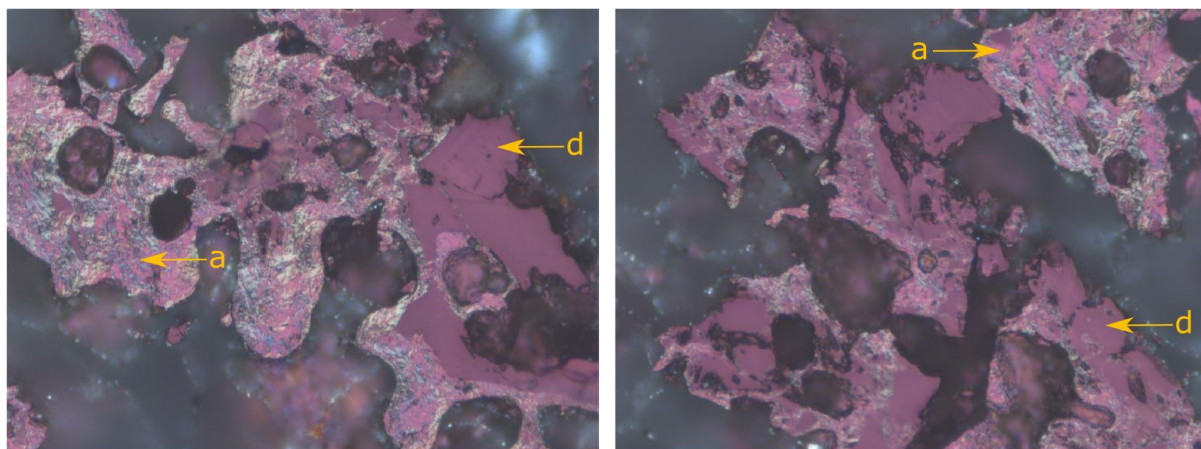
Figure 7. Micrograph of textured coke made from Coal C after 5 minute of microwave treatment. Identified components are: (a) Lenticular and (d) isentropic (scale of 390 microns x 308 microns)

Coal D only contained between 8-14 % filler, which is surprising since Coal D is high in inertinite (38.4 % fusinite and 25.6 % semi-fusinite), and it would be expected that the inertinite fraction would form filler (under conventional coking).[41] However, the microwave treatment resulted in extremely low percentages of filler, with circular and lenticular anisotropic morphologies formed instead. It is proposed that the semi-fusinite is possibly more reactive than the fusinite, and potentially more prone to forming anisotropic structures during coking. Coal E,

however, created a coke with 90 % filler and only small amounts of anisotropic coke. The lower reflectance of the vitrinite in Coal E makes it impossible to form anisotropic structures[42]. High levels of liptinite and low reflectance inertinite are also problematic for Coal E as they are ineffective components in coke formation, the liptinite will devolatilize during heating and the inertinite will remain as isotropic 'filler'. The results for Coals C and E suggest that non-coking coals could still be potential candidates for coking in microwave systems, as microwave treatment can form anisotropic coke morphological structures from inertinite structures, which cannot be formed with conventional coking methods.

Reflectance provides an indication of the degree of coking as a result of the re-ordering of the molecular structure of organic constituents in the coke.[50] Optical reflectance is related to the stages in the crystallinity of the carbon from amorphous to graphitic forms. The crystal structure causes directional variations in the transmission or reflection of polarized light,[51] which provide the reflectance values. Table 4 summarizes the coke reflectance of the cokes in comparison to a conventional commercial UK coke. The length of microwave treatment time greatly impacted the reflectance of the coke produced, with treatment time for optimal reflectance treatment varying by coal type. Coal B reflectance continued to increase up to the maximum treatment time of 15 minutes, while Coal C showed an increase in reflectance up to 7.5 minutes, whereupon the reflectance plateaued (within experiment error). Coal D peak reflectance was at 8.5 minutes, and decreased thereafter.

Table 4. Vitrinite reflectance of microwave treated coals in comparison to UK commercial coke

Sample	Time (mins)	Reflectance			
		Average %	Minimum %	Maximum %	St. Dev.
Coal A	10	7.1	5.1	11.1	1.4
	15	6.2	4.7	10.7	1.2
	20	6.1	4.6	10.7	1.2
Coal B	10	5.8	3.9	9.5	1.3
	15	6.3	4	11.1	1.4
Coal C	2	5.6	3.4	9.2	1.3
	5	7.1	4.3	11.8	1.6
	7.5	7.4	4.5	11.3	1.5
	10	7.2	4.2	11.6	1.7
	15	6.3	4.0	10.1	1.3
	20	6.4	4.1	10.5	1.5
Coal D	8	6.9	4.1	11.1	1.4
	10	6.6	4.1	12.0	1.6
	15	6.0	3.9	11.5	1.4
	20	6.6	4.1	11.8	1.6
Coal E	10	5.2	3.3	8.2	1.0
	15	5.1	3.7	8.6	0.9
	20	5.1	3.9	8.6	0.8
Conventional UK Coke		7.5	4.9	13.1	1.6

Fig. 8 shows that the reflectance of non-coking Coal C is comparable to that of a conventional commercial UK Coke after only 7.5 minutes of microwave treatment. Coal A had slightly lower reflectance range than the UK Coke, while Coals B, C, and D all produced cokes with comparable random reflectance to that of commercial UK Coke (Table 4). The study highlights how the composition of the base coal is fundamental in dictating the coking structure and reflectance of the subsequent coke produced. Reflectance also changes with the length of exposure to microwave energy. Reflectance depends on the area of the ordered graphitic planes, and is not affected by degree of cross-linking.[52] In addition to coal properties, reflectance is dependent on the

carbonization conditions.[51] Apart from the previous studies by the authors,[8,20] no other microwave coking studies have used petrographic or vitrinite reflectance to assess coke quality. In non-microwave studies, similar values of reflectance have been observed for lab scale experiments in a Jenker Retort oven.[53] Piechaczek[9] used petrographic analysis to assess anisotropy, which showed similar textures to those observed in this study, and has shown that the multifractal dimension of texture correlates strongly with reflectance and CRI/CSR.[54]
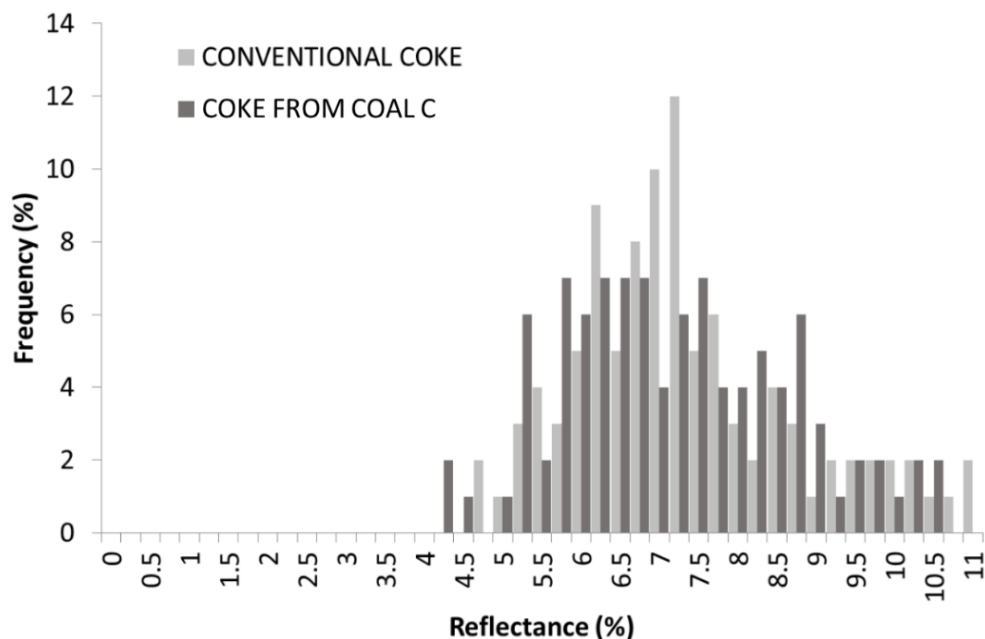
Figure 8. Random reflectance comparison for microwave treated Coal C after 7.5 minutes of treatment and conventionally produced coke

Table 5 summarizes the proximate analysis and intrinsic reactivity of the coals before treatment, as well as the impact of the various treatments on their properties compared to the commercial coke. No moisture remained in the samples after the treatment, and all the samples showed lower volatile contents than the conventional UK coke for all treatment conditions. This supports the petrographic analysis, which showed no coal or green coke was present in the cokes (Table 3). Coal E showed the lowest fixed carbon and highest dry ash contents between 30-40 %.

Table 5. Proximate and intrinsic analysis of microwave treated coals compared to UK commercial coke

| Sample | Time (Mins) | Proximate Analysis | | | | Intrinsic Reactivity | |
		Moisture %	Dry Volatiles %	Dry Fixed Carbon %	Dry Ash %	Peak Temperature °C	Burnout Temperature °C
Coal A	Initial	0.7	24.1	58.8	17.0	524	647
	10	0.0	0.1	79.6	20.3	729	807
	15	0.0	0.1	74.0	25.8	735	818
	20	0.0	0.3	73.0	26.7	746	835
Coal B	Initial	0.9	28.4	63.5	8.1	538	690
	10	0.0	0.3	80.2	19.5	736	840
	12	0.0	0.2	74.6	25.2	738	861
	15	0.0	0.1	81.7	18.3	773	872
Coal C	Initial	0.9	22.9	66.3	10.8	539	626
	2	0.0	0.4	86.9	12.7	734	846
	5	0.0	0.1	88.7	11.1	787	863
	7.5	0.0	0.4	86.3	13.3	748	848
	10	0.0	0.3	86.2	13.5	760	865
	15	0.0	0.3	87.6	12.1	755	853
	20	0.0	0.3	81.1	18.6	753	866
Coal D	Initial	1.0	26.7	62.2	11.1	547	640
	8	0.0	0.3	85.5	14.3	758	878
	10	0.0	0.5	86.4	13.2	773	874
	15	0.0	0.3	78.4	21.3	760	858
	20	0.0	0.5	73.0	26.4	762	863
Coal E	Initial	3.3	35.5	41.7	22.8	449	550
	10	0.0	0.4	70.2	29.4	739	841
	15	0.0	0.2	70.3	29.5	745	846
	20	0.0	0.4	58.8	40.9	775	871
UK Coke	-	0.0	2	86.9	11.6	697	882

Coal A also showed high ash contents, with dry ash between 20-27 %. Given that the standard coke require less than 10 % ash,[7] this could potentially be an issue if these two coals were to be used to make coke without blending with lower ash coals. The intrinsic reactivity results in Table 5 indicate that all the samples show higher peak and burnout temperature than the conventional UK coke.

The surface area (Fig. 9) of the microwave produced cokes for their optimal petrography conditions ranges between 5.2 and 6.7 m^2g^{-1}, while the conventional UK coke had an average surface area of 11.97 m^2g^{-1}. Blast furnace coke surface area is in the range of 1-66 m^2g^{-1},[18,55–57] and thus the surface areas observed fall within the expected band for cokes. The low surface area of cokes indicates that melting occurred in parent coals during carbonization.[38,58] The melting process destroys the original pore structure and only large pores form during the re-solidification stage of carbonization. The low surface area of the cokes means that surface area will have little influence on the reactivity of cokes.[18] The micropore volume was also in the range seen for coke breeze (0.002 cm^3g^{-1}),[55] indicating that the short microwave treatment has produced a coke with surface areas and micropore volumes within the range of commercial cokes, which has not previously been demonstrated in literature.

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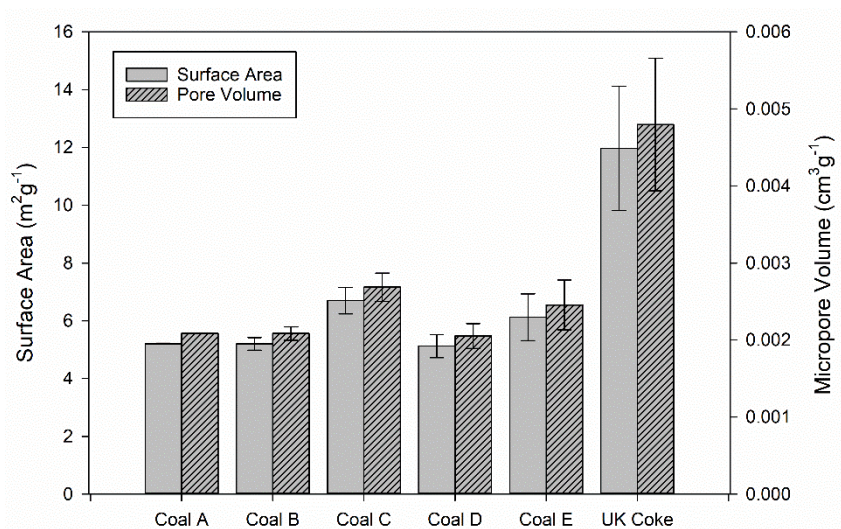
Figure 9. Surface area and micropore volumes for treated coals and UK Coke. Optimal treatment times: Coal A – 20 minutes, Coal B – 15 minutes, Coal C – 7.5 minutes, Coal D- 8.5 minutes, and Coal E 20 minutes

The Coke Reactivity Index (CRI) equivalent denotes the percentage weight loss to the original coke after reaction in CO_2 over 30 and 120 minutes for coke lump fragments.[37] Fig. 10 shows the CO_2 reactivity (RCO_2) of the microwave produced cokes for their optimal petrography conditions versus the conventional UK coke. In industry, the CRI values for conventionally produced cokes are around 20-30 %.[44,59,60] The industrial coke returned an average reactivity over 2 hours ($R120CO_2$) of 15 % in this study. While none of the microwave cokes matched this reactivity, several had $R120CO_2$ values within the acceptable CRI range for blast furnaces. Coal D obtained the lowest $R120CO_2$ (23 %), followed by Coal B (27 %), and Coal C (30 %). Coal A was just above the upper limit with a $R120CO_2$ value of 31 %, while the poorest performing coke was Coal E, with a $R120CO_2$ value of 43 %, which is in line with the other results of this study. Compared to conventional coking studies of Victorian brown coal,[18,38] the reactivity over 30 minutes ($R30CO_2$) was significantly lower, which showed reactivity range of 38-75 %. In the study by Mulloah *et al*,[18] industrial coke obtained a $R30CO_2$ value of 6 %, which corresponds to $R30CO_2$ of 7 % obtained for UK Coke in this study. Fig. 10 shows that some of the microwave cokes had very low $R30CO_2$, with Coal D obtaining a value of 9 % and Coal C at 12 %. To date, no other microwave coking studies have reported CRI/CSR values.
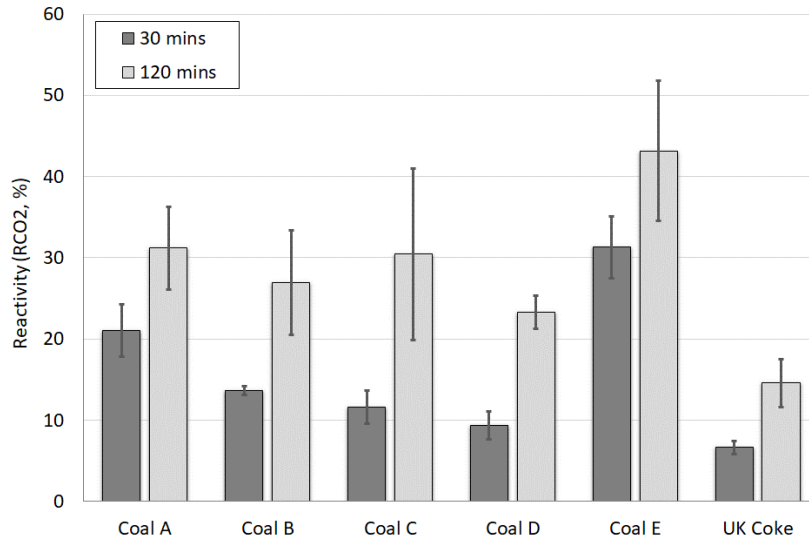
Figure 10. CRI equivalent values of CO_2 reactivity of the treated coals and UK Coke. Optimal treatment times: Coal A – 20 minutes, Coal B – 15 minutes, Coal C – 7.5 minutes, Coal D- 8.5 minutes, and Coal E 20 minutes

Unfortunately it was not possible to measure the coal strength after reaction (CSR) as only 20 g of coke was produced from the microwave coking process, where 200 g of material would be required for the standard CSR test [61]. Discrepancies have been noted between CSR and CRI values obtained from cokes produced in industrial ovens and those produced in laboratories, with industrial ovens producing higher quality cokes than experimental cokes for conventional coking processes.[62] Given that the mass of the coke 'stack' in the coking oven plays a significant role in the development of coke reactivity and strength,[7] without replication of these conditions on an experimental scale, it is not be possible to replicate the CRI/CSR values of industrial ovens. Correlations have been observed between reflectance and CRI/CSR, with high reflectance indicating higher CSR and low CRI values.[63] This study exhibited the same trend, with Coal E having a reflectance of 5.2 % and $R120CO_2$ of 43, while Coal D has a reflectance of 6.9 % and $R120CO_2$ of 23.

3.4. Influence of Microwave Heating and Densification on the Coking Process

This study has demonstrated that microwave heating can achieve coking of coking and non-coking coals in minutes. Microwave heating enables rapid coking as it is a volumetric heating process. It is also dependent on the dielectric properties of the coal. These change with temperature and are rank dependent, and start between 200-400 °C for bituminous coal, and 500-700 °C for anthracite.[64] The dielectric constant of coal is believed to be related to polarizability of the π-electrons in the clusters of aromatic rings within the chemical structure of coal.[20] Heating coals leads to an increase in the aromaticity of the carbon within the coal, due to the release of volatiles, and a re-ordering of the carbon structure to more plate like graphitized aromatic sheets.[8] This results in a higher degree of conductivity and thus higher levels of heating from electromagnetic energy due to the loss of hydroxyl containing radicals and the enhanced transfer of π-electrons between the aromatic sheets.

However, to achieve microwave coking under 2 minutes as demonstrated in this study, densification of the coal is also required. The shortest previous recorded studies took over 70 minutes to produce coke structures in powder form using microwave energy.[8,20] The densified microwave coking process used in this study fused two densified coal pellets into one solid lump coke. It is proposed that by densifying the coal prior to treatment, the bound water in the coal cannot escape easily and this superheated water rapidly heats up the transparent coal matrix, and thereby raising the bulk temperature, increasing the dielectric loss and susceptibility of the coal itself to microwave absorption. By the time the water has vaporized, thermal runaway of the coal is underway, allowing coke structures to form within minutes. While densification or stamp charging increases productivity and allows for the use of lower quality coking coals in conventional coking,[65] it does not result in a drastic reduction in coking times as noted in this

study. Without densification, the microwave coking of coal would not be able to produce fused coke samples or coke structures with a high reflectance in a matter of minutes. Further studies will explore the impact of moisture content on the process.

This study used small masses (30 g), and for the system to become a disruptive process at larger scale, larger scale systems need to be developed. Coetzer[24] used a 5-7 kg microwave system to produce coke, however the process took 2-3 hours with the addition of susceptors. A key aspect in maintaining short processing times with microwave processing is understanding the penetration depth of the microwave energy for a given material. Beyond this penetration depth, microwave heating becomes ineffective and heating occurs via thermal conductivity,[26] and the microwave coking process will take longer to achieve. As noted by Binner *et al.*,[20] the penetration depth of any microwave coking system would need to be in the order of centimeters for the whole bed to be heated with microwaves. In this study, the penetration depths ranged from 125-505 mm at atmospheric temperature to 14-25 mm at 650 °C for 2470 MHz for packed samples with densities similar to the coal pellets (~1100 kg.m^{-3}) (Table 6). Lower frequencies have greater penetration,[26] and the frequency of 910 MHz has greater penetration depths than at 2470 MHz for the coals used in this study (Table 6). The penetration depth issue would mean that a new process would need to be designed in order to scale the microwave technology. The batch system as used in conventional coking batteries systems (modern coking batteries produce typically 1.5–2.5 million t.yr^{-1} coke[66]) would not be fit for this purpose. Whilst scale-up of the system will require overcoming several technological challenges, this study has proved the potential for cokes to be produced in very short periods of time using microwave energy.

Table 6. Penetration depths of the coals at ambient temperature and 650 °C based on dielectric properties ε' and ε''

Coal	Penetration Depth at 20 °C (mm) - 910 MHz	Penetration Depth at 650 °C (mm) 910 MHz	Penetration Depth at 20 °C (mm) 2470 MHz	Penetration Depth at 650 °C (mm) 2470 MHz
A	1354	32	505	17
B	1214	47	483	16
C	581	48	483	17
D	399	37	125	14
E	550	66	185	25

4. Conclusions

This paper is the first to show that densification is the key step in reducing coking process to minutes when using microwave energy. This novel study demonstrated for the first time that densifying coal enables a dramatic acceleration of the coking process when combined with targeted high microwave power densities in the heated phase. This results in coke formations in non-coking coals which cannot be achieved through conventional coking. By utilizing a comprehensive set of coke analysis techniques, it was demonstrated for the first time that anisotropic coke structures were formed in a non-coking coals with only minutes of microwave heating without susceptors. Coke structures were formed from non-coking coals which could not be achieved in conventional coking meaning that even low rank, low vitrinite content coals could become potential candidates for coking.

Petrographic and thermal analysis both show that some of the cokes produced were equivalent to a commercially produced coke. All cokes formed solid fused entities, with anisotropic coke

structures forming within 2 minutes of microwave treatment. The optimal treatment time varied with feed composition. Several of the microwave produced cokes had CRI equivalent values of reactivity (R120CO2) within the acceptable range of CRI for blast furnaces (20-30) within 10 minutes. This study has shown the potential for a step change in microwave coking, which could dramatically reduce production time, and allow for non-coking coals to produce high quality cokes.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Microwave energy absorbed by coal

Fused coke formed in <2 minutes

Coke structures identified

Comparable reflectance to conventional coke