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A Review of Microwave Coal Processing

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ABSTRACT

This paper reviews the application of microwave energy in coal processing and utilisation. It brings together all of the published work on the microwave treatment of coal. The majority of the work was carried out at lab scale, although a few processes have made it to pilot or even industrial scale. The processes with more immediate promise for scale-up are identified, as are those that require further laboratory scale experiments to establish whether microwave processing should be pursued at a larger scale. The importance of dielectric properties of the materials to be processed is emphasized, and the reasons behind the need for a multi-disciplinary approach to the design and operation of electromagnetic experiments are explained. Microwave coal processing is a diverse area, which has the potential to aid in coal upgrading, cleaning and comminution, thus improving efficiency and reducing harmful emissions of coal usage. Other promising research areas include the investigation of microwave processing for coking, liquefaction, enhancing fluid flow in coal beds and coal characterisation. The paper concludes by discussing the barriers to scale-up that these processes face.

KEYWORDS: Dielectric, microwaves, beneficiation, coal cleaning, coal drying, coal grindability, coal.

INTRODUCTION

Clean coal technology is a very important area of research and development as it has enormous potential to reduce harmful emissions and improve fuel efficiency. Microwave heating technologies can potentially reduce the energy requirements and environmental impacts of some processes. Many papers are published each year exploring the potential

for microwaves to improve coal processing efficiency, but very few of these applications reach industrial scale. This paper presents a timely review of the current state of research into the microwave processing and utilisation of coal in order to assess the reasons for the low conversion of the technology from laboratory to industrial scale, and to inform future research and development decisions in this area. A brief introduction to microwave processing and the considerations required in the design of industrial microwave processes is given. Coal, as a fuel and as a feedstock for other products, is introduced and the areas where microwaves have been identified as having potential application in coal utilisation are highlighted. The main body of the paper summarizes the information available on the microwave heating characteristics of coal (dielectric properties), and reviews the work to date on microwave processing of coal. Where possible, industrial or pilot scale examples are discussed, along with a consideration of the significant hurdles that exist scaling from bench or pilot scale systems to industrial sized units. The paper concludes by identifying scientifically promising areas for further development of microwave coal processing and areas where further work would be required to establish the potential efficacy of the process. It also highlights that the economic case for the commercial development of most of these processes is yet to be made, and major financial investment would be required to operate most of these systems at industrial scale.

INTRODUCTION TO MICROWAVE PROCESSING

Conventional heating occurs from the outside of a body towards the centre through conduction, convection and radiation mechanisms. Microwaves, however, can penetrate inside most non-metallic materials and, therefore, have the advantage of heating volumetrically. How the material will heat depends on the dielectric properties of the individual components [Meredith, 1998]. When a material contains more than one component, and with quite different dielectric properties, selective heating will occur. It is usually this selective heating, coupled with the thermal properties of the material components, that dictates whether microwave heating will provide any advantages over conventional heating. The volumetric and selective heating capabilities of microwaves mean that heating times can often be reduced to less than 1% of conventional heating techniques [Meredith, 1998]. This rapid selective heating can also result in phenomena that would not be possible in conventional heating, such as superheating in processes that operate at atmospheric pressure and fracturing of materials [Kingman, 2006]. Shorter treatment times also enable equipment to be scaled down significantly. Therefore microwaves can be used to great advantage in certain applications. To exploit this potential, a multi-disciplinary approach is essential, as an in-depth understanding of microwave heating mechanisms, electromagnetic field patterns and dielectric properties of materials, and the industrial process in question is required in the design of effective microwave equipment.

Microwave heating mechanisms

In the presence of microwave radiation, materials can be classified into one of three groups: insulators, conductors and absorbers [Chen et al., 1984]. Most carbon based materials are absorbers of microwaves, depending on structural composition. Insulating materials like quartz or PTFE are microwave transparent, while conductors such as aluminium or stainless steel can reflect microwaves (when they are present as sheets or blocks). Materials that can absorb high frequency electromagnetic waves are known as dielectrics and can heat in various ways [Meredith, 1998; Whittaker, 2005a; Scaife, 1989]. In the industrial high frequency heating range (10^7 – 3 x 10^9 Hz), which includes radio frequency and microwaves, the predominant heating mechanisms are dipolar polarization, conduction and interfacial polarization [Metaxas and Meredith, 1983]. The conduction mechanism results from having limited free charge in the material matrix, as in graphite, and is usually substantially constant at low microwave frequencies, falling away as frequency increases to around 100 MHz [Meredith, 1998]. The load behaves like a poor electrical conductor, and the movement of the free charge results in heating through electrical resistance [Scaife, 1989]. The dipolar polarization mechanism arises from the molecules within the dielectric exhibiting a dipole moment. In the presence of an externally applied electric field, these dipoles align themselves in the direction of the field [Metaxas and Meredith, 1983; Whittaker, 2005b]. As the alternating electric field (resulting from the application of microwaves) changes, the dipoles oscillate, producing an increase in the internal energy of the dielectric. This internal energy can be lost as friction, thus heating the material [Metaxas and Meredith, 1983]. Dipolar polarization is frequency dependent and usually dominates in microwave heating applications above 1 GHz [Metaxas and Meredith, 1983]. Interfacial (or Maxwell-Wagner) polarization relates to the build-up of charge particles at interfaces in heterogeneous dielectrics. It is thought to be important in the heating of heterogeneous dielectrics at frequencies less than 5 x 10^7 Hz [Metaxas and Meredith, 1983].

The significance of dielectric properties on heating potential

The way a dielectric absorbs microwaves and converts them to heat is described by the complex permittivity (ε^*), where the real part is the dielectric constant (ε') and the imaginary part is the dielectric loss (ε''), as in the following equation.

$$\varepsilon^* = \varepsilon' - j\varepsilon''$$

The dielectric constant is a measure of the ability of charges and dipoles in a material to store electromagnetic energy. It also defines the velocity of propagation of an electromagnetic wave through a dielectric and can be related to refractive index [Meredith, 1998; Fletcher, 1995]. The dielectric loss factor is a measure of the ability of a dielectric to dissipate internal energy stored in the material as heat. The ratio between the dielectric loss factor and the dielectric constant provides a measure as to how well a material absorbs the electromagnetic energy and dissipates it as heat throughout the material. This property, called the dissipation factor or loss tangent, $tan\delta$, is often used to describe the ability of a material to heat in an externally applied electromagnetic field [Meredith, 1998].

Dielectric properties can vary greatly with composition, temperature, frequency, and density [Salsman, 1991; Nelson, 1988; Altschuler et al., 1963]. It is therefore important to characterise them across the whole range of processing conditions when planning microwave experiments and designing industrial microwave equipment.

Some considerations in electromagnetic design and scale-up

Not only the dielectric properties, but the microwave frequency and electric field strength, govern the power absorbed by the sample and must be considered when designing electromagnetic equipment. This relationship is demonstrated in the following equation.

$$P=2\pi f \varepsilon_0 \varepsilon''_{eff} |E|^2$$

The electric field strength and distribution are affected by the cavity type and dimensions as well as the dielectric properties of the materials in the microwave zone.

The penetration depth of microwaves given in the equation below is inversely proportional to the dielectric loss [Meredith, 1998], which can severely limit the scale of high dielectric loss systems [Kingman, 2006].

$$Dp \approx (\lambda_0 \sqrt{(\varepsilon')}/2\pi\varepsilon''$$

where λ_0 is the microwave wavelength.

This can be overcome to some extent by using a lower microwave frequency, but this solution is by no means trivial. Careful selection of the materials used in the microwave zone, for example the conveyor belt in a conveyed system, is also required [Meredith, 1998].

A detailed discussion of electromagnetic design and scale-up is beyond the scope this paper and can be found elsewhere [Meredith, 1998; Metaxas and Meredith, 1983], suffice it to say that it is a complex process requiring a multi-disciplinary approach, and close co-operation between the manufacturer of the microwave equipment and the end-user.

COAL PROCESSING

Coal is by far the most prevalent fossil fuel, with 860 Gt of coal reserves [World Coal Association, 2012c]. At current consumption rates, it will outlast oil and gas combined. Coal-fired power plants generate 41% of the world's electricity, while in some countries, coal accounts for over 90% of electricity generation [World Coal Association, 2012a]. Coal is also a very important resource for industry and is needed to produce 68% of the world's steel [World Coal Association, 2012b]. The average efficiency of coal power plants around the world is around 34% [World Coal Association, 2012c]. For each 1% improvement in efficiency, CO_2 emissions are decreased by 2 – 3% [World Coal Association, 2012a]. Therefore, research and development focusing on improving the efficiency of coal utilisation can make a significant contribution to world CO_2 emission reduction.

The research reviewed here has been split into three sections: coal dielectric properties, coal pretreatment in power generation, and other microwave coal applications. Coal is a heterogeneous material, and its composition and properties vary wildly from lignite to anthracite. Therefore the characterisation of the dielectric properties of coal is not straightforward and has been the subject of several papers. Microwave pretreatment has been investigated as a potential upgrading process, to remove minerals or water prior to combustion, or to improve grindability, thus saving on energy costs and reducing harmful emissions. Other applications include the investigation of microwave processing for coking, liquefaction, enhancing fluid flow in coal beds and coal characterisation.

Many of these techniques have been shown to work at laboratory scale, but have yet to reach full scale commercialisation. In some cases this is due to the fact that the application didn't offer efficiency advantages over conventional heating. In other cases, the multi-disciplinary approach required for successful and efficient microwave process design was not undertaken. This paper surveys the existing knowledge on coal microwave processing and attempts to identify areas where further development would be fruitful.

DIELECTRIC PROPERTIES OF COAL

Coal structure and composition vary enormously between coals of difference rank and origin, and therefore so do the dielectric properties. The dielectric constant of Run Of Mine (ROM) coal at 2.45 GHz can range from 1.5 – 10, and the dielectric loss from 0.04 – 3 [Marland et al., 2001; Chatterjee, and Misra, 1990]. The loss tangent, $\tan\delta$, can therefore range from around 0.01 to 0.2, making coals low – medium microwave absorbers as bulk materials [Kappe et al., 2009]. The bulk dielectric properties can be misleading, however, and it is more useful to consider the dielectric properties of the constituent parts. Coal is a heterogeneous material and can be difficult to characterise because it is formed through a complex set of inputs, depositional environments, and geological and chemical processes including dehydrogenation, de-oxygenation, and condensation reactions. As well as large variations in the organic component, the inorganic component (mineral matter) and moisture content can vary immensely.

Organic component

The aliphatic hydrocarbon structures in coal tend to have poor microwave absorbing potential [Metaxas and Meredith, 1983] whereas functional groups such as hydroxyl, aldehydes, ketones, and carboxylic acids can affect a molecule's otherwise non-polar structure resulting in an increase in microwave absorbing capability. Aromatic structures have free charge available that increases a coal's response to microwave energy [Whittaker, 2005b; Von Hippel, 1954; Mingos and Baghurst, 1991]. The ring of carbons with a shared charge is the primary component of all aromatics, and functional groups and aliphatics are commonly bonded to aromatic rings. Polyaromatics can be networks of rings, and can also include these groups. As with single aromatic rings, the presence of free charge should facilitate microwave heating through conduction or interfacial polarisation. With increasing chain length or larger branched structures, electrical conductivity has been shown to increase [Inokucki, 1951]. As the number of free charge carriers increases, microwave responsiveness should also increase [Hairetdinov, et al., 1998].

As coal rank increases, the structure becomes more aromatic and more ordered [Van Krevelen, 1993; Web Reference , 2005; Cartz and Hirsch, 1960]. Lignite (or brown coal) consists largely of single aromatic rings, with functional oxygen groups such as carboxylic acid, aldehydes and alcohols (-COOH, -OH, etc.). There is approximately one oxygen atom per 3-4 carbons. The effective cross-links between the rings are mostly secondary (hydrogen bonds) with a few aliphatic and ether links. Subbituminous coals still contain mostly single rings with aldehyde and alcohol groups, though there are some larger rings, and fewer functional groups than lignite, with approximately 5-6 carbons per oxygen atom [Blom et al., 1957]. Hydrogen bonds still provide many cross-links but oxygen bridging structures (ethers -O-) also contribute a significant proportion, in addition to the fewer aliphatic links that exist [Crelling, 1989]. Bituminous coals are a fairly broad category, which includes many larger structures of several rings, in addition to some smaller groups and branches [Van Krevelen, 1993]. The number of functional oxygen groups are also greatly reduced, with predominantly alcohol groups present and as low as 1 oxygen per 20 carbon atoms for the highest rank [Stach, 1982]. With increasing rank, the nature of the cross-links gradually decreases from a mixture of aliphatic and aromatic links, to almost entirely aryl bridges. Anthracitic coals are the most aromatic coals, with very few functional groups, with around one oxygen atom existing per 100 carbon atoms [Van Krevelen, 1950]. With anthracites, almost entirely aromatic-aromatic cross-links are present, resulting in large and relatively ordered structures [Van Krevelen, 1993].

The relationship between coal petrography and chemical composition (C/H, C/O etc.) is well known [Van Krevelen, 1993] and since there is a correlation between carbon structure and dielectric properties, it is fairly likely that a link also exists between coal petrology and dielectric properties. Vitrinites have been shown to behave as semi-conductors, with electrical conductivity increasing with increasing rank and aromaticity [Schuyer and Van Krevelen, 1955]. Inertinites have the highest carbon content of the maceral groups, followed by vitrinites then liptinites [Choi et al., 1989]. The aromaticity of the contained macerals is likely to dictate microwave response through interfacial polarisation due to delocalised pi electrons, as is the case when considering bulk properties of coal [Slowik and Wieckowski, 2003].

Wardle [2010] measured the dielectric loss factor for ten coal samples on a dry and ash-free basis. The coal samples were chosen to span a relatively wide rank range, and were dried and de-mineralised so that the contribution of the organic component of the coals to their dielectric properties could be assessed. The dielectric constants ranged from 1.9 to 2.8, and the loss from 0.016 – 0.12. This corresponded with tan δ ranging from 0.008 – 0.044, meaning that all dry-ash-free samples could be considered as 'almost transparent' [Kappe et al., 2009]. The results showed that dielectric loss increased with increasing rank (Figure 1).

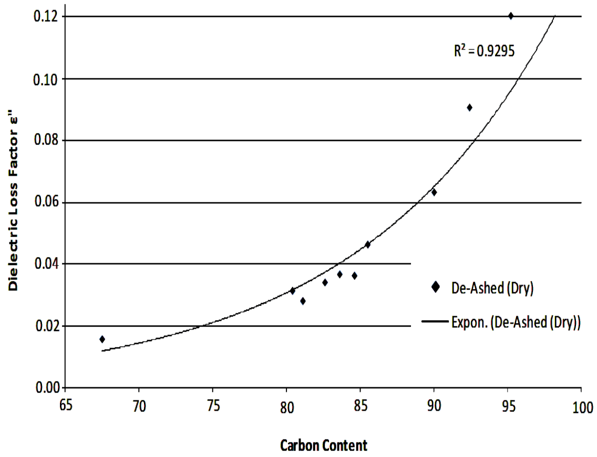

Figure 1. Relationship between dielectric loss factor measured at 2.45 GHz and carbon content for all coal samples on a de-ashed dry basis [Wardle, 2010].

Marland et al., [2001] showed that the dielectric constant increased with rank for low ash-yielding dried coals. The increase in microwave responsiveness of the organic component of coal with rank is caused by the increase in the number of charge carriers with increasing aromaticity.

Inorganic component

The mineral matter content and composition can affect the dielectric properties of coal. Pyrite and ash have been reported to have relatively high dielectric constants of 7 and 4.6 respectively [Chatterjee, and Misra, 1990; Shuey, 1975; Huang and Rowson N., R., 2001] when compared with the organic component measurements of Wardle [2010]. Marland et al., [2001] measured the dielectric properties of some selected (commonly coal associated) minerals. They found that, with the exception of pyrite, all minerals tested are expected to have a lower microwave heating rate than a medium-rank coal. However, pyrite is expected to have a much higher microwave heating rate and, therefore, may have a significant impact on the microwave heating properties of coal.

Iron sulphide (FeS_2) can occur in two crystalline forms, pyrite (cubic) and marcasite (orthorhombic), but pyrite is the more common form and so the term pyrite is usually used to refer to both [Wardle, 2010]. Dielectric heating studies of pyrite and marcasite found that marcasite exhibited a higher heating rate than pyrite [Huang and Rowson N., R., 2001]. It has been proposed that pyrite doesn't behave as a true dielectric, but as a conductor [Groves, 2007]. The heating mechanism would therefore be through the conductive heating mechanism, or 'skin heating', where high frequency currents flow through a conductor, causing eddy currents to flow in the opposite direction and covering the surface in a thin skin [Groves, 2007]. As a semiconductor, the conductivity of pyrite varies significantly depending on the impurities present, [Pridmore and Shuey, 1976] and therefore the contribution of the conduction mechanism to its dielectric properties is expected to vary accordingly. Dipole orientation is also likely to occur, due to point defects with a permanent dipole moment [Shuey, 1975]. Interfacial polarisation may play a role at low frequencies, and this will be affected by the distribution of pyrite in the coal [Shuey, 1975].

The mineral matter content in coal can commonly range from approximately 1.5% [Li, 2004] up to 49% [Schweinfurth, 2009] and higher, and the pyritic sulphur content ranges from 0 – 8% [Schweinfurth, 2009; Attar and Hendrickson,1982]. As the mineral matter is heated it transforms, further complicating the behaviour of the ash yielding materials [Falcone and Schobert, 1986; Huffman and Huggins, 1986; Richardson et al., 1986].

Moisture content

Bed moisture contents in ROM coal can be as much as 70% [Allardice et al., 2004]. Coal moisture is not present as pure water, however. Heteroatoms in the coal form soluble functional groups such as carboxylates and amines [Attar and Hendrickson, 1982]. Inorganics such as sodium (Na^+), calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions can be bonded to the carboxylate ($-COO^-$), and can therefore be present as salts in the coal moisture [Hayashi and Li, 2004]. Some of the minerals present (kaolinite, quartz and calcite for example [Renton, 1982]) also exhibit some solubility.

Water has a dielectric constant of 77 and a loss factor of 13 at 2.5 GHz and 25 °C [Meredith, 1998], meaning that it has a $\tan\delta$ of 1.9, and absorbs microwaves very strongly. The dielectric constant of water decreases slightly with the addition of sodium chloride (NaCl): it is 68 in a 0.5 molal solution at 2.5 GHz and 25 °C [Meredith, 1998]. The effect of dissolved NaCl on dielectric loss is less straightforward, but in general it causes an increase; the dielectric loss at 2.5 GHz and 25 °C is 54 in a 0.5 molal solution [Meredith, 1998]. It is also important to note that the dielectric properties of water and aqueous salt solutions change with temperature. While the dielectric properties of pure water decrease with increasing temperature, the opposite may be observed at low moisture contents and higher salt contents [Metaxas and Meredith, 1983]. This means that heating efficiency may decrease or increase with increasing temperature, depending on the coal. Likewise, dielectric properties change with frequency, and the addition of NaCl has been shown to affect this frequency dependence [Nörtemann et al., 1997]. The dielectric properties of bound water are also different from those of free water, and this further complicates the dielectric response [Metaxas and Meredith, 1983]. Obviously the moisture content, composition and form will vary from coal to coal and therefore it is important to measure the dielectric properties for the sample in question.

It is clear that the coal moisture dictates the microwave heating characteristics of many coals. This was demonstrated by measuring dielectric properties during heating and cooling of coal. A substantial reduction in dielectric properties occurring between 80 °C and 180 °C are a result of moisture loss [Marland et al., 2001] (see Figure 2).

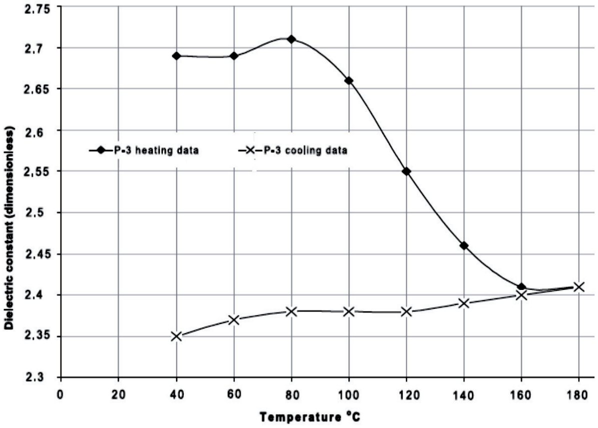

Figure 2. Dielectric constant during the heating and cooling of coal measured by Marland et al. [2001].

COAL PROCESSING USING MICROWAVES

Beneficiation and mineral liberation

There is renewed interest in the beneficiation of coal for reduced greenhouse gas emissions [Katalambula and Gupta, 2009; Domazetis et al., 2008] particularly with the need for mineral matter removal in lower quality coals [Katalambula and Gupta, 2009], e.g. the reduction of inorganic sulphur, other minerals and concurrently mercury and arsenic [Katalambula and Gupta, 2009, Huggins et al., 2009; Ward, 2002; Spears et al., 1999]. Many nations now require pre- or post-combustion sulphur oxide mitigation strategies to meet compliance and so the pre-processing of coals to reduce sulphur etc. is of interest.

Microwave processing of coal for beneficiation has specifically targeted the removal of pyrite (for sulphur reduction strategies), with early desulphurisation work using microwaves dating back to the 1970s [Zavitsanos, 1978]. As reported in the inorganic component section, most coal associated minerals such as quartz and alumina are relatively transparent to microwave radiation as a result of their low dielectric properties [Marland et al., 2001]. Pyrite however has higher conductive losses than coal and most other associated minerals [Huang and Heating, 2001]. Several workers [Marland et al., 2001; Shuey, 1975; Fanslow et al., 1980] studied the dielectric properties of coal and pyrite to predict heating rates. They suggested that magnetic separation was successful because the conductive losses of coal and pyrite were sufficiently different, thus allowing the pyrite to absorb more electromagnetic energy and thus heat faster than the coal. These properties therefore gave an indication of the heating characteristics of the selected minerals and it was consequently expected that pyrite should heat readily in a microwave environment, with the other, low loss, materials exhibiting a lower heating rate.

There have been many studies that suggest that the magnetic susceptibility of pyrite in coal can be significantly improved by heating it to sufficient temperatures as to shift its stoichiometery toward magnetic phases [Rowson and Rice, 1990a]. This can be achieved by conventional heating techniques [Thorpe et al., 1984], but heating consequently causes the pyrolysis of the coal matrix. Since pyrite has such a high thermal (and electrical) conductivity it would suggest that the pyrite heating mechanism would be through conduction or surface heating [Al-Harahsheh and Kingman, 2004]. Weng and co-workers [Weng and Wang, 1992] showed that by exposing coal to microwaves, localised heating occurs and pyrite decomposes according to the following reaction;

$$FeS_2 \rightarrow Fe_{1-x}S \rightarrow FeS \text{ or } FeSO_4 \ (0 < x < 0.125)$$

There have been several attempts to induce this transformation using microwave heating, and this has been discussed in a previous review by Jones and co-workers [Jones et al., 2002]. Briefly, the use of low microwave powers (<500 W) to increase the magnetic susceptibility did not induce the desired transformation [Rowson and Rice, 1990b]. Increasing the power [Butcher,1995; Uslu and Atalay, 2004] and residence time [Uslu and Atalay, 2004] showed some success, although recovery rates were still poor. The addition of magnetite as a microwave receptor was found to improve the recovery rate up to 58% and enable a reduction in treatment time [Uslu and Atalay, 2004] by increasing the bulk heating of the coal matrix. The use of microwave receptors to increase heating rates is common in the academic literature when the dielectric properties of the sample (or slurry) are not sufficient to absorb microwave energy. However, the use of this type of material changes the major heating mechanism from volumetric microwave heating to conventional conductive heat transfer from the receptor. Selective heating in the sample itself is no longer the main mechanism by which reactions can occur.

Microwave treatment of crushed coal in a caustic solution of sodium hydroxide (NaOH) or potassium hydroxide (KOH) showed up to 60% sulphur reduction with an improvement in magnetic separation [Rowson and Rice, 1990b; Waanders et al., 2010]. The mechanisms at work are now further complicated by the addition of caustic solution, which itself is an excellent microwave absorber. The penetration of the microwaves into the slurry would certainly be different from dry treatment or even water based slurry processing, resulting in the heating in the coal matrix through conduction from the hot caustic solution.

Relatively few reports exist that investigate the mechanism by which pyrite is transformed into pyrrhotite. Mossbauer spectroscopy was used to demonstrate the impact of different exposure times (30 to 100 s) at 2.45 GHz with 1.5 kW on a Chinese coal in the transformation of pyrite into pyrrhotite and troilite [Weng and Wang, 1992]. There was a reduction in the inorganic sulphur content (up to 44%) with the release of H_2S (and possibly other gases). Mossbauer spectroscopy in the study of Waanders and co-workers showed no evidence of pyrite transformation, probably indicating that the required temperature for the reaction had not been reached [Waanders et al., 2010].

Microwave treatment has been shown to enhance the dissolution of both inorganic sulphur and some organic sulphur with peroxyacetic acid [Jorjani et al., 2004], copper (II) chloride and tri-iron dodecacarbonyl [Bodman et al., 1997], and hydrogen iodide (HI) [Elsamak et al., 2003]. When compared with thermal heating, microwave heating was found to reduce reaction times significantly, and this was attributed to localized superheating and thermal runaway affecting the reaction kinetics [Elsamak et al., 2003]. However, the claims of weakening C-S and Fe-S bonds [Jorjani et al., 2004] are effectively impossible when the energy in a microwave photon at 2.45 GHz is considered. A total of 36% sulphur reduction was achieved when a -400 micron (40 mesh) coal was treated at 1000 W for 80 s, with pyritic sulphur reduction of 50% increasing to 80%, and organic S reduction increasing from 24% to 35% [Jorjani et al., 2004]. Optimised sulphur reduction of 65% was achieved with smaller mesh sizes (-300 μm/50 mesh) and 120 min of peroxyacetic acid leaching at 55 °C [Jorjani et al., 2004]. This again challenges any claim of selective heating, suggesting that the reactions are actually predominantly mass transfer controlled. Microwaves have been investigated as the heat source for the solvent extraction of coal in the production of 'ashless' coal from three high ash-yielding Turkish coals [Sönmez and Giray, 2011]. Polar solvent n-methyl-2-pyrrolidinone, dielectric constant 32.6, was used as the solvent and microwave absorber. The advantage of this process over conventional heating is the much shorter extraction time (10 min versus 2 h). However, the coal is not selectively heated in this process and therefore any differences in yield or ash removal are likely due to the heterogeneity of the sample, the difference in solvent/coal ratio, and the temperature.

Microwave processing of brown coal has been shown to increase triboelectrostatic separation efficiency [Turcaniova et al., 2004]. In this case larger sized coal particles of <3 mm were exposed for 10 min at 900 W under nitrogen then pulverised to <70 μm. The ash yield dropped from 49% to 18% [Turcaniova et al., 2004]. The beneficiation mechanism may relate to the formation of cracks inside larger particles, as a result of selective heating of the mineral phases, which are then liberated after grinding. Other workers have tried to enhance this liberation effect by combining ultrasound (to improve penetration of solvents post treatment) with microwaves, which was shown to improve the desulphurisation rates of high sulphur coals over microwave treatment alone [Mi et al., 2007].

Flotation pretreatment is another area that has been investigated. Low-rank coals are hydrophilic due to the presence of oxygen functional groups and high intrinsic moisture content, and are therefore poor candidates for flotation. Drying improves coal flotation, and microwave drying has been compared with oven drying as a pretreatment for coal flotation [Ozbayoğlu et al., 2009]. It was found that both oven drying and microwave drying improved flotation in heptanol and octanol, and that the best results for microwave drying were generally comparable with oven drying.

The selective heating of the water was thought to potentially dry the coal without oxidising the surface, potentially offering advantages over conventional drying. FTIR analysis of the microwave dried samples revealed little change to the abundance of acid functional group such as –OH and –COOH [Ozbayoglu et al., 2009]. Oxidation of coals during storage also reduces flotation efficiency and microwave pretreatment has been investigated as a means to remove hydrophilic groups such as –OH and –COOH [Xia et al., 2013]. Microwave treatment was found to decrease the concentration of these functional groups, and this was almost certainly through moisture removal (the coal was dried from 6% to well below 1%) [Xia et al., 2013].

Coal drying

There are significant calorific gains that can be achieved through the removal of water from coal. An enhancement of around 104 Btu/lb is achieved for each weight per cent of moisture that is removed from Powder River Basin coal [Sarunac et al., 2009]. It has been estimated that a reduction in moisture from 6% to 2.6 - 2.8% in lignite burned in US power stations would result in annual savings of $1.3 million [Karthikeyan et al., 2009]. The majority of the work in this area has attempted to use waste heat and steam drying although other novel methods such as mechanical thermal compression [Bergins, 2003] and acoustic treatment [Ensminger, 1988; Swamy et al., 1988; Fairbanks, 1984] do exist. Microwave energy can be used since the unwanted phase in the coal (water) has the highest loss factor [Marland et al., 2001; Standish et al., 1988; Seehraet al., 2006; Learey, 2010] so it will be selectively heated whilst the bulk coal remains effectively microwave transparent.

The drying rates of brown coal agglomerates (spheres of 20-30 mm diameter or 20-30 mm diameter cylinders) using microwave heating (2.45 GHz over five power settings with full power being 650 W) were found to be one to two orders of magnitude quicker than conventional thermal drying (80 °C) [Standish et al., 1988]. The selective mechanism of the moisture was attributed to “liquid pumping” of the convective fluid flow, created by pressure build up within the particles [Standish et al., 1988]. Microwaves have been shown to produce higher heating rates (of an order of magnitude) on a coal with 52 wt% moisture whilst operating at 2.45 GHz and 800 W [Seehraet al., 2006], again as a result of selective heating over conventional heating mechanisms. Economic estimates of $3/ton were provided for a 10% reduction of moisture [Seehraet al., 2006]. Total moisture removal was not possible using microwaves since any residual moisture was thought to remain in the fine capillaries of the bituminous coal. The authors also demonstrated that a bench scale conveyor system could be used at kg quantities [Seehraet al., 2006]. The effect of particle size, output power, coal sample weight and ash yield on the drying of three low-rank coals in a 1300 W microwave oven has been investigated [Tahmasebi et al., 2011]. Drying was shown to improve with increasing particle size due to a reduction in proportional heat losses as the particle size increased. As would be expected, increasing the output power and reducing sample size both resulted in an increased drying rate. Shenhua no. 5 (18% ash yield as-received) was found to dry more rapidly than the Shenhua no. 6 (3% ash yield as-received), and this was attributed to the higher dielectric constant of mineral matter compared with organic matter in coal. However, the differences in moisture content (and potentially other differences in the sample composition) were not ruled out as contributing factors to this result. Binner et al. [2013] investigated the drying of Morwell brown coal (ROM moisture content ~60 %) in a 2 kW single mode cavity (Figure 3). They found that the energy required to remove the bulk and loosely bound water was comparable to other thermal drying processes. However, energy requirements

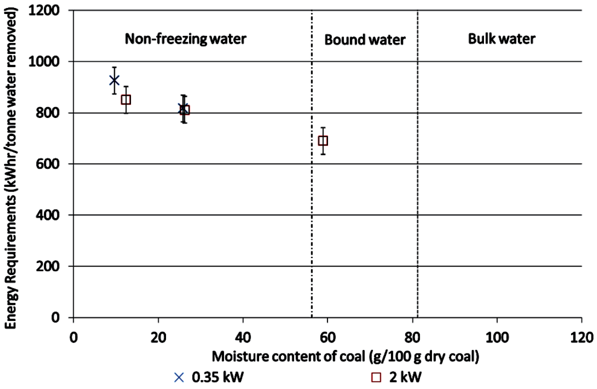

Figure 3. Energy requirements for Morwell brown coal drying in a 2 kW single mode cavity (Run of Mine moisture content ~60%) measured by Binner et al. [2013] Bound water content estimated based on Hayashi et al. [2004] and non-freezing water content based on Allardice et al. [2004].

increased through the non-freezing water region. The overall energy input, and not the power input or treatment time, determined the degree of drying.

One specific concern with microwave treatment is the possible alteration of the coal's structure. Whilst the heating of coal is selective, heat transfer occurs from the potentially superheated moisture into the bulk [Lester and Kingman, 2004a]. Low-rank coals are more susceptible to low-temperature thermal modification due to their oxygen functionality although this is again dependent on power density, treatment time and cavity design. ^{13}C NMR analysis of microwave dried subbituminous coal (300 and 600 W over selected periods of exposure for a few minutes) showed no major structural changes although several coals had minimal changes (± 2%) in apparent aromaticity [Miknis et al., 1996]. Fourier transfer infrared (FTIR) spectroscopy showed that microwave drying of a Chinese lignite resulted in a significant decrease in the concentration of oxygen-contained functional groups, a slight reduction in aliphatic hydrogen and little or no effect on aromatic carbon [Tahmasebi et al., 2012]. Higher powered treatment resulted in the heating of the whole coal sample generating additional transformations [Wilson, 2009].

There have been attempts to scale up the microwave drying process. Early work was based on drying lignite, subbituminous, and bituminous "fine" ¼ inch coals on a moving fiberglass-Teflon mesh belt running through a 6-foot oven with two 6 kW microwave sources [Lindroth, 1986]. A maximum of 1.54 kg of water was removed per kWh. The mean peak temperature of the coals was 73 °C implying some bulk heating from the selective heating of the moisture [Lindroth, 1986]. Interestingly this level of moisture removal is remarkably close to the theoretical limits that can be achieved but it is likely that hybrid heating and controlled use of recycled heat would be needed for it to be viable. When scaled up, coal fires (spontaneous or otherwise) have been shown to be a safety concern requiring continuous monitoring, or in more extreme cases physical removal of "smoking" coal lumps [Wilson, 2009]. Problems of entrainment of fine particles out of the bed by the rapid evolution of water vapour have also been reported [Allardice et al., 2004].

The Drycol commercial plant in Kentucky (USA) had a system to continuously process 15 tons of coal per hour. Figure 4 shows the Drycol process in 2010. The coal was kept to a temperature lower than 90 ºC to avoid loss of volatiles and minimise the risk of fires by spontaneous combustion. The main challenge for scale up of this process is in the design of an appropriate microwave cavity that minimizes residence time through the use of high power densities whilst avoiding bulk heating.

The Drycol process appears to show no changes in the proximate analysis (apart from a 50% reduction in moisture content) as a result of microwave processing. Coaltek has also been developing a coal drying system to create upgraded fuels for pulverised coal combustion and gasifiers using microwaves. The process claims a 50% increase in calorific value through moisture removal operating at 120,000 ton/year plant [Wilson, 2009].It is clear that significant commercial drivers exist

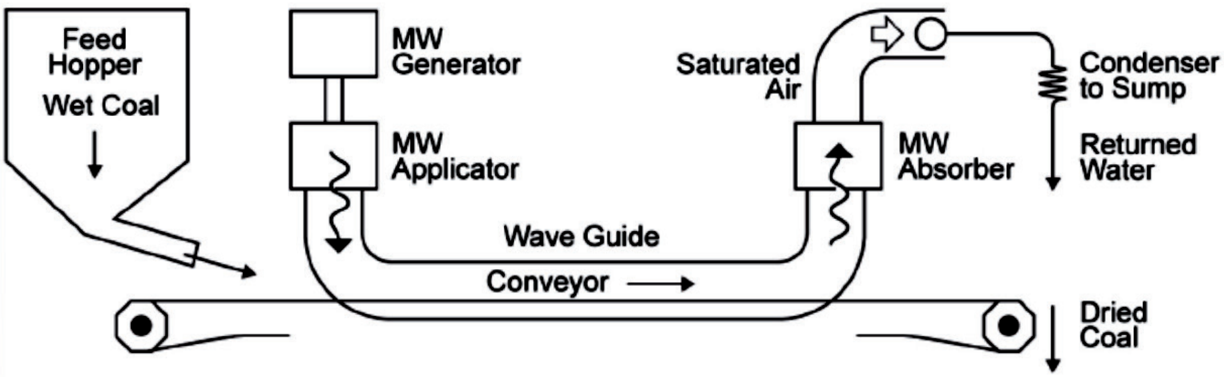

Figure 4. The Drycol continuous coal drying process.

while there are massive coal reserves across the globe, provided that low cost microwave systems can reduce the cost of transport and increase the calorific value of these low-rank coals for improved efficiencies and concurrent emission reductions.

Improved grindability of coal

Coal that is fired in a pulverised form requires drastic size reduction of the feed to a standard of 75% < 75 μm (200 mesh) to give acceptable burnout performance. Poor grinding is a problem to the power industry since oversize particles inevitably cause burnout problems [Shibaoka, 1986] even when the coals are reactive with high-volatile yields [Clokeet al., 2002].

Conventional heating of a coal can be used to reduce grind strength [Harrison and Rowson, 1997], although it is unlikely that this would be economically viable unless waste heat was utilized [Key World Energy Statistics, 2011; Lytle et al., 1992]. In addition, prolonged heating may affect the combustion properties of the coal. Volumetric heating of selected phases using microwave heating again presents an opportunity to reduce processing times. At low powers (and therefore lower power densities) workers have demonstrated that microwave treatment can significantly reduce the strength [Achimugu, 2007] and therefore improve the grindability of coal particles [Batar, 2004; Marland et al., 2000]. The authors concluded that the economics were poor with much more energy being added to the process than could be potentially saved but this is directly as a result of the high treatment times required when working at such low powers. Another study [Ruisánchez et al., 2012] looked at the effect treating wet and dry coke in a 700 W multimode oven with 1 s and 3 s power pulses. Shorter (1 s) pulses were found to be more effective for the same treatment time (energy input) than longer pulses. Dry coke was found to respond better than wet coke. This was attributed to the fact that the water in coke is added as part of the quenching process, and is therefore present as surface water, which has no effect on the coal structure as is volatilises. It was also found that the initial treatment had the greatest effect on grindability, and therefore the optimum treatment time was short. Based on direct scale-up of these experiments, economic analysis suggested that the overall grinding costs could be reduced, and the number of particles <1 mm could be increased, with a microwave pretreatment step.

At higher powers the processing times can be drastically reduced in order to avoid bulk heating of the coal. Lester and Kingman showed how treatment of a single UK coal in a TE_{10n} single mode microwave cavity operated at 8 kW and at 2.45 GHz and with exposure times of several seconds improved the grindability significantly [Lester and Kingman, 2004a]. The paper investigated how petrographic and proximate characteristics also showed minimal changes after treatment. In a follow-on study, five coals were treated at 8.5 kW and 2 s [Lester and Kingman, 2004b]. Despite the improved grindability there were minimal changes in petrography, proximate content, and reactivity.

Another study [Wu et al., 2005] showed that the residence times in the microwave cavity could be reduced to 0.1 s and still achieve significant changes in the grindability of various world coals. The grindability increased by an average of 100%, demonstrating that longer residence times were not necessary if the cavity design (and therefore electric field strength and distribution) was appropriate. The economic implications of this finding are important as well as the demonstration that coal could be treated under free fall conditions through a microwave cavity rather than on a conveyor belt or similar transport system, and therefore operate at industrially relevant residence times.

In the same paper [Wu et al., 2005], the expansion of moisture within the coal matrix was proposed as the mechanism for causing cracks and breakage. Whilst these faults lead to an increased grindability it was also noted that the moisture content of the coals did not drop significantly. This implies that high power density treatments at short treatment times mobilizes the moisture around the coal matrix without expelling the moisture. This is a fundamentally different process to coal drying with microwaves, where the initial moisture levels are much higher, i.e. 30-50 wt% as opposed to <5%.

The recent work by Toraman shows that lignite can also be processed using high power microwaves over short treatment times (2 s) to increase by grindability >100% [Toraman, 2010] The process appears to be identical to that used by others [Lester and Kingman, 2004a] whereby a charge of coal is dropped using pneumatic controls through a single mode TE_{10n} single mode cavity. The author concludes that 20 kW increases the Hardgrove Grindability Index (HGI) but also produces the largest quantity of fines (-75 μm).

The process of increasing grindability through microwave pretreatment has been demonstrated at small scale and should be scalable. This has not been achieved to date despite promising results and recent work in this area [Wang et al., 2011; Sahoo et al., 2011].

OTHER APPLICATIONS

Coke making

Whilst coke making via the slot oven design has been optimised over the last 100 years, the fundamental processes surrounding the technological transformation of coal to coke has remained essentially the same. Whilst many aspects of production have been improved, conventional ovens still heat coal feed stocks for at least 16 hours [Fess, 1957], mainly due to the poor thermal properties of the coal [Gupta et al., 2008]. Microwave heating of coal offers an alternative means of coke making [Lester et al, 2006] through the selective heating mechanism. Initial heating can occur because minor components such as moisture and bound hydroxyl groups have significantly higher dielectric properties (as with pyrite, discussed in the inorganic components section).

With sufficient power density and residence time the bulk temperature of the coal sample will be raised by the superheating of the moisture in the carbon matrix [Wang et al., 2008]. The carbon matrix, which is relatively microwave transparent at temperatures below 300 °C, then becomes more susceptible to absorbing microwave energy. As coal turns into coke, the aromaticity increases [Marland et al., 2000] as a consequence of the loss of the volatile component and restructuring of the carbon which, in turn, increases the conductivity due to increasing electron mobility through the transfer of π bond electrons along the aromatic layers [Honda, 1959; Pilawa et al., 2009; Peng et al., 2012]. As temperatures continue to increase from 400 to 1000 °C, the mobility of electrons and level of free charge per unit volume increase. Increased carbonization increases the dielectric loss factor and thus increasing the rate conversion of microwave energy to heat allowing temperatures in excess of 1000 ºC to be achieved [Lester et al, 2006; Gray, 1987]. This marked increase in microwave absorbing capability does pose the problem of a marked reduction in penetration depth, which was measured to be 0.008 and 0.003 m at 915 and 2450 MHz respectively for a bituminous coal [Peng et al., 2012].

Commercial work on microwave coke applications began in the 70's [Wagener and Horst, 1978] and 80's [Tetsuo and Sumio, 1985] although patents are still being filed [Coetzer, 2009]. The patents tend to fall in three main categories. Firstly the use of dielectric properties for remote sensing of coke quality during conventional manufacture [Enami Yoshihiko, 2004], coke manufacture with microwaves where additional microwave receptors are used [Steiner, 1979], and direct microwave heating of the coal [Nushishiro and Igawa, 1995].

One study reports results for heating a high-volatile UK bituminous coal at 8 kW in a multimode microwave oven for 70 min [Lester et al, 2006]. The degree of anisotropy, the intrinsic reactivity and dielectric properties of the treated coal were similar to that of conventionally prepared commercial cokes. As well as drastically reducing coking time, the coal used in the study was low grade and not suitable for use in a traditional coking plant.

In a recent study, [Binner et al., 2014] demonstrated coking of a range of coals. Characterization tests showed that at least 13,600 kW/t was required in the non-optimised cavity to produce a commercially comparable material (Table I). Binner et al., [2014] noted that the energy requirements would need to be reduced by at least an order of magnitude to be comparable with conventional coking. They also pointed out that the dramatic reduction in penetration depth during the coking process would mean a complete redesign of the furnace.

Therefore, microwave coking represents a potential step change in the

Table I. Random reflectance measurement and dielectric properties for microwave-treated Coal A (a high-volatile English bituminous coal), untreated Coal A and commercial cokes, measured by Binner et al. [2014].

Sample	Power (kW)	Treatment time (min)	E input (kW/t)	Average Random Reflectance Rran (%)	ε' at 2.45 GHz	ε" at 2.45 GHz
Coke A1	0.75	30	1700	3.93	7.44	1.44
Coke A2	0.75	60	3400	3.95	11.20	1.75
Coke A3	0.75	120	6800	4.82	14.35	3.04
Coke A4	1.5	30	3400	4.03	10.43	1.17
Coke A5	1.5	60	6800	5.49	19.69	4.94
Coke A6	1.5	120	13600	5.87	24.32	7.6
Coke A7	3	15	3400	4.36	6.65	1.07
Coke A8	3	30	6800	5.47	16.46	3.43
Coke A9	3	60	13600	5.77	28.90	10.67
Coke A10	3	120	27200	5.95	39.38	12.54
Coke A11	4.5	40	13600	6.22	25.49	7.02
Coal A				0.86	3.12	0.02
Commercial Coke 1				6.49	30.77	9.36
Commercial Coke 2				6.35	30.56	9.80

coke making industry, increasing the range of coals that are suitable for coking and drastically reducing heating times. However, energy requirements are currently excessive when compared with conventional coking. Optimizing the process would require further work to develop a system that was able to efficiently heat the initial coal to the target coking temperature followed by lower power heating to allow the coal to carbonize. The control of power input into a material that has rapidly changing dielectric properties and hence penetration depth is a key challenge in the design of a larger commercial process. Reactor design allowing for millimeter penetration depths, rapidly changing material properties and the potential for arcing and thermal runaway would pose major challenges, and an innovative, multidisciplinary approach would be essential in what in reality is a massively challenging application to scale up to a meaningful level.

Liquefaction and liquefaction pretreatment

Due to the abundance of coal, its direct liquefaction is appealing for the domestic production of transportation fuels and chemicals [Shui et al., 2010]. Liquefaction is considered to be one of the most effective ways of reducing CO_2 emissions from low-rank coals, as well as having the potential to convert them into high-value transportable fuels [Okuma and Sakanishi, 2004]. Microwave treatment has been explored as a pre-drying step and also as a heat source for liquefaction itself, potentially improving reaction yields and selectivity.

The efficiency of the coal liquefaction process can be improved by pre-drying the coal. There have been several studies to determine whether the drying process used, including microwave drying, affects the efficiency of liquefaction. Variable exposures and power levels (1 – 15 min and 150 – 600 W) of microwave pretreatment (under nitrogen) of a low-rank coal showed a coal conversion increase of 3 – 7% with 9 – 22% increase in combined oil and gas yields [Ishak et al., 2007] Accompanying the loss of moisture was a decrease in volatile matter and changes in the elemental composition, most notably sulphur. Decreasing volatile matter following microwave exposure has also been reported in other work [Jie and Jiankang, 1994] although it is likely that this was through excessive heating. These treatments may convert pyrite to pyrrhotite and troilite with the loss of gaseous sulphur compounds [Rowson and Rice, 1990b; Waanders et al., 2010]. Thermal, microwave and chemical drying were compared as potential liquefactions pretreatment methods [Miknis et al., 1996]. Liquefaction yields were found to decrease after microwave and thermal drying, and increase after chemical drying. NMR analysis did not show any significant changes in the general chemical structure of the coal for any of the drying methods investigated. Solvent swelling ratios were used to indicate the level of cross-linking in the coals. Chemical drying was found to decrease the cross-linking in the coal, whereas microwave and thermal drying increased it. It was concluded that this increase in cross-linking was due to the partial devolatilization of the thermally and microwave-treated coals, and that this effect was slightly greater in the case of microwave treatment due to the 'intense localized heating' of the coals. The reduction in liquefaction yield was therefore attributed to pore collapse, which then influenced solvent accessibility. These studies all report loss of volatiles during coal drying, which may have led to a decrease in the liquefaction yield. However, as discussed in the coal drying section, microwave treatment can effect coal drying without the loss of volatiles, and therefore should not be ruled out as a potential pre-treatment step in coal liquefaction. Having said that, these studies suggest that microwave-dried coal offers no advantage over a conventionally dried product. Therefore superior efficiency would have to be demonstrated, and the safety issues arising from microwave drying would have to be addressed, before a case for microwave drying were made.

Microwaves have also been investigated as the source of heat during liquefaction. It has been suggested that microwaves are more effective at generating free radicals than other heating methods, and therefore may pose an advantage in liquefaction, which is described mostly as a free radical process [Şimşek et al., 2001a]. Conventional heating of the liquefaction process can lead to long heating and cooling periods. Therefore the yields of oils, asphaltenes and pre-asphaltenes obtained using microwave heating are different from those obtained using conventional heating because of the difference in heating profiles and, consequently, reaction kinetics [Simşek et al., 2001b]. It is therefore the bulk heating property, which enables rapid heating of dielectric materials, that is exploited in this application. The addition of ‘microwave receptors’ (V_2O_5, CuO and TiO_2) has been investigated in the belief that they would ‘increase the interaction between coal and microwave energy’ as well as acting as catalysts [Yagmur and Togrul, 2005; Yagmur et al., 2008]. However, bituminous coals were found to absorb microwaves more strongly than the receptors, and therefore liquid yields were not improved. The V_2O_5 and CuO improved liquid yields for all of the lignites tested, whereas the TiO_2 improved liquid yields for Beypazari and Muğla-Yatağan lignites but decreased it for Tunçbilek. The results were attributed to the microwave receptors effecting changes in the interaction between the microwaves and the reaction media, the catalytic effects of the microwave receptors, and differences in the elemental composition of the coals. Dielectric properties were not measured, and would likely have shed light on the results. Microwaves have also been investigated as a potential heat sources in the treatment of liquefaction residue [Wang et al., 2008]. Again, further knowledge of the dielectric properties of the different phases present and the heat transfer mechanisms at work would help to explain the differences in the reaction products between microwave and conventional heating. Microwaves are a potential heat source for coal liquefaction, and bulk heating has the potential to facilitate rapid heating rates, thereby potentially improving reaction yields and selectivity. Future work should focus on the dielectric properties of the coal, solvents and catalysts to enable comparison with other heating options. Catalyst optimisation has been identified as a major area for improvement in coal liquefaction [Okuma and Sakanishi, 2004], and the consideration of the dielectric properties of potential new catalysts will be useful if microwave heating of liquefaction is to be pursued.

Enhancing fluid-flow in coalbeds

Building on the earlier work that showed the formation of cracks following exposure to microwave energy [Marland et al., 2000; Kingman et al., 2007], it was postulated that an in-situ microwave treatment could enhance coalbed methane extraction or carbon dioxide injectability for CO_2 sequestration and enhanced coalbed methane production [Kumar et al., 2011]. A microwave-transparent polycarbonate pressure vessel constrained the bituminous coal core with argon gas to simulate isostatic pressure. The fracture network was determined using X-ray computed tomography before and after exposure following short-bursts of microwave energy (3 s at 15 kW). New fractures were generated along with aperture enhancements for the existing fractures. Optical microscopy was used to calibrate the X-ray computed tomography volume, with enhancements estimated to increase the fracture volume from 0.5% to 5.5%. A higher enhancement was observed for a non-constrained core (1.8% to 16.1%). It was thought that stresses generated by the production of superheated steam, from the inherent moisture, were responsible for the induced fractures and aperture enhancements. Depth of penetration issues will need to be addressed if work in this area is to continue, although coal under gas pressure will be more brittle and fractures may well extend beyond the microwave penetration depth.

Analytical techniques

Various analytical approaches have taken advantage of microwave energy for rapid drying (for moisture determination in small samples and on conveyor belts), as a digestion aid, and in the elucidation of water forms. Early work generated rank-dependent calibration curves at the laboratory scale before moving to conveyor belt demonstration [Hall et al., 1970a; Hallet al., 1970b]. Later work evaluated a wider range of frequencies determined thick layers worked better with frequencies >2 GHz to avoid the influence of sodium chloride (from coal washing). Prieto-Fernandez and co-workers provided a good review of the application of microwave energy to moisture determination [Prieto-Fernandez et al., 2002]. Their work examined attenuation with varying coal rank and particle size for three different coals. Additional conveyor belt work included natural gamma radioactivity coupled with microwave attenuation to determine, and correct for both moisture and mineral matter [Prieto-Fernandez et al., 2006]. Microwave energy (based on the reflected power) has also been used to determine coal-flow out of a pulveriser. The mass of coal in an air-blown coal line is difficult to determine thus microwave reflection provides a real-time continuous monitoring ability to aid optimisation of combustion systems [Blankinship, 2004].

Beary [1988] compared room temperature vacuum drying for 24 hours against microwave drying for 8 min, examining repeatability and direct value comparison. This particular microwave approach resulted in a lower moisture loss (1.03% compared with 1.26% in the vacuum oven) and greater standard deviation (0.07% compared with 0.02%). Unsworth et al. examined water forms by comparing NMR and microwave attenuation comparison for water forms [Unsworth et al., 1988]. With the microwave application they were exploiting the difference in microwave absorption between mobile (greater microwave energy uptake) and less mobile forms. By increasing the moisture content there was a clear distinction between bound and total moisture content. The response of individual macerals has also been investigated using microwaves [Slowik and Wieckwski, 2003].

For small samples a high-resolution (0.01 mg) thermogravimetric analyser (~20 g sample size) housed within a multimode cavity aimed at allowing larger sample sizes while maintaining even heating [Parkes and Williams, 2005]. Microwave assisted digestion of coal and coal fly ash has also been shown to be quicker than conventional heating techniques [Srogi, 2007], although often direct comparisons are not straightforward, particularly when only measuring bulk temperatures of fluids. Selective heating of the carbon or moisture phases during microwave heating can mean that higher temperatures exist in certain areas of the sample, whilst the bulk temperature is recorded to be significantly lower [Zhang and Hayward, 2006].

DISCUSSION

Coals as bulk materials are low to medium microwave absorbers. In low-rank coals it is the moisture content that is the major absorbing phase. As rank increases, the moisture content decreases and the dielectric properties of the organic component of coal increase, leading to an increase in microwave absorption by the organic component of the coal. Pyrite is a medium microwave absorber, and so is likely to contribute to the dielectric properties of some coals. Therefore coal can be selectively heated, and the components that are selectively heated vary depending on coal rank, moisture and mineral matter content and composition. Some coal microwave applications take advantage of this selective heating potential, whereas others use the volumetric heating property of microwaves to achieve rapid heating of a reaction mixture. Coke making with microwaves uses the changing dielectric properties of coal with temperature to induce thermal runaway. Table II summarizes the areas in which microwave coal processing has been researched for specific industrial applications. It gives the proposed mechanism by which microwaves are perceived to act in each process, states whether the experimental evidence supports the proposed mechanism, and recommends actions that would be required to either establish the benefits of microwave processing over other methods or, if that is already established, what the next logical

Table II. Summary of state of the art of microwave coal processing.

Application	Proposed mechanism	Outcome	Recommendation
Pyrite Removal	Selective heating of pyrite promotes desired reactions.	Not proven – advantage of microwave heating over conventional heating has not been demonstrated.	Need to confirm whether microwave heating has advantage over conventional heating.
Enhanced dissolution of impurities.	Volumetric heating reduces reaction time.	Proven - reduced heating time due to bulk heating.	Only advantage is reduced heating time – consider whether this is a driving factor for process development before proceeding.
Drying (for coal drying, or pretreatment for liquefaction and flotation).	Selective heating of water Reduced drying times.	Proven - but efficiency gains over conventional heating not demonstrated.	Economic analysis versus other drying methods and consideration of safety issues required.
Grindability	Rapid selective heating induces stress fractures.	Proven – high power density treatment for short time mean that the process could operate at industrially relevant residence times.	Scale up to enable optimization and economic assessment recommended.
Coke making.	Thermal runaway as coal aromatizes (increasing its dielectric properties).	Proven – has potential to reduce coking times by an order of magnitude and works on coals that are not suitable for conventional coking.	Further work to optimize process indicated.
Liquefaction	Microwave interactions with coal change reaction products.	Not proven – the differences in reaction products between conventional heating and microwave heating are caused by differences in kinetics resulting from different temperature profiles.	Rapid microwave heating may improve selectivity and yields. Further studies taking dielectric properties of coal, solvents and catalyst required.
Enhancing fluid-flow in coal beds.	Rapid selective heating induces stress fractures.	Proven – stresses generated by superheated steam.	Scale up of experiments required to assess potential.
Analytical techniques.	Based on knowledge of dielectric properties of different sample component.	Proven – works in various applications.	New applications may well follow the successes already in use.

step in development of the process would be. Where it is unclear whether selective heating has real advantages in terms of process effectiveness and efficiency (for instance in pyrite removal and coal drying), experiments designed to make direct comparisons between microwave heating and conventional heating are required. Where selective heating does not occur (for instance, as the result of addition of microwave receptors, or where the solvent has higher dielectric properties than the coal), the only advantage is in rapid volumetric heating; therefore careful consideration of whether this would justify the extra complexity and potentially increased energy requirements compared with conventional heating is required before further development is undertaken. The next step would then be to design further experiments that take into account the dielectric properties of all components of the system and how they change with temperature. The use of microwave receptors should be very carefully considered. If heating is not sufficient without the use of receptors, the electromagnetic design of the experiment should be revisited, as it is possible that the application of higher electric fields would enable heating without the addition of microwave receptors. Where selective heating has been demonstrated to offer real advantages (for instance in improving grindability), scale-up and optimization of the process is recommended to establish whether the process is economically and practically viable. Likewise, in the case of coke-making, which potentially represents a step change in the coke making process, further work to optimize and scale up the process is indicated.

The authors feel that it is worth noting a common misconception that has led to incorrect interpretation of results in some of the papers reviewed here. Microwaves do not cause unique reactions, i.e. there is no 'microwave effect', the addition of microwave receptors cannot 'increase the interaction between microwaves and coal'; any differences in chemical reactions taking place is caused by different temperature and pressure profiles affecting the reaction kinetics.

The importance of a multi-disciplinary approach in the design and operation of microwave processes cannot be stressed enough. Detailed understanding of dielectric properties of all process components and how they change under processing conditions is necessary. Design of a tailored microwave cavity means that treatment times can be shortened with the application of high electric fields, potentially achieving the desired effect without collateral damage to the sample. The ability to measure the absorbed power, and knowledge of the field patterns in the microwave cavity and how they are affected by the load, enable better understanding and consequently aid in process optimization.

The issues of scale-up are not trivial. The inevitably changing dielectric properties of the load pose challenges such as difficulties with impedance matching, thermal runaway and changing penetration depth. Scale-up often means operating at lower frequencies than were used at lab scale, meaning that the system performs differently. Moving to a larger cavity, potentially from single mode to multimode, means that the field pattern will change. Electromagnetic modelling is invaluable in this process. However, at the time of writing, the reality is that due to the scale of most industrial coal processing systems and the lack of availability of microwave hardware at power levels of above 100 kW, commercial applications of microwaves for coal processing are still some if not many years away. It is clear that there are some interesting applications which, from a scientific point of view at least, offer some potential to improve process efficiency or allow exploitation of different and potentially cheaper coal types through microwave upgrading. Whilst it is possible to develop microwave power to the megawatt level required, it is going to need a very strong value proposition coupled with an organization with high acceptance of risk to do so. Ultimately, the availability of high power microwave equipment able to work effectively in dirty, harsh environments is going to be the limiting step in the commercialisation of these opportunities.

CONCLUSION

Microwaves have been evaluated to assist with mining, beneficiation, drying, mineral liberation, liquefaction, improved grindability, coking and analytical techniques. Some of these processes, notably coke making, have been shown to work at laboratory scale, and to provide distinct advantages over conventional heating. Those processes have been identified and recommendations for future development have been given. Other processes were found to need further work to elucidate heating mechanisms and demonstrate whether microwaves really did offer potential benefits over other heating processes. In general, the success of microwave systems in industry has been through careful measurement of the dielectric properties of the target materials, a thorough understanding of the heating mechanisms, and the design of an appropriate cavity to ensure optimized delivery of the microwaves. We conclude that whilst there are some interesting applications from a scientific point of view, a very strong value proposition coupled with an organization with high acceptance of risk would be required to develop high power microwave equipment able to work effectively in dirty, harsh environments.

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