



Binner, Eleanor and Medeira-Munoyerro, Maria and Huddle, Thomas and Kingman, S.W. and Dodds, Chris and Dimitrakis, G. and Robinson, John P. and Lester, Edward (2014) Factors affecting the microwave coking of coals and the implications on microwave cavity design. *Fuel Processing Technology*, 125 . pp. 8-17. ISSN 0378-3820

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Factors affecting the microwave coking of coals and the implications on microwave cavity design

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Abstract

The work carried out in this paper assessed how processing conditions and feedstock affect the quality of the coke produced during microwave coke making. The aim was to gather information that would support the development of an optimised microwave coke making oven. Experiments were carried out in a non-optimised 2450 MHz cylindrical cavity. The effect of treatment time (15 – 120 min), power input (750 W – 4.5 kW) and overall power input (1,700 – 27,200 kWh/t) on a range of coals (semi-bituminous – anthracite) was investigated. Intrinsic reactivity, random reflectance, strength index and dielectric properties of the produced cokes were compared with those of two commercial cokes to assess the degree of coking produced in the microwave system.

Overall energy input and coal rank were found to be the major factors determining the degree of coking following microwave treatment. The dependency on coal rank was attributed to the larger amount of volatiles that had to be removed from the lower ranked coals, and the increasing dielectric loss of the organic component of the coal with rank due to increased structural ordering. Longer treatment times at lower powers or shorter treatment times at higher powers are expected to produce the same degree of coking.

It was concluded that microwave coke making represents a potential step-change in the coking industry by reducing treatment times by an order of magnitude, introducing flexibility and potentially decreasing the sensitivity to quality requirement in the feedstock. The main challenges to development are the energy requirements (which will need to be significantly reduced in an optimised process) and penetration depth (which will require an innovative reactor design to

maximise the advantage of using microwaves). Understanding and quantifying the rapidly changing dielectric properties of the coal and coke materials is vital in addressing both of these challenges.

KEYWORDS: Microwave; coke; dielectric properties; reflectance; intrinsic reactivity; penetration depth

1 Introduction

Over the last 100 years or so, knowledge about coke making and the slot oven design has been gradually optimised. However the fundamental process surrounding the transformation of coal to coke remains essentially the same, with the use of conventional ovens heating coal feed stocks for at least 16 hours [1]. Whilst many aspects of production have been improved with changes in furnace design, long processing times have remained, mainly as a result of the poor thermal properties of the coal matrix [2]. Another limitation of the existing coke making process is the need to blend coals to within a fairly narrow volatile content range in order to control pressure in the oven: some pressure between the coal particles is desirable, as it improves coke strength, but excessive pressures cause damage to the oven walls [3].

World steel production has increased dramatically over the past few years. Between 1970 and 2006 production almost doubled from less than 600 Mt to around 1.2 billion tonnes [4]. Almost 70 % of steel produced relies on metallurgical coal (coking coal) [4]. In addition, current coke making facilities are in need of refurbishment i.e. in 2004, 52 % of factories were over 20 years old and 26 % were over 30 years old [5]. The increasing demand for coke, coupled with aging coking facilities, may open investment opportunities to new coke making methods.

Microwave heating of coal has been identified as having the potential to offer a step change improvement in coke making. Microwaves heat volumetrically, meaning that non-metallic materials, like coal, can be heated effectively instantaneously, avoiding the heat transfer limitations of conventional heating and, therefore, drastically reducing treatment times. Microwaves heat selectively, the degree of heating of each individual component depending upon its dielectric properties. 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 [6-8]. There are also small but detectable variations in electromagnetic properties of macerals [8-10]. Bound water in porous particles has the potential to superheat to temperatures well above 100°C [6, 11-14]. This superheated water is situated within the microwave transparent coal matrix, heating it up and thereby raising the bulk temperature, increasing the susceptibility of the coal itself to microwave absorption. The transformation from coal to coke produces an increase in the aromaticity of the carbon material [7] as a consequence of the loss of the volatile component during the carbonisation and an increase in the degree of graphitisation. Increasing aromaticity results in an increase in conductivity due to increasing electron mobility through the transfer of π bond electrons along the aromatic layers [2, 8-10, 15-19]. As temperatures continue to increase from 400 to 1000°C, electron mobility and level of free charge per unit volume will also continue to increase through graphitisation of the carbon, resulting in an increase in dielectric loss factor and thus increasing microwave heating, allowing the high temperatures (>1000°C) required for coking of coal to be achieved [1, 3, 6, 8].

Coke making by the microwave heating of coal is not a new idea, and several patents for methods with and without the use of microwave receptors have been filed, dating from the 1970's to more recently [20-23]. Coetzer and Rossouw have used microwave treatment to produce high quality cokes from a Waterberg semi-soft coking coal in 2 – 3 hours using microwave receptors to heat the coal indirectly [24]. However, according to the theory presented above, some or even all coals could be heated to coking temperatures without the addition of microwave receptors. Since superheating of bound water is a major mechanism in the initial heating-up of the coal, it is vital to maximise the power density in the sample during cavity design. Lester et al. [6] have shown that it is possible to produce coke with similar properties to conventional cokes using a relatively low rank, high volatile bituminous coal without the use of receptors with only 70 min of heating in a multimode cavity. The cavity used was a non-optimised multimode cavity operating at 8 kW.

Initial indications from previous work are therefore that microwave heating may represent a step change in coke making through drastic reductions in coking times, and the ability to start-up and shut down the process within a short time frame. In other words, a complete redesign of coking plant equipment with a smaller footprint and the ability for flexible operation may be possible.

Prior to the development of any larger scale process, a more fundamental understanding of the microwave induced coking process is required. The importance of high temperature properties of coke is well established in the steel industry [25]. Coking conditions (such as bulk density, coking time, preheating of the charge, and the incorporation of non-coal materials) and the properties of the input coal or coal blend are the factors that determine the coke properties in conventional coking [25]. The aim of the work presented in this paper is therefore to investigate the effect of coking conditions and input coal properties on the quality of coke produced using microwave heating. The basic process variables in a microwave process are the power input and treatment time. A certain amount of input power is absorbed by the sample, and if this is measured over the duration of the experiments, the energy input can be calculated. As stated above, the input coal or blend is also a major determinant of coke quality. The coal rank, rheology and composition all affect the final coke quality [25]. In microwave processes, the dielectric properties of the material are also key factors in determining how a material will heat, and these change with temperature, pressure and composition [26]. This feeds back into the degree and distribution of power absorption, which can be expressed by the power density in the sample, as shown in Equation 1.

$$P_d = 2\pi f \varepsilon_0 \varepsilon'' |E|^2 \quad (1)$$

The power density, P_d , is the power dissipated within a given volume of material (W/m^3), f is the frequency of the applied electromagnetic wave (Hz), ε_0 is the permittivity of free space (8.85×10^{-12} F/m), ε'' is the dielectric loss factor and E is the electric field strength (V/m). P_d varies spatially and according to the cavity and sample dimensions and absorbed power, and these variations are

accounted for in the E term. It is therefore clear that there is a complex interdependency of process variables and material properties, and that the heat transfer properties that determine heating rate in conventional coking are largely replaced with the dielectric properties in microwave heating.

The dielectric properties also impact reactor sizing. As a wave progresses into a dielectric-heating workload, its amplitude diminishes owing to absorption of power as heat into the material. This attenuation is expressed quantitatively by the penetration depth, D_p , which is defined as the depth into the material at which the power flux has fallen to $1/e$ of its surface value [27]. When $\epsilon'' \leq \epsilon'$, D_p can be approximated according to Equation 2, where ϵ' is the dielectric constant and λ_0 is the microwave wavelength.

$$D_p \approx \frac{\lambda_0 \sqrt{\epsilon'}}{2\pi\epsilon''} \quad (2)$$

It is clear from Equation 2 that the penetration depth decreases as the dielectric loss of the material increases [27]. The practical implication of this is that microwaves cannot penetrate very far into materials that absorb microwaves strongly, and this limits the reactor dimensions.

For the purposes of this work, the process inputs varied were power input, treatment time and coal type. The aim was to determine the effect of these variables on coke quality. In order to optimise the process in terms of energy requirements, the E term in Equation 1 would need to be manipulated, and this would be done by optimising the cavity design. The information presented here would be vital developing the process further. It is likely that the energy requirements would be dramatically reduced with the development of an optimised microwave cavity. Such a cavity would need to be designed specifically for coke manufacture, and this will only be possible once the key parameters that govern the coking process are fully understood.

2 Materials and Methods

2.1 Coal Samples

The microwave coking of four different coals was investigated: a high volatile English bituminous coal (Coal A), a low rank semi-bituminous coal from Kaltim Prima (Coal B), a medium rank bituminous coal from Wales, UK (Coal C) and a semi anthracite from Wales, UK (Coal D). The petrographic characteristics and proximate analysis of Coals A – D are given in Table 1.

The coal samples were passed through a jaw crusher and sieved to a size fraction of 1 – 3.35 mm prior to microwave heating.

2.2 Microwave Experiments

The experimental setup is shown in Figure 1. All experiments used a variable power 6 kW microwave system (HF Dielectric Heater FDU 543VD-02) operating at a frequency of 2.45 GHz with a cylindrical cavity, waveguide and manual three stub tuner for impedance matching purposes. The reflected power was maintained below 10 % during the majority of the operating time. Each experiment used two hundred and twenty grams of coal held in a Pyrex beaker covered by glass wool. The glass wool acted as a dielectric barrier to protect the cavity from arcing and to contain the beaker in the event that it cracked during the experiment. All flanges were tightly sealed and the cavity was flushed with 15 L/min N₂ for 15 minutes (i.e. approximately six reactor volumes) prior to the experiments. The N₂ flow was reduced to 10 L/min during operation, and this maintained the inert environment as well as acting as a carrier gas to remove products that were evolved during processing.

Coke samples were prepared from Coal A using a range of microwave powers (750 W - 4.5 kW) and treatment times (15 - 120 min), representing a range of total energy inputs of 1,700 – 27,200 kWh/t. Coals B – D were treated at an energy input of 6,800 kWh/t in order to investigate the effect of coal type.

2.3 Product analysis

The properties of the microwave cokes were compared with two commercial cokes (Commercial Coke 1 and Commercial Coke 2).

Thermogravimetric analysis was used to determine the intrinsic reactivity of the original coal and the coke products using a non-isothermal program with a heating rate of 10°C/min in an air flow of 100 cc/min up to a temperature of 900°C [6, 28]. The burnout profile (the burnout temperature (BT) and peak temperature (PT) in particular) was used to provide a relative indication of carbon reactivity. The BT is the temperature at which the burnout rate reaches 1%/min, and the PT is the temperature at the maximum burnout rate. An isothermal TGA test that modified the British Standard (BS 4262-1984)

for measuring coke 'reactivity' towards CO₂ was also used [29]. The sample was heated in a N₂ atmosphere at 50 °C/min up to 1000 °C with a hold time of 10 min before switching to a CO₂ gas flow for 2 hours.

Oil Immersion Analysis was carried out using polished blocks of the samples, prepared with an epoxy liquid resin blend, examined under polarized-light microscope Leitz Ortholux Pol II BK with x32 magnification oil-immersion objective and x10 magnification eyepiece. Random reflectance was measured on each sample with the system calibrated using a silicon carbide light standard (7.51 % reflectance in oil) [30]. Colour and black and white mosaic images (3090 x 3090 pixels from 15 x 15 individual images) were captured using a Zeiss AxioCam attached to the microscope, connected to a computer using an optic fibre cable, and operated with KS400 V3.1 image analysis software. A minimum of 350 particles per sample were considered to identify and quantify porosity.

Strength tests were carried out using BS 1016-108.2:1992 modified for a smaller amount of sample [31-33]. In each case, the whole sample was crushed by hand to avoid the production of fines and maximise the quantity of particles between 3.35 mm and 9.5 mm. The sample was then sieved into two size fractions, and a twenty gram sample with a known size distribution (65 % between 9.5 - 5 mm size and 35 % between 3.35 - 5 mm size) was prepared. This sample was introduced into a small rotating drum consisting of three 30.2 mm steel balls bearings, each weighing 68.2 g, at a speed of approximately 30 rpm for a total of 200 revolutions. The coke was then sieved on a 2.36 mm screen to produce a >2.36 mm percent coke strength index, S. Each test was repeated twice.

Dielectric property measurements of the polished block samples (prepared for the oil immersion tests) were performed with the use of an open ended coaxial line terminating to a probe with an annular aperture. The other end of the coaxial line was connected to an Agilent 8753ES Vector Network Analyzer (VNA) with a frequency range 30 kHz – 6 GHz. Before each measurement, the system was calibrated with three different calibration standards: an open line, a short-circuited line and a reference liquid [34] of known dielectric response (ethanol). During the short circuit measurements the metallic shortening block was replaced in each measurement; experience has shown that achieving a good short circuit during calibration is paramount, as it introduces the largest residual errors during the procedure. After the measurement of the three standards the calibration coefficients were calculated and downloaded to the VNA. Details of this method can be found elsewhere [35]. During the measurement a swept frequency signal was transmitted from the VNA into the liquid via the coaxial line, and the reflection coefficient Γ was recorded. The amplitude and the phase of Γ were fed into a computer program, which utilised a modal analysis [25, 35-37] to calculate the real (dielectric constant, ϵ') and imaginary parts (dielectric loss, ϵ'') of the complex permittivity.

3 Results and Discussion

3.1 Thermal Reactivity – Intrinsic Reactivity in air

Figure 2 shows the differential weight loss with temperature for Coal A treated for 120 minutes at a range of powers from 0.75 kW to 3 kW. It shows that the PT and BT increase (and therefore reactivity decreases) with increasing input power. Similar results were observed when the treatment time was increased but the input power was held constant. Therefore if the energy input is increased, either by increasing the power or treatment time, the reactivity of the resultant coke decreases.

Table 2 shows BT, PT and the proximate analysis of Coal A treated under the full range of conditions, untreated Coal A and the two commercial cokes. The data in Table 2 show that when the power input and treatment times are multiplied to give total energy input (kWh/t), BT and PT are independent of power input.

Figure 3 shows BT and PT against total energy input for all powers and treatment times. There is more scatter in the peak temperature data than the burnout temperature data, but a clear correlation between total energy input and intrinsic reactivity is nevertheless observed. Based on the data in Table 2 and Figure 3, it is concluded that the reactivity of the microwave coke decreases with increasing energy input. Energy input can be increased by increasing the treatment time or power input, i.e. it appears to be possible to achieve a specific burnout reactivity using either a shorter residence time and a higher power input, or a longer residence time and a lower power input.

Table 2 also shows that the volatile matter content decreases with increasing residence time and overall energy input.

Based on the PT and BT values for the commercial coke samples, an energy input of approximately 20,000 kWh/t would be needed to create similar material using this microwave cavity, which would equate to a power input of 1.5 kW for 180 min or 3 kW for 90 min.

3.2 Thermal reactivity - Reactivity with CO₂

Similar to intrinsic reactivity, reactivity in CO₂ is a relative test for comparing different coke products. Metallurgical cokes that oxidise too easily in CO₂ will weaken and degrade into smaller particles, leading to permeability decreases, which can also lead to the blockage of the tuyères through the build-up of coke residues [25].

Figure 4 shows conversion in CO₂ versus time for Coal A treated for 120 min at three different input powers (750 W, 1.5 kW and 3 kW) and both commercial cokes. The 750 W and 1.5 kW samples were notably more reactive than either of the commercial cokes, in agreement with the PT and BT data in Table 2. The 3 kW sample, however, remains unreactive in CO₂ for longer than either commercial

coke, and the conversion followed the Commercial Coke 2 profile very closely from 50 min into the test. Therefore it appears that with sufficient energy input, microwave coke can show a similar reactivity to CO₂ as commercial coke.

3.3 Random reflectance R_{ran}

It is possible to see from Table 3 that reflectance values increase both with treatment time and microwave power. As the degree of graphitisation in the carbon material increases, structural ordering also increases and the reflectance of the material (under oil immersion) becomes higher [38, 39]. Figure 5 shows that the reflectance values, like the burnout temperatures, increase with overall energy input. In this case however, because of the rapid increase in reflectance from the original coal, the relationship appears to be non-linear. Even the lowest power input for a relatively short time produces a material with a reflectance of 4.0 % (from the initial coal at 0.8 %). The increase from 4.0 % towards the commercial coke values of >6.0 % requires significantly more energy input, either with longer treatment times or higher power input. The highest reflectance value of 6.2 % was achieved at 4.5 kW and 40 min treatment time (13,600 kWh/t); further increases in input energy did not increase the reflectance of the product. There is no evidence from these results that input power affects the reflectance of the product.

3.4 Coke strength

Coke strength is the key absolute property for coke whilst being a good relative measure for performance in the lower region in the furnace [1]. Table 4 gives the strength index of the cokes produced from Coal A by microwave energy at different operating conditions.

Interestingly, low power tests carried out at the same energy input, 6,800 kWh/t for example, using 750 W for 120 min and 1.5 kW for 60 min, produce strength index data that is very similar (53.2 and 54.3 % respectively), although more data would be needed to confirm this. At higher power input levels but the same energy input (13,600 kWh/t), a significantly higher strength index was produced at 1.5 kW than 3 kW, 61.9 compared with 56.8. This discrepancy also agrees with observations made with intrinsic reactivity (Table 2) and reflectance data (Table 3). These differences may be due to the impact of an increased heating rate i.e. the increased power input from 1.5 to 3 kW produces four times the power density.

It is evident from Table 4 that the commercial coke strength values of >65 were only achieved when the coal was treated with > 15,000 kWh/t.

3.5 Coke Porosity

The formation of pores is a critical feature of coke material not least because the porous structure is directly linked to coke strength [40] and, more importantly, the diffusion of reductive gases through

the coke bed in the blast furnace [41]. Figure 6 shows porous structures from Commercial Coke 1; it was found to have an average porosity of 48 %, which is similar to values previously reported for commercial coke materials[42]. Figure 7 shows the porosity of a single image of Coke A prepared at relatively low power input (3kW for 15 mins with a total input of 3,400kWh/t). In this case the porosity was an 'encouraging' 39%. The porosity produced by taking the same energy input (3400kWh/t) at increasing powers (1.5kW, 3kW and 4.5kW) seemed to produce small increases overall at 26%, 28% and 32% respectively. Figure 8 shows a large mosaic image of particulate coke, where the individual grains have been magnified and analysed for porosity. All cokes prepared using microwaves exhibit a reasonable degree of pore formation, with the 4.5 kW at 40 mins (13,600kWh/t) producing the largest porosity at 43%.

It is clear that porosity develops during microwave heating, which is encouraging. We are still developing a means of automated measurement of porosity with more samples, but it should be noted that these experiments were batch based, in a non-optimised cavity. Section 3.8 discusses further how a system might be able to produce coke more efficiently using microwaves. Porosity will be directly linked to the size of the sample (both weight and dimensions) as well as time temperature history [43, 44], so the final porosity from an optimised microwave based process is still unknown.

3.6 Coal type and microwave coking potential

Coals B, C and D (low rank semi-bituminous, medium rank bituminous and semi anthracite) were selected to investigate the effect of coal type on coking behaviour (Table 1). They were treated at 1.5 kW for 60 min. These conditions correspond to the absolute minimum energy requirement for Coal A (a high volatile bituminous coal) to form a coke like product (Table 2) and were therefore chosen to maximise the probability of identifying any differences in coking performance based on coal type.

Table 5 gives the values of the peak and burnout temperatures of the original coals together with the values corresponding to the cokes, and Table 6 gives the random reflectance and dielectric properties. The reactivity of each coke product was significantly reduced compared with the parent coal, although it is clear that coal characteristics can play a very important role in the behaviour of the coals in the microwave coking process. The PT and BT values (intrinsic reactivity) increase as rank increases, but more importantly, the response of the coal to microwaves changes. As rank increases, so does the degree of aromaticity, producing a more stable structure with lower H/C and O/C ratios [45].

Coke D has the lowest intrinsic reactivity, highest dielectric properties and highest reflectance of the microwave-made cokes, indicating that it is the best candidate for microwave coke making. This is almost certainly as a result of the reduced devolatilisation time (with only 6.6 % volatiles in the initial coal), and its higher (initial) aromaticity, which is already structurally more like coke material. Therefore using higher ranked coals appears advantageous, and the reasons for this are twofold:

firstly, they are already highly aromatic and so require less time to complete the coking/graphitisation process, and secondly, lower ranked coals inevitably have higher volatile contents, which will require longer pyrolysis times thus delaying the onset of the graphitisation process. Table 5 shows that Coal B (44.7 % volatiles) produced a coke with 11.4 % residual volatiles present and the lowest PT and BT values. There is still a marked increase in the BT and PT values between Coal B and Coke B, but the changes between Coal D and Coke D is far larger. This indicates that even though coal moisture in lower ranked coals can boost dielectric properties at low temperatures (since moisture and bound -OH groups are highly receptive to microwaves and these are generally inversely proportional to rank), the graphitisation process still requires time and hence lower ranked coals will require a longer treatment time. In addition, the moisture and bound water are undoubtedly lost during the initial heating phase of the coal material and, once this has happened, the carbonaceous material in the cavity is at a high temperature and highly microwave absorbent, requiring time in which to carbonise.

Figure 9 shows the reactivity of the coke products in CO₂. Coal B produced a material that is clearly the most reactive and the least comparable to the commercial cokes. Coal D produced a material that (at a relatively low energy input of 6800 kWh/t) had a similar profile to Commercial Coke 2, the less reactive commercial coke. The profiles for Coke A and Coke C also approached Commercial Coke 1, the more reactive commercial coke. It therefore appears from these results that the volatile content is a major factor influencing coking time, but that all coals tested could produce coke given enough treatment time and overall energy input.

3.7 Dielectric properties

As explained in Section 1, the dielectric properties of a material describe how it will heat in a microwave field. Knowledge of the dielectric properties and how they can be expected to change over time is therefore important in microwave process design.

The dielectric properties of treated and untreated Coal A at 2450 MHz, as well as those of the commercial coke, are shown in Table 3. As with the other characteristics, both the dielectric constant and loss factor increase with increasing energy input which, in turn, is effectively a measure of the level of graphitisation in the sample [6, 46]. When interpreting the results it is important to be aware of the potential errors in the measurement technique. Coaxial probe measurements are most accurate for high dielectric loss materials, where it is possible to obtain uncertainties of the order of $\pm 3\%$ or less [47]. The measurements here indicate that the $\tan \delta$ (which is the ratio $\epsilon'':\epsilon'$ and is used as an indicator of the how well a material absorbs microwaves [48]) is <0.1 for the untreated coals and within the range 1.0 – 0.5 for the cokes. This means that the coals were all classified as low microwave absorbers and the cokes were medium microwave absorbers, increasing in uncertainty beyond that for high loss materials [48]. In addition, hard specimens were used, and the potential for small air gaps in the surface of the samples also increases the uncertainty in the measurements [49].

Despite the relatively high levels of uncertainty in the dielectric measurements, clear trends are seen within the results.

Figure 10 shows the variation of the dielectric properties of the microwave cokes against overall energy input. As with intrinsic reactivity and reflectance, the total energy input appears to correlate well with changes in both the dielectric constant and loss. Based on the data in Table 3, a dielectric constant of around 30 and loss of around 10 are expected to be required for microwave coke to be comparable with commercial coke; referring to Figure 10, this equates to an energy requirement of around 15,000 kWh/t, which is close to with the previous figure of 20,000 kWh/t that was quoted based on the intrinsic reactivity data. Whilst the general trends seen in Figure 10 are clear, it would be useful to carry out more repeat experiments at lower energy input (<10,000 kWh/t) to clarify whether the relationship between dielectric loss and energy input is linear or logarithmic.

In addition to informing microwave process design, the correlation observed here may have a potential application in monitoring the progress of (conventional or microwave) coking processes. The fact that dielectric properties increase with temperature means that a thermal runaway effect can be achieved at high temperatures. This means that the maximum temperature of the coking process is not limited in the same way as in a conventional furnace, and therefore higher processing temperatures may be achieved. This may lead to an improvement in coke quality over conventional coke.

3.8 The relevance of the results to cavity design and scale-up

The results reported here show that energy input correlates well with all measured characteristics, implying that high powers at shorter treatment times do not achieve better products than lower powers with longer treatment times. It follows that power input could be calculated if a residence time was chosen. However, emphasis must now be given to minimising energy requirements in the cavity design process. Knowledge of the dielectric properties and how they will change during processing will be vital to the design of the microwave cavity from the point of view of maximising the conversion of energy to heat, and also because the dielectric properties influence penetration depth. Table 7 shows the calculated penetration depth of the coke materials at a frequency of 2450 MHz. These figures show that if a microwave system was designed to work at a bed thickness that was similar to a conventional coke furnace, only a fraction of the total mass would be heated by microwaves, with the rest of the material being heated through conventional heat transfer. In addition, the penetration depth would decrease further when operating at typical coke bed temperatures (>1000 °C), meaning that the penetration depth would decrease from tens of centimetres to a few millimetres. The coal samples in these experiments were prepared in the form of cylinders 8 cm diameter and 13 cm high, and the penetration depth reduced to less than the sample dimensions during treatment in all cases. The implication is that only the outer few millimetres of the

sample would have been absorbing microwaves by the end of the experiment, and therefore conventional heat transfer from the part of the sample that was still able to absorb microwaves was responsible for continuing to heat the inside of the sample. Therefore, if thinner samples had been used (in the order of millimetres), the coking process would have been quicker since volumetric heating by microwaves is effectively instantaneous, whereas conventional heat transfer is not. This reduction in treatment time may also have led to a reduction in heat losses, making the process more energy efficient. It should be noted that wavelength (or its reciprocal, frequency) influences penetration depth [26]. This means that operating at typical industrial frequencies such as 433 MHz or 896 MHz rather than the 2450 MHz used here would increase the penetration depth. However, it is clear that the final stages of microwave coking will not be possible in a large coking furnace, and that a novel design will be required for this process to work.. Although this would be a major engineering challenge, it would provide the opportunity for the design of new coking plant equipment with a small footprint and the option for flexible operation.

As initially stated, the success of conventional coking is largely dependent on careful control of the properties of the coal or coal blend used as the raw material. This is largely due to the presence of an optimum volatile range, below which the coke produced is not strong enough, and above which high pressures cause damage to the oven walls [3]. The coals treated in this work represent a wide range of volatile contents, and the initial indication is that, given enough energy input, a coke-like material could be produced from each coal. Further testing would be required to confirm this. However, the rapid temperature increase of liquid in pores caused by volumetric heating can lead to internal pressure build-up on a scale that is not possible in conventional heating processes [26]. It may therefore be that the internal pressures required to achieve the necessary coke strength [3] could be achieved in microwave processing without the presence of the same degree of volatile matter. Since volumetric heating was not achieved throughout the entire duration of the experiment (due to decreasing penetration depth), the heating rate, and therefore devolatilisation rate in the core of the sample, was not maximised, as conventional heat transfer for the outer layers was now the mode of heat transfer; poor heat transfer properties are known to be a limitation in conventional coking [2]. Further testing in an optimised cavity would be required to elucidate devolatilisation kinetics and confirm whether superheating in the sample can be used to enhance coke strength. The issue of excessive pressures damaging the oven walls is also something that would have to be assessed separately for microwave processing, given that the oven design would be completely different from the current slot oven design. Since the sample would have to be of the order of millimetres thick, it is possible that the pressure build-up would be significantly less and therefore may not be an issue. Of course a lot more work is required before these questions can be fully answered, but it could be that microwave coke making could be used on feedstocks with a larger volatile content range than is currently the case. If this is true it would be a major driver for the development of this technology.

Another important point to note is that very high temperatures and rapidly changing dielectric properties can lead to thermal runaway, and so controlling the power into the material through careful electromagnetic and engineering design would be paramount to ensure a safe and sustainable process.

4 Conclusions

Work reported here and elsewhere [6] shows that microwave heating of coal without the addition of microwave receptors can produce coke in timescales that are much shorter than the conventional coking process. Each sample becomes more graphitised with increasing treatment time and/or power input, resulting in an increase in the level of free charges per unit volume that produces an increase in the dielectric constant and loss factor values.

The first major finding of the work reported in this paper is that the overall energy input determines the degree of graphitisation of a given coal. A range of characterisation tests showed that at least 13,600 kW/t was required in the non-optimised microwave cavity to produce a commercially comparable material using a high volatile coal as a feed material. This figure would have to be reduced by an order of magnitude to compare with conventional coking, which uses approximately 1,000 kW/t [50]. The second major finding is that it is possible to produce coke from a range of coals, including those that are not suitable for conventional coking. Further work investigating the devolatilisation kinetics in an optimised cavity is required to elucidate the relationship between volatile content and coke strength during microwave treatment. Our results show an inverse relationship between coal rank and energy requirement. It is suggested that the energy required to devolatilise lower rank coals is the main cause of this effect. In addition, although the higher water content of lower rank coals facilitates microwave absorption in the first instance, once the water is removed, the less graphitised, more amorphous, lower rank coals absorb microwaves less effectively than their higher ranked counterparts. This leads to lower heating rates, which affects devolatilisation behaviour and coking time. Blending lower and higher ranked coals may be an excellent way of producing a high heating rate in the feedstock without creating subsequent problems with uncontrolled devolatilisation and flow type anisotropy in the product.

Possibly the most significant conclusion from this work concerns the importance of penetration depth. Rapidly decreasing penetration depth will have a major influence on process design. Only the outer few millimetres of a coke sample in the late stages of treatment are heated with microwave energy at a frequency of 2.45 GHz, and although lower frequencies could be used to increase the penetration into the sample, practical sample dimensions would still remain significantly less than the dimensions of a conventional coking furnace.

Bulk sample temperature was not measured for practical reasons since thermocouples that remain transparent to microwaves at high temperatures and operate at temperatures of 1000 °C are not

readily available. However, temperature data would help to clarify the reaction kinetics. Ash and sulphur analysis would also be of interest in future work, to help to understand devolatilisation behaviour and also to confirm whether ash and sulphur content of the feedstock need to be within strict limits, as is the case in conventional coke making [3]. Further investigations should take place in an optimised cavity, in order to determine scalable energy requirements, and also to simulate the coking conditions that would be experienced in an industrial microwave system.

To summarise, microwave coke making represents a potential step-change in the coking industry by reducing treatment times by an order of magnitude, enabling flexible operation, reducing the equipment footprint, and potentially decreasing the sensitivity of the product quality to the feedstock.

The main challenges to development are the energy requirements, which will need to be significantly reduced in an optimised process, and the penetration depth, which will require an innovative reactor design to maximise the advantage of using microwaves. Understanding and quantifying the rapidly changing dielectric properties of the coal and coke materials is vital in addressing both of these challenges. This work provides inputs that will be required in future research and development work, but the engineering challenges in developing a scaled microwave coking system will be significant.

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Captions

Figure 1. Schematic of the cavity for coke making process by microwave heating

Figure 2. TGA profiles for Coal A and coke samples treated for 120 min at different powers

Figure 3. The effect of energy input on burnout temperature (BT) and peak temperature (PT)

Figure 4. CO₂ reactivity tests - the impact of power input with a treatment time of 120 min

Figure 5. Variation of the random reflectance values of the cokes made from Coal A as a function of the energy input applied at four different powers (0.75, 1.5, 3 and 4.5 kW)

Figure 6. A binary thresholded mosaic of Commercial Coke 1 with internal porosity shown in black and coke walls in white. Image width is 1mm.

Figure 7. An example of how the porosity is segregated in the Coal A at 3kW for 15 mins with a total input of 3,400kWh/t. The original image (left) captured using oil immersion lens (32x objective and 10x internal lens). Image size is 270 microns wide. This image is showing 39% porosity, with pores shown in red (right).

Figure 8. A larger mosaic image (15x15) showing particulate coke particles at 3kW for 30 mins equating to 6,800 kWh/t. This sample is showing 33% porosity.

Figure 9. CO₂ reactivity tests – the effect of coal type on coke reactivity the same total energy input (1.5kW for 60 minutes).

Figure 10. Dielectric constant (ϵ') and dielectric loss (ϵ'') vs overall energy input.

Table 1. Petrographic and proximate analysis of coal samples

Table 2. Results of the TGA characterisation of Coal A and cokes samples (E = energy, BT = burnout temperature, PT = peak temperature, VM = volatile matter, db = dry basis)

Table 3. Random reflectance measurement and dielectric properties for treated Coal A, untreated Coal A and commercial cokes

Table 4. Coke strength index values for the cokes made from Coal A (average of 2 measurements)

Table 5. Results of the TGA characterisation of the parent coals and cokes produced at a power of 1.5 kW, treatment time of 60 min and energy input of 6,800 kWh/t

Table 6. Results of the random reflectance measurement and dielectric properties values for different parent coals and microwave cokes produced at a power of 1.5 kW, treatment time of 60 min and energy input of 6,800 kWh/t

Table 7. The penetration depth of the coal and coke materials at 2450 MHz