

Highly Selective Microwave Decomposition of Plastic Waste

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ABSTRACT

Growing amounts of plastic waste material pollute the planet contributing to a global ecological and environmental crisis. Common hydrocarbon-based plastic materials do not quickly or safely biodegrade, but their high hydrogen and carbon contents present an opportunity for extraction of valuable materials. Of the potential materials that could be produced, two of the most interesting are hydrogen gas and carbon nanotubes, which themselves could be used for a range of useful applications such as clean energy generation, improved battery systems and biomedical applications.

This thesis presents an investigation into the use of microwave heating to rapidly produce valuable products from waste plastic material. Microwave heating offers benefits compared to conventional methods including rapid heating and material selectivity. In particular, the use of the magnetic field of a microwave resonant cavity is explored for its potential to be even more rapid and selective even when compared to standard microwave dielectric heating mechanisms. With relatively few materials that can be effectively heated by a high-frequency magnetic field, the useful energy can be more effectively directed into a chosen catalyst, increasing efficiency and maximum temperatures.

Cost effective and abundant iron oxide powders are chosen for the core exploration. These are magnetite (Fe_3O_4) and haematite (Fe_2O_3) and are characterised using microwave cavity perturbation techniques to determine their complex permeability and permittivity. This is performed across a range of frequencies and at elevated temperatures up to 198 °C to provide a detailed electromagnetic profile and investigate potential frequency and temperature dependencies. Practical demonstrations of microwave magnetic heating are performed, illustrating the nature of selective heating.

Magnetite is assessed for its suitability as a catalyst for rapid microwave-assisted plastic decomposition, showing rapid heating potential to temperatures above the thermal decomposition requirements of common household plastics ($> 620\text{ }^{\circ}\text{C}$). This is achieved with limited power inputs typically under 100 Watts. This heating technique is applied to mixtures of magnetite and common plastics, focusing on polyethylene.

Rapid decomposition of plastics was achieved with produced gaseous mixtures and solid residues analysed. This revealed limited hydrogen content and the most significant quantities consisting of alkane hydrocarbons including methane, ethane and propane. Analysis of solid residues revealed frequent reduction of magnetite to wüstite (FeO) and iron (Fe) which was theorised to be enabled by available hydrogen or carbon monoxide. No crystalline carbonaceous materials were detected.

Microwave magnetic heating has the potential to be a useful tool for a range of uses across fields of catalysis, chemical synthesis, and material treatment, including for the application of rapid plastic decomposition. This work demonstrates that magnetically-driven microwave heating enables selective, low-power catalytic decomposition pathways distinct from conventional dielectric microwave approaches.

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ABBREVIATIONS

AC	Alternating current
CNTs	Carbon nanotubes
DC	Direct current
EM	Electromagnetic
FEM	Finite element modelling
FID	Flame ionization detector
GC	Gas chromatography
GHGs	Greenhouse gases
IR	Infrared
LWIR	Long wave infrared
MCP	Microwave cavity perturbation
MW	Microwave
PA	Power amplifier
PE	Polyethylene
PET	Polyethylene terephthalate
PMA	Portable microwave applicator
PP	Polypropylene
PS	Polystyrene
PTFE	Polytetrafluoroethylene
RF	Radio frequency
RTD	Resistance temperature detector
SEM	Scanning electron microscopy
SWIR	Short wave infrared
TCD	Thermal conductivity detector
TE	Transverse electric
TEM	Transverse electromagnetic
TM	Transverse magnetic
VNA	Vector network analyser
XRD	X-ray diffraction

PHYSICAL CONSTANTS

Permeability of Free Space	μ_0	$1.257 \cdot 10^{-6}$	H m ⁻¹
Permittivity of Free Space	ϵ_0	$8.854 \cdot 10^{-12}$	F m ⁻¹
Speed of Light	c	$2.998 \cdot 10^8$	m s ⁻¹

COMMON UNITS

GHz	gigahertz
MHz	megahertz
kHz	kilohertz
°C	degrees Celsius
K	degrees Kelvin
s	seconds
min	minutes
m	meters
mm	millimetres
µm	micrometres
g	grams
kg	kilogram
mL	millilitres
W	Watts
kW	kilowatts
F	Farads
H	Henries
S	Siemens
dB	decibel
dBm	decibel-milliwatt
kJ	kilojoules
MJ	megajoules
mol	moles
Mt	million tons

Chapter 1

1 INTRODUCTION AND MOTIVATION

1.1 MOTIVATION

1.1.1 PLASTIC POLLUTION

The current level of plastic pollution constitutes an environmental crisis. The total amount of plastics humans have produced since the beginning of their mass production in the 1950s exceeds 9 billion tonnes, and around 75 % of that has ended up dumped in landfill or marine environments [1]. Plastic pollutants threaten both human and animal health directly and also put many ecosystems at severe risk of collapse [2]. Along with human-induced climate change, this is one of the most pressing global environmental issues that requires significant attention from the scientific community. This issue was identified many years ago, but as plastic production continues to grow and global recycling measures remain insufficient, we must develop new and more efficient ways of dealing with existing and future plastic waste. One method of removing plastic waste that is currently employed is incineration, which sometimes includes energy recovery to extract energy intrinsic to the plastic. However, incineration of plastic waste produces greenhouse gases (GHGs) [3][4] such as carbon dioxide which exacerbate the issue of climate change.

As many plastics are derived from hydrocarbon sources, they contain long chains of carbon and hydrogen atoms. Recently there have been investigations into extracting energy or useful products based on this knowledge, as well as processing plastic materials using microwave energy [5][6][7][8]. Many studies also report success in extracting value from plastics with the use of microwave treatment, producing high purity

hydrogen, carbon nanotubes, and hydrocarbon fuels [9][10][11][12]. These ideas are key to this work as they present promising results in which plastics can be converted into useful clean fuel sources such as hydrogen for fuel cells while producing negligible amounts of GHGs. The ability to produce valuable materials, including a source of clean energy, from abundant waste materials would be an incredibly important development that could benefit a great number of people.

1.1.2 SELECTIVE MICROWAVE HEATING

To achieve the chemical degradation and decomposition of plastic material microwave (MW) heating will be employed. Microwave heating has a number of benefits when compared to conventional heating; it is much more rapid and provides more uniform heating of small particles as it is volumetric [13][14][15]. Perhaps the most important characteristic of MW heating in this application is that it is selective. This means it will only be absorbed by and therefore only heat particular substances, depending on their electric and magnetic characteristics. For example, water is a substance with a significant electric dipole moment, meaning it can be heated strongly by an oscillating electric field [16]. A core aim of this work is to use an intense magnetic field to cause rapid heating only in a magnetically susceptible catalyst material and not the plastic reactant. The rapid heating in the catalyst will then cause heat transfer to adjacent plastic pieces. The plastic will then reach the necessary temperature for degradation, rapidly degrading into useful products.

A key difference between this work and existing works in the literature [9][10][11][12] is the focus on the use of the magnetic field in the electromagnetic (EM) radiation. Many other microwave studies have used primarily regions of intense electric field [17][18][19], or even multimode solutions such as a domestic microwave oven [20][21] but far fewer studies have utilised the potential of regions of intense magnetic field [22][23]. The magnetic field combined with a suitable catalyst material

could provide much greater selectivity in heating processes when compared to microwave electric field heating, and potentially greater energy efficiency as a result. This is because far fewer materials have a significant magnetic permeability (loss) value than those which have significant dielectric permittivity values. This is further compounded by the use of microwave frequencies of the order of a few GHz, where fewer materials are considered to be magnetic.

1.1.3 GENERATING VALUABLE PRODUCTS

As the global population increases, the demand for energy much like plastics, is higher than ever before and continues to increase. Most of the world's energy still comes from greenhouse-gas-emitting sources; coal, oil and natural gas [24]. Shown in Figure 1.1 [25] is the increasing energy generation since 2000 and the contributions from each source type. Fossil fuel sources still provided around 60 % of the world's energy in 2024. Implementation of renewable energy generation is however increasing, with increasing proportions of electricity being generated by wind and solar energy especially. Renewables are seeing the greatest use

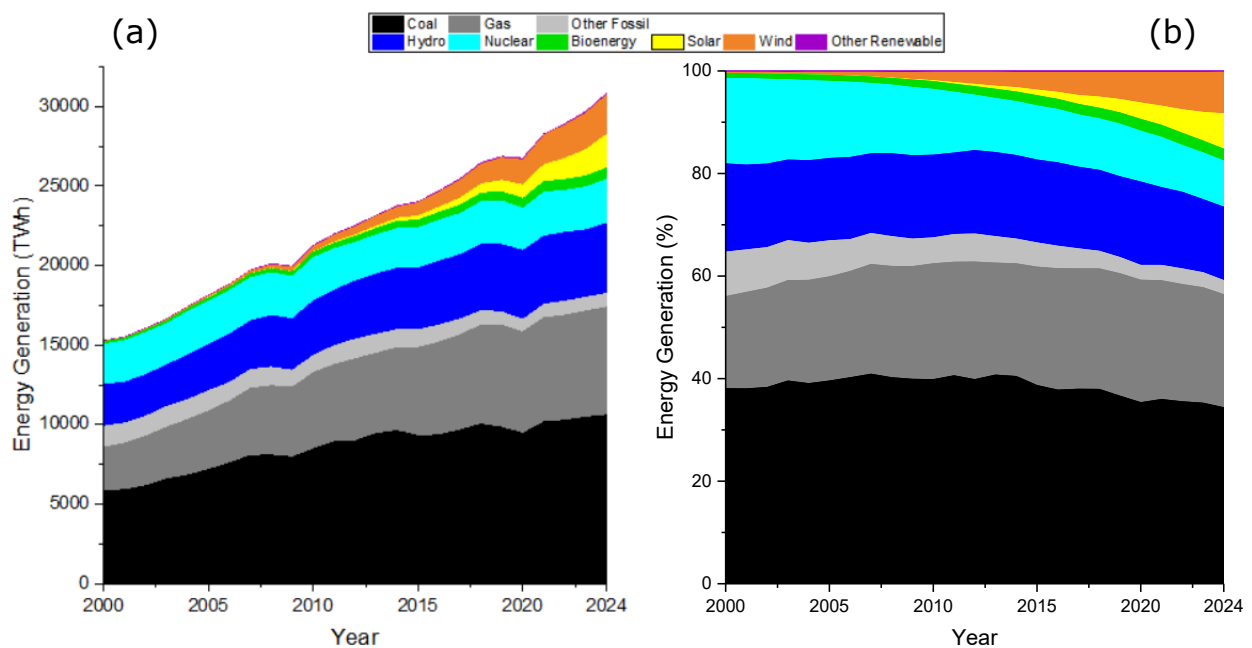


Figure 1.1 – World energy generation 2000-2024 by source shown in (a) TWh and (b) percentage of total energy generation per year [25]

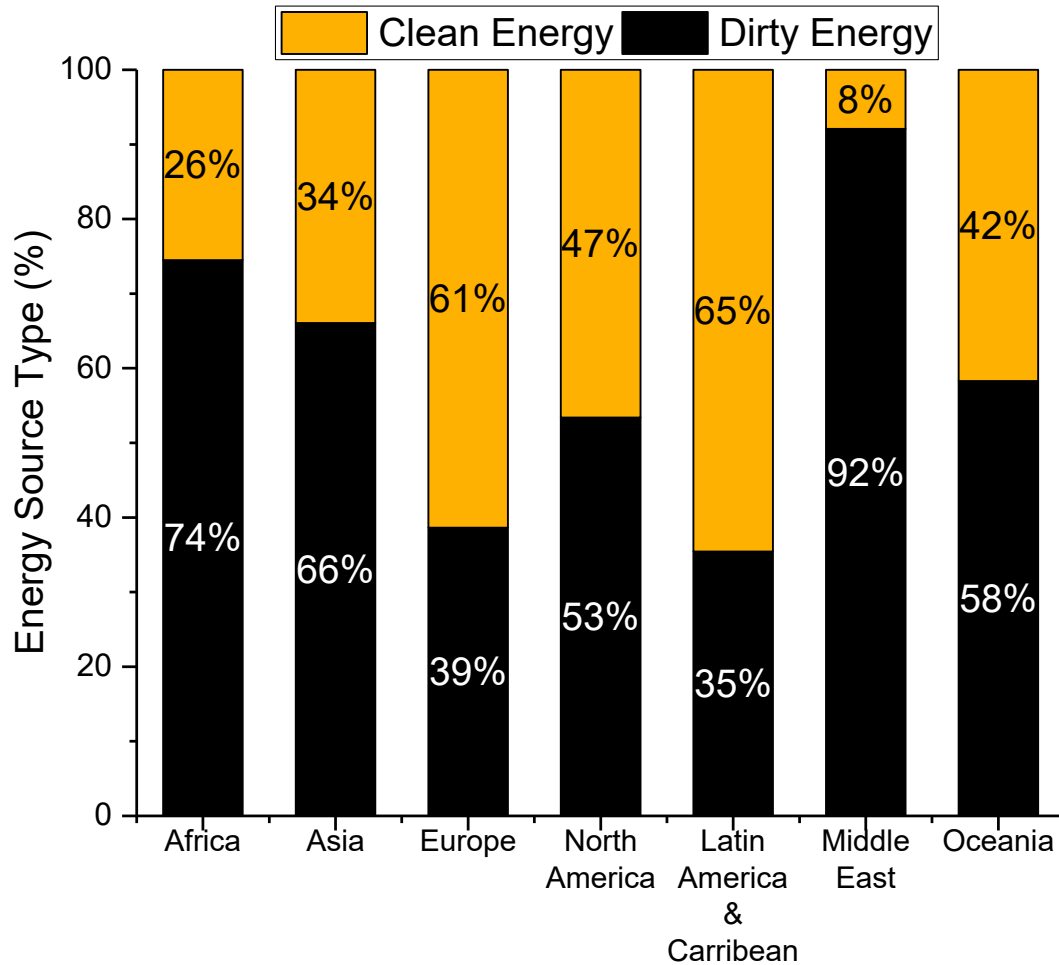


Figure 1.2 – Clean and dirty energy generation in 2024 by region [25]

across South and Central America, Europe, North America, and in the Asia-Pacific region. Figure 1.2 [25] shows the energy generation in 2024 split by source type into clean and dirty energy with clean energy being all renewables, hydro, bioenergy and nuclear, and dirty energy being all fossil fuel sources emitting significant greenhouse gases. Even in those regions with the greatest adoption of renewable energy generation methods there are still significant proportions of energy generation from non-renewable sources which produce harmful emissions. Carbon emissions are still too great to meet key targets concerning climate change, such as the Paris Agreement [26]. One of the biggest obstacles to further clean-energy adoption is the knowledge and advancement of relevant technologies to make them practically feasible, financially viable and economically attractive for those with the resources to invest in them.

The necessity for greater investment and more innovation in low-carbon and carbon-neutral energy generation sources is obvious.

Hydrogen as a fuel exhibits a high gravimetric energy density, much higher than that of common fossil fuels. Hydrogen contains approximately 120 MJ/kg while natural gas has 54 MJ/kg, petrol 47 MJ/kg and coal has less than 35 MJ/kg [27][28][29][30]. As hydrogen is a chemically simple fuel the only products from a fuel cell are water, heat and electricity. Hydrogen fuel seems like a promising alternative to fossil fuel systems but one of the greatest difficulties in large-scale implementation is initial generation of the hydrogen.

Hydrogen is produced on an industrial scale from a number of sources. The primary sources are derived from fossil fuels, primarily natural gas and coal [31]. Unfortunately, less than 1 % of hydrogen generated in 2024 was achieved using low-emission technologies including renewable-powered water electrolysis [32]. Most hydrogen production comes from natural gas in the form of methane steam reforming [33] which produces carbon monoxide as a by-product.

The potential to produce carbon nanotubes (CNTs) is exciting. CNTs have elicited great interest in both academic and industrial settings. They have been reported to have excellent electrical, thermal and mechanical properties that lend themselves well to a broad range of applications. These include but are not limited to battery materials, wearable technology, flexible electronics and highly absorbing microwave materials [34][35].

The use of consumer plastic waste to generate high-purity hydrogen and useful carbon-based materials could tackle two environmental issues simultaneously. While diverting plastics from potential landfill or incineration, this method could also produce an alternative hydrogen generation stream. This could potentially make energy generation from

hydrogen fuel a more appealing option, environmentally, practically and financially.

1.2 BACKGROUND

1.2.1 MICROWAVE HEATING

Microwaves are a type of electromagnetic radiation like radio waves, X-rays or visible light. They have a frequency range higher than radio waves but lower than infrared light in the range 300 MHz to 300 GHz. Microwave heating has been used domestically and industrially for many decades and is well established as having certain advantages over conventional heating methods. Microwave heating is rapid, volumetric, selective and non-contact [36]. These advantages lead to other benefits depending on the application such as reduced processing times, greater product yields and better overall energy efficiency.

One of the most important attributes of microwave heating for this work is the selectivity of heating. Using conventional heating methods such as conduction or convection typically involves heating materials other than the reactants. This can include the air inside a reaction vessel or the vessel itself. Heating these materials is representative of wasted energy and is typically undesirable. Microwaves heat materials by interacting directly with them and causing changes which induce heating within the material. This is the basic operating principle of domestic microwave ovens which heat food primarily by heating the water content. Water molecules are polar, meaning that they are electrically asymmetrical having a positive and negative “end”. This polarity means the molecule reacts to an external electric field as the charged ends attempt to align with the opposite charges of the field. This causes molecules to rotate and if an alternating field with sufficient frequency is used the molecular friction dissipates energy as heat [37]. This is an example of dielectric heating.

Dielectric heating is a selective process as materials like water will heat well but materials like quartz are effectively transparent to microwaves and therefore do not absorb microwave energy. The list of materials able to be heated via dielectric heating is still long, so one method of increasing selectivity further is to instead use the microwave magnetic field to induce material heating. Far fewer materials can be heated by magnetic field interactions. For example, while water is strongly heated by electric field fluctuations it has no magnetic properties and thus the magnetic field fluctuations will have no impact on it. Primarily using the magnetic field for material heating allows greater control over the reaction as the vast majority of absorbed energy will be absorbed by a suitably chosen magnetically stimulated susceptor material.

This work focuses on the utilisation of the magnetic field to heat materials, particularly for applications where they may be mixed with other non-magnetic materials. Like other microwave heating processes this should be rapid, volumetric and selective, and its selectivity should be increased when compared to the common electric-only usage. Microwave heating experimentation is discussed largely in Chapter 5, with application-specific usage shown in relation to plastic degradation in Chapter 6.

1.2.2 MICROWAVE CHARACTERISATION

Microwave cavity perturbation techniques were developed in the mid-20th century [38][39] and have since been used extensively in the fields of microwave engineering, chemistry, physics and materials science [40][41][42][43][44][45]. Under a resonant condition a cavity is very sensitive to changes in the filling material or shape of the cavity structure. By introducing a very small shape or material perturbation, the well-defined electromagnetic fields do not change significantly from their unperturbed state. Through very small changes in the resonant frequency and Q -factor (a dimensionless figure of merit representing the energy

storage efficiency of a resonant system) of the cavity, the electromagnetic qualities of the introduced material can be calculated. These are known as the material's permeability and permittivity.

It can be very useful to characterise materials this way as they give an indication of how a material will respond to electromagnetic radiation, for example when heated with microwave radiation. Cataloguing the permittivity and permeability of materials can be useful for assessing their suitability for all manner of applications. These qualities can vary with frequency, temperature, chemical state or particle morphology.

Materials will be characterised using the microwave cavity perturbation method in Chapter 4 to assess their permeability and permittivity across frequency and temperature ranges. Details of this method and supporting fundamental theory are found in Chapter 3 and 4.

1.2.3 MICROWAVE CATALYSIS

Microwave heating is a multidisciplinary tool used widely by fields other than microwave or electrical engineering. A field which often utilises microwaves outside of engineering is chemistry where microwaves can be used for one or more of their qualities including selective heating, rapid heating rates, high energy density or higher reaction yields. Some examples of microwaves used specifically for catalysis include natural gas dehydroaromatisation [46], methane reforming [47], production of syngas [48], conversion of ethane [49], ammonia synthesis [50], desulfurisation [51][52], dechlorination of PVC [8] and pyrolysis [21][53][54]. As microwave catalysis is broadly applicable it is attractive for researchers and industry alike to apply to new problems or improve existing processes.

When performing catalysis it is important to choose a catalyst material suitable for the application. For microwave catalysis this largely involves considering the permittivity and permeability of a substance, especially the complex part of each which indicates how lossy that material is and

thus how well it will heat in response to microwave energy. Materials can be selected primarily for their role as an effective microwave susceptor, or as a useful chemical catalyst, or a combination of both. A common type of susceptor used in microwave reactions driven by dielectric heating is carbon-based materials like graphene, activated carbon or carbon nanotubes. These materials have relatively high dielectric loss values so they will absorb microwaves well and heat up, rapidly providing lots of heat energy for the reactants.

1.2.4 PLASTIC PRODUCTION, RECYCLING AND DISPOSAL

Plastics are a broad category of materials that vary wildly in properties and chemical structure. The primary focus of this work is those plastics which present the greatest problem in the environment. The most commonly produced plastics are high-density polyethylene (HD(PE)), low-density polyethylene (LD(PE)), polyethylene terephthalate (PET) and polypropylene (PP) [55]. These plastics are incredibly useful as they offer lightweight, cost-effective solutions for all manner of applications but they do not safely degrade in landfills or marine environments. Over 63 % of the cumulative global plastic production as of 2018 consisted of these four plastic types [56]. These plastics only contain carbon, hydrogen, and in the case of PET, oxygen atoms as part of their chemical structure. The polymer structure diagrams are shown in Figure 1.3.

It is estimated that over 80 % of all plastic has accumulated in soil and oceans, as much as 9.7 Mt per year [57]. The composition of this total waste figure includes 3.2 Mt/yr of polyethylene and 1.3 Mt/yr of polypropylene which are some of the biggest contributing polymer types to accumulated waste. This work intends to focus on polyethylene when attempting plastic decomposition. Other types of common plastics will also be investigated. Tackling the most common plastics is important to maximise the environmental impact and be the most applicable to any real-world applications.

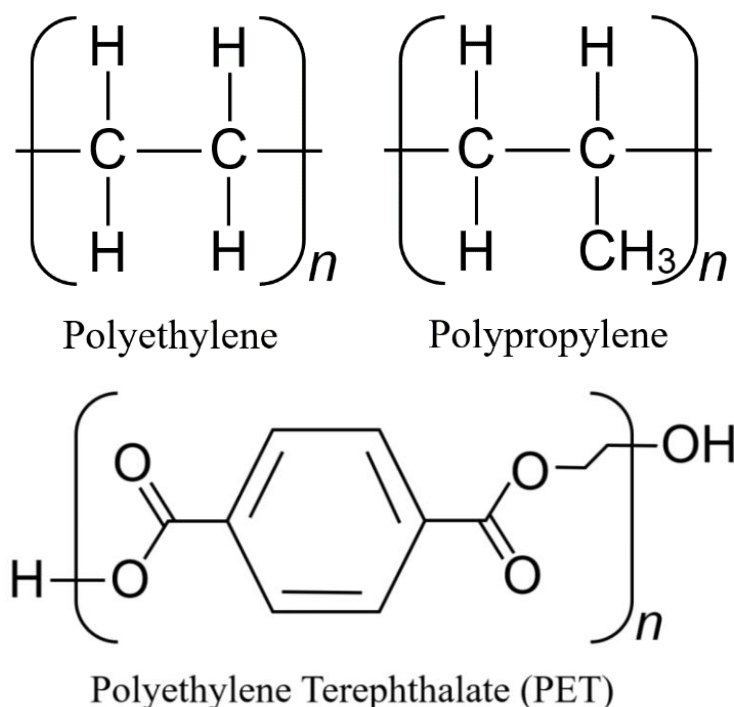


Figure 1.3 – Chemical structures of common polymers polyethylene, polypropylene and polyethylene terephthalate

The degradation of these plastics is chemical rather than mechanical in nature. Mechanical degradation means to break plastics into smaller and smaller pieces through crushing, ripping and cutting. This occurs in current recycling processes to create pellets that can be formed into new materials such as bottles or packaging trays. Chemical degradation means to break up the plastic on a molecular and atomic level by separating hydrogen-carbon bonds. If this can be achieved under the correct conditions, it could produce valuable products such as pure hydrogen and carbon while minimising the production of harmful by-products like carbon dioxide. This would mean extracting value from hydrocarbon (fossil fuel) sources while decreasing or eliminating the effect on global warming.

Consumer plastics often contain additives other than the polymer itself. These can include but are not limited to pigments, stabilisers, plasticisers, flame retardants and other fillers. Some examples of particular chemicals found in consumer plastics include triethyl citrate ($\text{C}_{12}\text{H}_{20}\text{O}_7$), octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate ($\text{C}_{35}\text{H}_{62}\text{O}_3$), and 2-

Hydroxy-4-methoxybenzophenone ($C_{14}H_{12}O_3$) [58]. Alongside the more common organic additives, inorganic additives can also form a significant part of a post-consumer plastic's composition [59]. These additional chemicals can change the electromagnetic response of the plastics and also the composition of any products formed from the destruction or degradation of the plastics.

1.3 PROJECT AIMS

A brief introduction has been provided here which discusses the key motivating factors for pursuing this work. These are:

- the growing global environmental issues associated with plastic waste
- the vast quantities of plastic waste that currently exist, and the increasing amounts that are being produced which lead to more waste
- common plastics being a potential valuable source of hydrogen and carbon
- renewable energy becoming ever more crucial in modern infrastructure, with clean hydrogen-based energy generation an emerging technology
- the applicability of microwave heating for rapid achievement of elevated temperatures
- the selective nature of microwave heating, particularly in magnetic fields, which allows energy to be targeted at specific materials, potentially increasing energy efficiency

These factors all contributed to the decision to experiment with microwave magnetic materials and assess their suitability as effective microwave catalysts for the application of plastic decomposition.

The targeted aims of this work are:

1. Investigate common magnetic powder materials in iron oxides (Fe_3O_4 -Magnetite, Fe_2O_3 -Haematite) using microwave cavity perturbation techniques to determine their electromagnetic properties across a range of frequencies and temperatures.
2. Experiment with these powders using mono-mode magnetically-driven microwave heating with low power levels assessing their capability to rapidly reach sufficient temperatures to fully decompose plastic materials. Compare their response to electric field-driven heating.
3. Perform decomposition of polyethylene and other plastics using a suitable magnetic susceptor/catalyst to produce gaseous mixtures containing significant quantities of hydrogen gas and solid carbonaceous residual material i.e. high-value materials.

1.4 CHAPTER SUMMARIES

The following pages detail the progression made towards these aims, including details of methods and equipment used, presentation and discussion of relevant data and conclusions or lessons learned from experimentation. Included below are short summaries of each chapter provided for convenience of the reader.

Chapter 2 provides a literature review of iron oxides and their applicability in research and industry, as well as the mechanisms behind microwave heating using both magnetic and electric fields. Also discussed are the relevant works and options in plastic waste valorisation, with a key focus on the transformation of polyethylene into hydrogen gas and carbon nanotubes.

Chapter 3 provides detail on fundamental electromagnetic theory, working from Maxwell's equations through to the derivation of waveguide and cavity boundary conditions. Determination of cylindrical cavity frequency

and quality factor is shown alongside relevant resonant modes utilised later. This chapter concludes with discussion of *S*-parameters and signal bandwidth which are used to interact with cavities for measurement and heating, and assess their characteristics.

Chapter 4 shows experimental data obtained from microwave cavity perturbations of magnetite and haematite powders. Measurements of frequency and *Q* allow calculation of relative complex permeability and permittivity of both powders. Measurements are made across a range of frequencies and a temperature ramp from room temperature up to 198 °C. The construction of both specialised cavities used in the perturbations is explained, including their dimensions, relevant modes and associated frequencies, *Q*-factors, and geometric cavity scaling factors required for calculation. Details of other utilised equipment and a general procedure is also included.

Chapter 5 further studies magnetite and haematite using practical microwave heating equipment. Both magnetite and haematite are heated for short durations at low power levels to study the degree of microwave absorption they exhibit. The powders are heated concurrently to highlight the selective nature of microwave heating. Magnetite is further explored using increased power levels to achieve sufficient temperatures for catalysis applications and the decomposition of plastic. Dedicated sections are provided to discuss the importance of infrared pyrometry and its challenges and limitations which are relevant to microwave heating. Magnetite is heated using the magnetic field and the electric field to observe differences in its response with the final part of this chapter illustrating the ability of magnetite to be heated repeatedly in an inert atmosphere.

Chapter 6 discusses the application of magnetite as a microwave magnetic catalyst for the one-step decomposition of common plastic materials. High-density polyethylene is the primary polymer in focus as it represents a common plastic with a simple molecular structure that can

take significant energy to break down. The study of PE decomposition provides an excellent benchmark test for the applicability of the microwave catalysis process. Decomposition is performed and gaseous and solid products analysed. This is further explored with other plastic types such as PP, PET and PS.

Chapter 7 concludes this thesis with discussions of the conclusions drawn from earlier chapters, limitations of the work and potential for future work. This includes both small experimental work that expands on that performed here and larger projects that may be tackled as individual works.

Chapter 2

2 LITERATURE REVIEW

2.1 APPLICABILITY OF IRON OXIDES

Iron and its various oxides and alloys are widely applicable for many different processes. Iron is one of the most abundant metals in the Earth's crust and has been used extensively for manufacture of tools and structures. Iron exists in many forms in nature with some of the most common being iron oxides. Common iron oxides include Fe_3O_4 (magnetite), $(\alpha\text{-})\text{Fe}_2\text{O}_3$ (haematite or hematite), $(\gamma\text{-})\text{Fe}_2\text{O}_3$ (maghemite) and FeO (wüstite). These are generally inexpensive, chemically stable and non-toxic with a wide range of applications such as pigmentation, cosmetic ingredients, steel production, water treatment, cancer treatment and more [60].

2.1.1 IRON OXIDES AS CATALYSTS

The most relevant applications of iron oxides to this work are those which utilise the magnetic properties or employ them as catalysts for chemical processes. Magnetite and haematite in particular have been studied extensively with uses as catalyst materials for wastewater treatment [61] photocatalysis [62], extraction of nitrate [63], methane oxidation [64], degradation of herbicides [65], oxidation of alcohols [66][67], oxidation and cracking of hydrocarbons [68][69][70] and generation of hydrogen from water (water splitting) [71][72].

These iron oxides are often investigated as potential catalysts for these reactions due to their chemical structure. Iron can easily move between oxidation states (e.g. Fe^{2+} and Fe^{3+}) and oxides typically have high surface areas for reactions to take place. This is also influenced heavily by

particle size; nanoparticles of iron oxides, particularly magnetite have seen detailed investigation over a range of applications such as magnetic resonance imaging [73], conversion of waste cooking oil to biodiesel [74], and photocatalytic degradation of textile dyes [75].

2.1.2 IRON OXIDES AS MICROWAVE SUSCEPTORS

Iron oxides are also used for their effective interactions with microwave radiation, performing well as microwave susceptors. Microwave heating can be used to heat rapidly and provides a path of efficient energy transfer to drive the initial heating of the susceptor particles. The microwave heating method can generate heat selectively at the microwave susceptor particles and not necessarily within the reactant particles, creating localised hot spots at the reactant-catalyst interface. Recent work has explored the creation of iron carbon composite materials where enhanced microwave absorption has been observed [35][76][77][78][79].

As with their uses as a typical chemical catalyst, iron oxides can also act as a microwave susceptor in many applications too. This is commonly driven by a microwave electric field source, especially in multidisciplinary work where microwave application equipment is used as an alternative method for supplying heat to a reaction. Magnetite in particular has interesting applicability with microwaves as it is one of the few materials which has an appreciable magnetic loss at microwave frequencies. This fact has been used for magnetic microwave hyperthermia for cancer screening and therapy [80][81][82], providing a method of selectively heating particular sites (tumours) to around 42-45 °C while minimising damage to healthy cell tissue.

Another valuable use of iron-based materials as microwave susceptors is in the decomposition of hydrocarbon sources to produce valuable products. Key research in this area has focused on production of both hydrogen gas as a clean energy source and carbon nanomaterials such as

CNTs for their value across many potential industrial and research sectors. This has been performed with hydrocarbon waxes and liquids [11][18] as well as biological sources [83]. Microwaves are often noted for their potential to enhance reaction metrics, such as yield or efficiency due to rapid and volumetric heating of particles, limiting the initiation of side reactions that may happen when using conventional heating methods.

Microwave heating of iron oxides has been used to significantly reduce energy input for existing reactions. For a water splitting reaction creating oxygen and hydrogen from water using a metal oxide composite in cycles of oxidation and redox, microwave heating of iron-based materials has been shown to significantly reduce the temperature required for generation of gaseous products [84]. Temperatures typically required for the reoxidation reaction are in excess of 1000 °C but this was achieved at only 478 °C, representing a significant reduction in input energy. Power consumption was also significantly reduced using microwave heating equipment based on reduced reaction time (30 min. microwave vs. 325 min. conventional heating), the selectivity of microwave heating, and the efficiency of equipment. Estimated values for energy consumption for the entire reaction were 0.07 kWh for the microwave method and 1.66 kWh for the conventional heating method, representing an estimated 95 % reduction in energy consumption.

2.2 ELECTROMAGNETIC LOSS MECHANISMS

2.2.1 MAGNETIC LOSS MECHANISMS

Magnetism arises in materials due to the motion of the negatively charged electrons, their orbitals, and spin. The movement of electrically charged particles creates a magnetic field and the organisation of atoms and collective magnetic moments generated by the electrons determine a material's bulk "level" of magnetism. Diamagnetic materials are those which have no net magnetic moment, typically because the electron

orbital shells are filled and there are no unpaired electrons, meaning the magnetic fields generated cancel each other out [85]. Quartz and water are both examples of this type of materials that we would typically consider “non-magnetic”. Paramagnetic materials are similar but may have unfilled orbitals or unpaired electrons with minimal net magnetic moment. Both diamagnetic and paramagnetic materials show weak repulsion or attraction in the presence of an applied external magnetic field but cannot maintain an independent field. Some metals such as chromium and titanium are considered paramagnetic.

When magnetic materials are discussed it primarily refers to ferromagnetic and ferrimagnetic materials. These are materials which have significant net magnetic moments and interactions between these moments. Ferromagnetic materials display parallel alignments of molecular magnetic dipoles meaning significant levels of magnetisation can be generated. The most famous and eponymous material displaying ferromagnetism is iron. Other common ferromagnetic materials include nickel and cobalt. Ferrimagnetic materials display antiparallel (parallel but in opposite directions) alignments of magnetic dipoles, with different magnitudes that then still result in a significant net magnetic moment. Magnetite is an example of a ferrimagnetic material in which oxygen ions form a cubic structure, with iron ions filling the gaps in between. The iron ions can be part of a tetrahedral (surrounded by 4 oxygen atoms) or octahedral site (surrounded by 6 oxygen atoms) and these two types of site form two antiparallel sublattices [85].

Another type of magnetism is antiferromagnetism. as the name would suggest it is very similar to ferromagnetism in the structure of particles and ions, but the antiparallel dipoles are typically equal in magnitude, resulting in zero net magnetic moment. If the alignment of electron spins is not exactly antiparallel this means they do not exactly cancel out and a small net moment can be observed. This is the case for haematite, a canted antiferromagnetic material.

An important dependence exhibited by all magnetic materials is that of temperature. As a material is heated, the thermal energy increases resulting in increased random motion and disordering of particles. At a certain point the thermal energy is great enough to disorder enough electron spins and reduce the net magnetic moment to zero [86]. The temperature at which this happens is known as the Curie temperature (T_C) and is material dependent. Above the Curie temperature a material will no longer display typical magnetic properties and effectively becomes paramagnetic.

There are a number of ways materials can exhibit loss from magnetic fields. These include hysteresis or eddy current losses, domain wall resonance, natural or broadband ferromagnetic resonance, as well as Brownian or Néel relaxation.

Hysteresis and loss from eddy currents are dominant loss mechanisms in highly conductive magnetic materials like iron. Eddy currents arise due to the resistance in materials like iron in response to a low frequency AC electric field. Hysteresis occurs due to friction between material impurities or domain walls when a magnetic field is applied [87]. As a material becomes magnetised and domains align there can then be more molecular friction and therefore heat generated when applying an opposing magnetic field that demagnetises the material. Both these mechanisms are prominent at low frequencies and are typically the concern of those dealing with high power systems and transformers. This is still relevant for small particles if they are sufficiently conducting but less so for those powders with lower conductivity, like oxides [88].

Domain wall resonance describes the regions of similarly aligned magnetic dipoles i.e. domains, which will rotate to align with an applied magnetic field. In a bulk material there will typically be many domains with different alignments which will have boundaries or walls between them [85]. Using a field which alternates at sufficient speed (frequency) there can be a lag introduced between the applied field and the domain

alignment which causes losses realised as heat. This is highly significant between 1 MHz and 1 GHz with significant loss still present above and below this range [89].

Brownian magnetic relaxation describes the motion in fluid-suspended magnetic nanoparticles when exposed to a magnetic field. An applied field will cause the whole particle to rotate to align with the field, rather than an internal domain. The viscosity of the suspension fluid is important as it will slow down the particle rotation and thus generate heat [90][91]. This typically shows maximal magnetic loss in the kHz to MHz range of AC frequencies.

Néel relaxation is similar but concerns the rotation of magnetic moments derived from electron spins. This mechanism is associated with the time taken to rotate the moment(s) without physically rotating the particle (as with Brownian relaxation). This occurs only in very small particles (nanometre-scale) at which point they can be described as superparamagnetic where only a single domain can be accommodated in the particle and it can undergo spontaneous magnetisation reversal [85]. Néel relaxation displays the greatest loss at frequencies in the MHz to GHz range, overlapping with the effects of domain wall resonance and ferromagnetic resonance [92][93].

Ferromagnetic resonance is when energy from an AC electromagnetic wave is absorbed by the resonating magnetic moments [92][94]. The magnetic moments undergo gyroscopic precession at the Larmor frequency [95] and when the applied magnetic field frequency matches this precession significant energy absorption can occur. The frequency range for ferromagnetic resonance is field-strength dependent but typically considered to be in the GHz range i.e. most microwave frequencies [92][93].

The complex permeability of magnetite has been investigated over a wide GHz frequency band in relation to particle size [98]. This demonstrates

the broadband ferromagnetic resonance peak of magnetite well, spanning many gigahertz and increasing in centre frequency with decreasing particle size. A sample of magnetite powder with sizes 38-62 μm has a peak in this resonant frequency at approximately 2.59 GHz. From 2 GHz upwards the particle size has little impact on the imaginary permeability (loss) of the particles, with the more influential factor being relative density. Values around 1.0 can be seen for frequencies near 2.45 GHz and relative densities between 45 and 55 %. For decreasing relative density (i.e. more air in the measurement) the permeability drops closer to 0.5 for relative densities around 20 %.

Relating these loss mechanisms to frequency is important for understanding what mechanisms we may or may not be utilising when heating magnetic particles. Shown in Figure 2.1 is an estimate of relative complex permeability behaviour over a wide range of frequencies [96].

For near-DC frequencies the losses from eddy current and hysteresis dominate. For frequencies around MHz to GHz Brownian and Néel

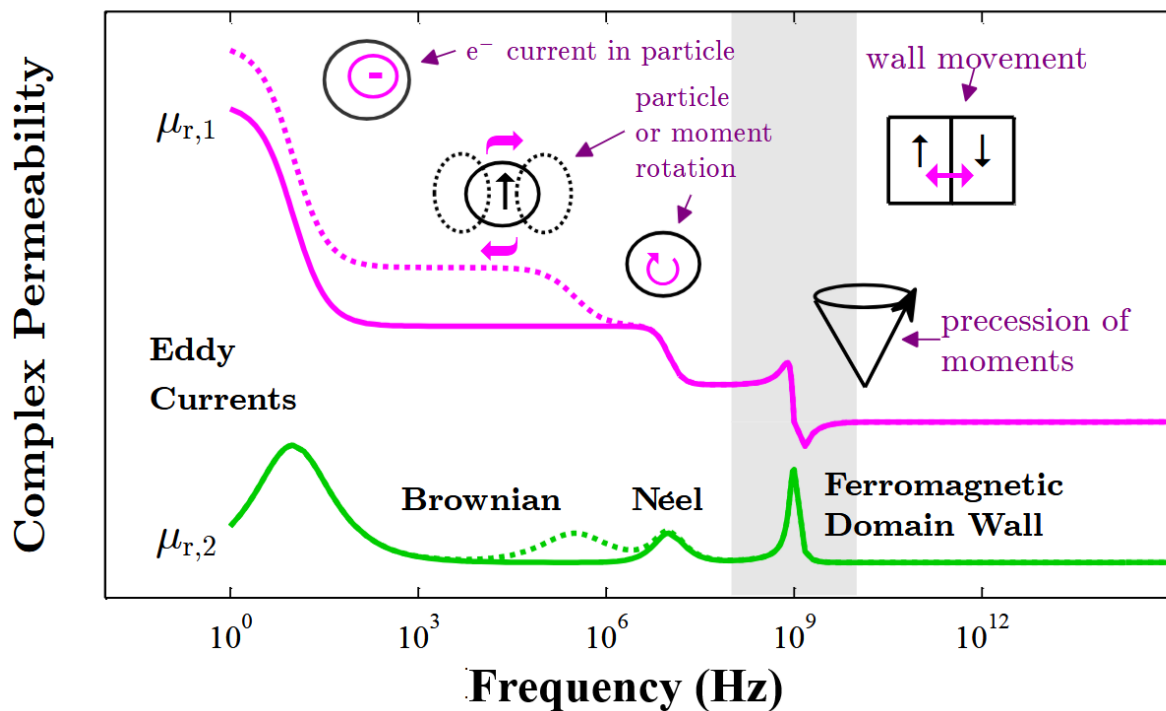


Figure 2.1 – Estimated frequency dependent relative complex permeability [97]. Reproduced from [96].

relaxation mechanisms are the most prominent, however these are generally concerned with very small particles (nano) or those in a fluid. At near-GHz and GHz frequencies i.e. microwaves the dominant loss mechanisms are domain wall rotation and ferromagnetic resonance. Given the materials of interest in this work are primarily metal oxides with relatively low conductivity and particle diameters much smaller than their skin depth at microwave frequencies, we can expect that even with low values of relative microwave loss (0.1) that significant heating will still be possible [88].

2.2.2 ELECTRONIC LOSS MECHANISMS

Materials also experience losses via interactions with electric fields. Losses can be sourced from conduction or material polarisation, which is related to the material permittivity, or dielectric constant. Like magnetic losses, there are a number of understood mechanisms by which electronic losses can be realised in a material. These include conductive or ohmic losses, space-charge polarisation, ionic or atomic polarisation, dipole rotation and electronic polarisation. These are all frequency-dependent mechanisms, with key frequency ranges where their loss contributions are most relevant [97].

Conductive losses are those that arise from the movement and interaction of charged particles (electrons and ions). In DC or low frequency AC electric fields the losses from the resistivity of the material are generally much larger than those introduced by any form of electronic polarisation. This is caused by electron collisions with the atomic lattice or impurities within the material and generates heat energy. In conductive materials like metals with lots of free electrons, an external electric field can become screened by the electrons. Using an alternating field will also induce a magnetic field and opposing electric field inside the conductor which pushes the electrons to the surface. This is known as the skin effect and increases with frequency i.e. the effect becomes stronger and the

region in which conduction can occur near the material surface, known as the skin depth, becomes smaller. Shrinking the region of conduction and thus the area requires the resistance to increase. As the skin depth decreases proportional to the inverse of the square root of frequency, the resistance increases proportional to the square root of frequency. Losses due to conduction therefore increase as frequency increases, but losses from other sources increase much faster or dominate more readily in other frequency ranges meaning the effect of conductive loss is primarily limited to low frequencies (near-DC or kHz).

Ionic polarisation happens only in ionic crystalline solids. Ions have a net charge so can be influenced directly by electromagnetic fields, even though the bulk material may have a net neutral charge. Taking a basic ionic compound of sodium chloride (NaCl) as an example, the positive sodium ions (anions) and negative chlorine ions (cations) form a cubic lattice held together by the mutual attraction of opposite electrically charged ions [86]. When an external electric field is applied to the ionic material the charged ions are displaced in opposite directions [99][100]. For an alternating field this displacement is constantly occurring, creating an oscillating motion. When the motion of these ions matches their natural resonant frequency, this causes the greatest difference between internal forces and the applied field, resulting in the greatest loss. When the field frequency increases too much the ions cannot react quickly enough to displace and loss is reduced [101]. This can also be called atomic polarisation, referencing the stretching of atoms themselves to give each individual atom a net electrical dipole. The peak loss for this mechanism occurs in the region of 10^{12} - 10^{13} Hz.

Electronic polarisation is mechanically similar to ionic polarisation, but occurring with smaller particles, namely the electron clouds or orbitals surrounding atoms. As it is a mechanism inherent to each atom it is a type of polarisation that happens to all materials, although it is generally weak in comparison to other mechanisms of electric loss. Atoms are in

essence a dipolar system with a positive nucleus and a cloud of surrounding negative electrons. By applying an electric field this can displace the electrons relative to the nucleus. Similarly to ionic polarisation, if an alternating field is used it can cause an oscillating or vibratory motion that, given the suitable frequency, can dissipate energy [97][100][101]. Electronic polarisation losses are maximised at higher frequencies than ionic polarisation due to the fact the electrons are less massive than whole atoms and thus can move quicker under a similar applied force, taking less time to respond to field changes. Electronic polarisation is most significant around 10^{15} Hz.

One of the most important electric loss mechanisms for microwave experimentation is that of dipole rotation, sometimes also called dipole polarisation or orientational polarisation. This is a loss mechanism which results from electrically asymmetrical molecules being exposed to an electric field. These molecules with a permanent dipole are normally randomly ordered due to thermal energy but will attempt to align with an applied electric field [97][101]. Molecular friction among the rotating molecules when exposed to an alternating electric field requires energy which is dissipated as heat. The classic example of a common polar molecule that demonstrates this process well is water. Dipole rotation is particularly significant around microwave frequencies (10^9 Hz) and as such is widely studied in microwave applications.

While water is a well-known microwave-absorbing material, it is often other materials with polarity which are more applicable for research, especially carbon-based materials with surface functional groups or defects that allow dipole polarisation to act on them and dissipate heat. These include graphene, carbon nanotubes and carbon fibres [102][103][104][105][106].

Included in Figure 2.2 is an estimate of complex relative permittivity behaviour over a wide range of frequencies, and the most relevant loss mechanism for each frequency region. At microwave frequencies (shaded)

the most relevant loss mechanism is dipolar rotation but there are significant contributions from the decay of low frequency conductivity losses and the atomic and electronic polarisation mechanisms [96].

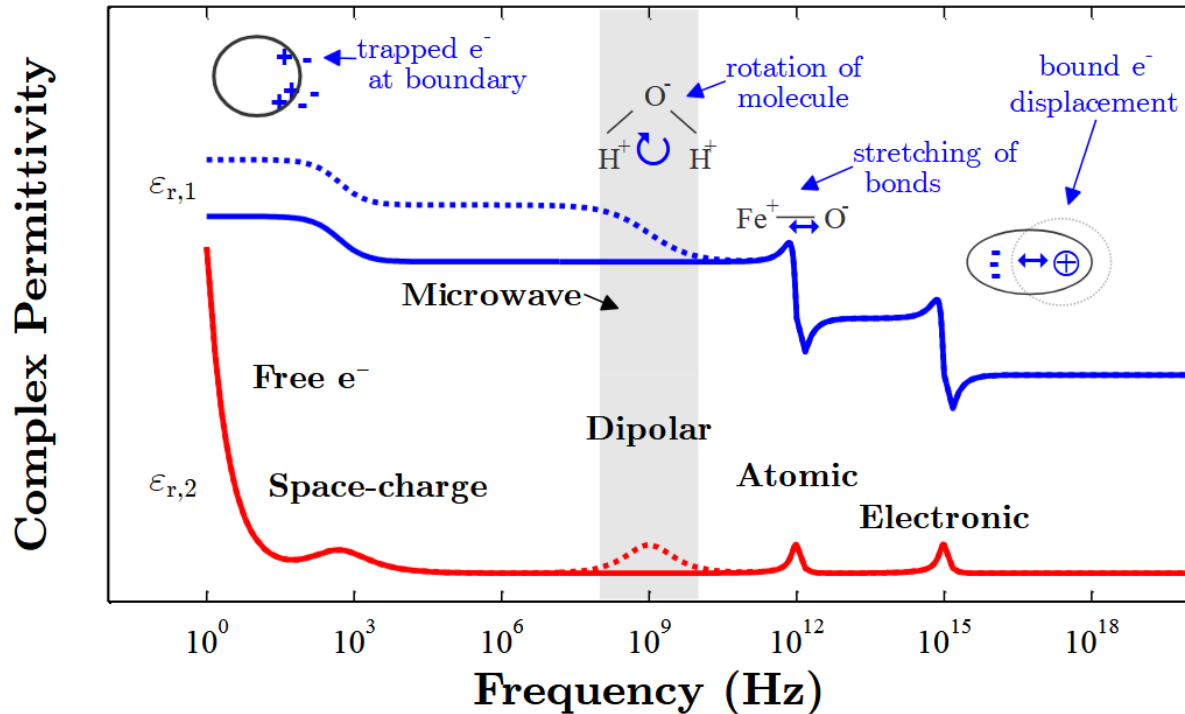


Figure 2.2 – Estimated complex relative permittivity behaviour over frequency. [97] Reproduced from [96]

2.3 PLASTIC WASTE TREATMENT

Plastic has only been produced for a relatively short time frame of less than 100 years, but the generated waste has recently become a mainstream societal concern. It is important to understand the context in which this work aims to address plastic waste and the other options and structures that currently exist.

This includes an overview of the hierarchy of plastic waste, what options are preferred and a more in-depth view of the potential applications of specialised tools like microwave-assisted pyrolysis.

2.3.1 PLASTIC WASTE HIERARCHY

One way of assessing and understanding the generation and fate of plastic material is through a waste hierarchy. This aims to graphically demonstrate the preferential order of actions taken to minimise waste or

its impact on the environment. Shown in Figure 2.3 is an example for a plastic waste hierarchy from [107].

This highlights the most preferred actions are those to reduce or avoid production of waste altogether, followed by reuse and then by recycling and finally recovery of basic materials or energy before landfill should be considered. Moving from the top of the hierarchy to the bottom represents a number of key factors including a product's life cycle and ideally, the volume of material that should be handled at each stage i.e. most material should be dealt with by avoidance and minimal material should be landfilled, thus reducing environmental impact. Elements higher up the hierarchy can be the most impactful but are often mobilised through societal factors, governments and legislation.

Another interesting development surrounding plastic waste research is the idea of a circular economy [107][108]. This is the idea that products or materials that would become waste can be returned to the economic

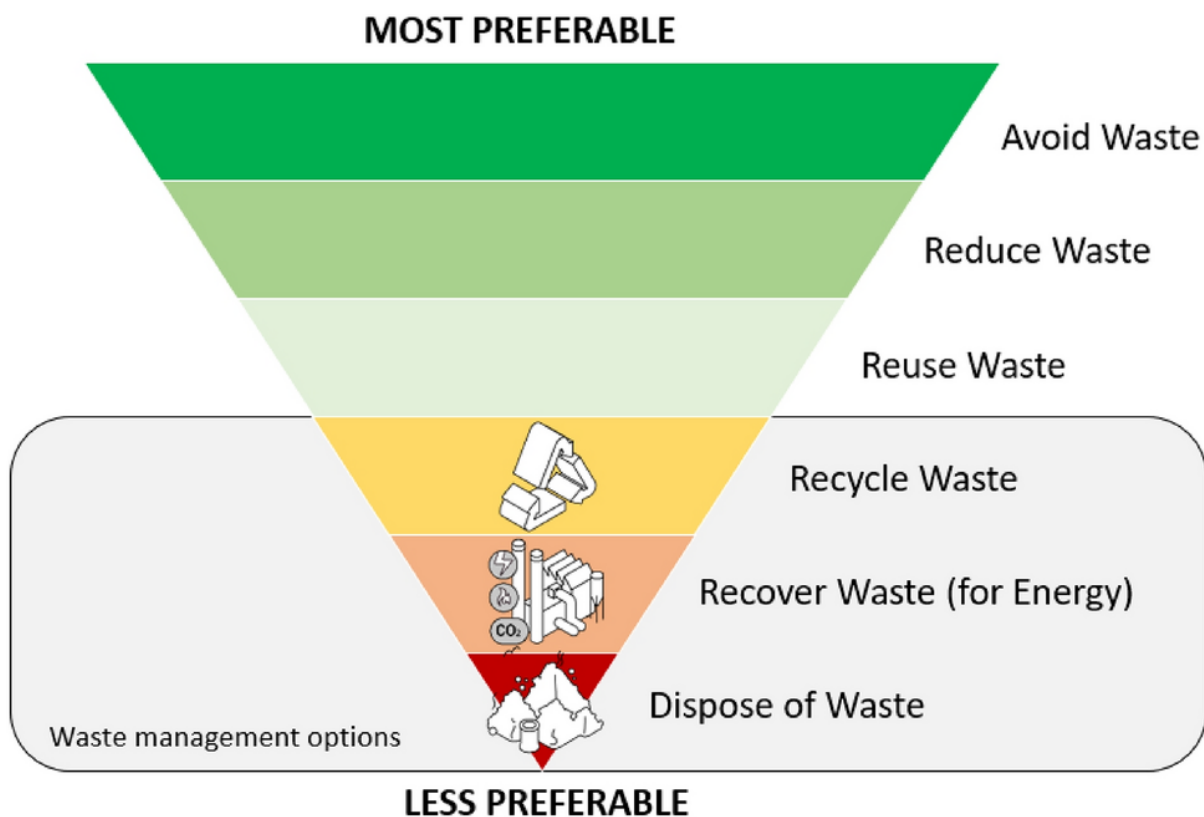


Figure 2.3 – Plastic waste hierarchy [107]

chain through such practices as mentioned in Figure 2.3; reduction, recycling and recovery. This concept emphasises sustainability of processes through reduction of waste material at production, extension of product life and recycling of used material in the creation of new products which is particularly relevant for non-biodegradable plastic material.

As with the methods for waste management detailed in the hierarchy, circular economies are often more effective the higher up the hierarchy they can be implemented. Techniques used nearer the base of the hierarchy can still have significant value. Often, at the recovery stage chemical, electrical or mechanical methods are employed to extract useful energy from waste plastic or to use plastic as a feedstock to produce valuable materials with other uses. This can include production of monomers which can be used in the reproduction of polymer material or used for other purposes. Other generated products can include fuels; either more traditional long-chain diesel-type hydrocarbons or hydrogen gas for generation of clean energy. Valuable solid materials, especially carbon-based ones like carbon nanotubes can also be produced. These methods can contribute to circular economies directly by producing new plastic material or indirectly by extracting a valuable material from the plastic waste to be used in other products or processes (e.g. CNTs).

The work regarding plastic decomposition contained in the following chapters sits within the "Recovery" tier of the hierarchy which is only one step removed from disposal. It is important to understand that this does not aim to provide a solution for all plastic waste, especially given the current volumes produced. If plastic waste generation can be tackled to be more in line with that presented by the hierarchy in Figure 2.3 then the amount of waste available for energy and material recovery will be much smaller and more suited to specialised solutions such as microwave pyrolysis.

Hydrogen is particularly targeted as an effective and environmentally friendly energy vector. Hydrogen gas is incredibly energy dense at 120

MJ/kg (gravimetric density) but has a number of challenges associated with its storage, transportation and usage. To calculate the amount of hydrogen in a plastic we can simply work out the proportion of molecular mass constituted by hydrogen and multiply that by the mass of plastic in question. For polyethylene consisting of two carbon atoms (12.01 g/mol) and four hydrogen atoms (1.008 g/mol) per repeating unit we can determine it is approximately 14.37 % hydrogen by weight. In this case, if all hydrogen contained in polyethylene could be extracted without losses it would take approximately 7 kg of PE to generate 1 kg of hydrogen. Using hydrogen in a fuel cell to generate electricity can produce up to 23 kWh/kg_{H₂} [109], meaning theoretically, from 7 kg of waste plastic you could run most of a typical home's appliances for a whole day or more [110]. This includes energy intensive items such as washers, dryers, ovens and refrigerators which could be powered primarily from waste plastic. This is one of the reasons research into all aspects of the hydrogen energy generation network is so important and so promising.

2.3.2 DECOMPOSITION OF PLASTIC WASTE

There are a number of methods used to decompose plastics through various thermal, chemical or electrical means. These include pyrolysis, solvolysis, gasification, liquefaction, photocatalytic degradation and catalytic oxidation. Each method can be further complicated by its process parameters which may include, reaction temperature, heating rate, residence time, feedstock mass, catalyst-to-feedstock ratio, reaction pressure, particle sizes and feedstock composition. Some methods may also involve multi-step processes that require pre- or post-processing of materials to achieve the desired results. Given the wide array of means available to process plastics and the many variables relevant to the success of the reaction it is important to focus on the most relevant subset of methods for the proposed microwave-based reactions performed later in this work. We are primarily concerned with the thermal

degradation of plastics and how microwave heating can change, enhance or otherwise benefit this process.

2.3.2.1 TYPICAL PYROLYSIS METHODS

Traditional thermally-driven pyrolysis of plastic waste often yields significant proportions of liquid hydrocarbon product and can progress at reaction temperatures from around 350 °C to 750 °C [110][112][113]. This type of pyrolysis is often considered relatively low-cost as it requires a heat source, reaction vessel and product collection mechanisms and can produce significant quantities of liquid fuel or monomers for recycling use. Produced pyrolysis oil exhibits useful properties, primarily its high energy density, and therefore it is valuable as an energy resource. This is a useful alternative to incineration or landfill of plastics as valuable energy can be extracted but the process typically requires a large amount of energy to achieve due to the high temperatures involved, and the product selectivity is often limited.

Some research into plastic pyrolysis focuses instead on production of hydrogen gas and sometimes useful solid carbon products [114][115][116][117][118][119]. This is more appealing to aims including reduction of greenhouse gas emissions and reduced environmental impact as it reduces production of liquid fossil fuels and instead produces a clean, highly dense energy source in the form of hydrogen gas. Many standard plastic pyrolysis procedures utilise a two-step method of first pyrolysing the plastic at 450 °C to 550 °C and then using either steam reforming or chemical vapour deposition (CVD) at temperatures often in excess of 800 °C to create the final hydrogen/carbon products.

2.3.2.2 MICROWAVE ASSISTED DECOMPOSITION OF PLASTIC

Recently, important work has advanced the understanding of the plastic pyrolysis process and enabled a one-step method with the aid of microwave energy and suitable transition-metal-based catalysts [9]. This

work uses a range of iron, aluminium and carbon-based materials to deconstruct waste HDPE with the focus on hydrogen production. Among the best performing catalysts are magnetite and haematite but the most promising catalyst is their iron-aluminium oxide FeAlO_x which was able to generate a H_2 yield of >55.6 mmol per gram of plastic, extracting more than 97 % of the hydrogen contained in the plastic. This was done over a relatively short time-scale of 180 s, with over 650 mL of gas evolved in the first 90 s and much of the deconstruction happening in under 30 s from microwave initiation.

Heating of the catalyst alone with the 1000 W microwave equipment recorded absorbed power levels between 250 and 450 W in the first 30 s, falling to approximately 250 W over the remaining experimentation time. This catalyst heated from room temperature to approximately 500 °C in 40 s. Combining catalyst and HDPE plastic saw a more rapid heating profile but a lower recorded maximum temperature of approximately 350 °C in just 25 s. The temperature remained at 350 °C for 10 s and then began to steadily decrease to 300 °C by 70 s into the experiment. Recorded absorbed power levels in this experiment rise exponentially from 100 W to 450 W over the first 20 s of heating then show a similarly rapid decay to between 150 and 200 W for the remainder of the heating duration. This work demonstrates that rapid absorption of microwave energy can produce significant proportions of hydrogen gas and carbon nanotubes from waste plastic, with recorded temperatures much lower than typical conventional thermal pyrolysis routes requiring process temperatures in the region of 450 to 550 °C.

Other works have investigated similar methods using iron carbide catalysts and a multi-mode microwave cavity with a maximum output power of 800 W [120]. This research achieved excellent hydrogen yields for deconstruction of LDPE, HDPE and PP plastics of 69.4, 70.7 and 71.2 mmol per gram of plastic, respectively. There is no direct reaction temperature recorded but tests involving the microwave input power

indicate increasing from 400 to 700 W increased proportions of gaseous yield and decreased the quantity of produced oils. Also investigated was the catalyst-to-plastic weight ratios which found high ratios (1.8 to 3 times catalyst relative to plastic) also generated greater proportions of gaseous products. When analysing post-reaction carbon residue it was also found that amorphous carbons and CNTs decomposed differently in relation to temperature, with CNTs decomposing most prominently in the window of 500-550 °C while amorphous carbons began decomposing earlier at 450 °C. Both carbon types generally finished thermal decay by 700 °C.

Similar to the work of Jie et al. [9], studies have been performed using microwave power and iron-aluminium oxides but with investigations of microwave input power and its effect on reaction outcomes [10]. This work used microwave input power levels ranging typically from 300 to 900 W, measuring temperatures between 150 and 330 °C after the initial rapid temperature rise, often continuing to climb gradually as the reaction progressed. They also concluded that increased microwave input power led to increased gas yield (33.11 % at 300 W to 57.04 % at 900 W) and increased hydrogen efficiency. Increased power also produced more organic gas compounds such as methane, carbon dioxide and notably carbon monoxide, contributing to a reduction in relative hydrogen content of produced gases. This work utilised a long reaction time of over 40 minutes and a stepped and pulsed approach to microwave application. Initially the reactants are exposed to 700 W of microwave power to rapidly achieve reaction-level temperatures over 220 °C, then the power is dropped to a steady 300 W for approximately 10 minutes. The temperature is increased closer to 300 °C using 400 W pulsed power (10 s power on, 50 % duty cycle; 20 s power on, 66 % duty cycle) for a further 10 minutes. Similar pulsed approaches (50 % duty cycle) are used at 500 W and 600 W to further elevate the temperature. It was found that the most effective temperature range for gas production rate and relative

hydrogen production was when the recorded temperatures were in the region of 300-330 °C.

A key point to note about microwave-based heating works is that the recorded temperatures are often at the particle or reactor surfaces, and the internal reaction temperatures can often be significantly higher. For traditional thermal decomposition of plastics we expect temperatures in the region of 500 °C which will be similar across the reaction vessel and particle exteriors, but requires time for heat to travel to particle centres. Volumetric heating of particles with microwaves and enhancement of field strengths can lead to localised temperature hotspots exceeding those required for plastic degradation, but the temperature of the reaction vessel or particle surfaces may be much cooler. Again, conduction of heat is an important parameter as it will take time to transfer from the microwave-absorbing particles to the surrounding atmosphere and reactants. If a microwave-induced heating reaction is sufficiently rapid there may be an observed lag or reduction in apparent reaction temperatures.

2.4 CONCLUSIONS

The relevance of iron oxides for their role as catalysts and microwave-absorbing materials has been discussed, highlighting their broad applicability and versatility. An outline of key magnetic and dielectric loss mechanisms is provided, with particular interest in their relationship to frequency, especially in the microwave frequency range. Relevant literature around decomposition of plastics is discussed both for traditional thermal pyrolysis techniques and microwave-assisted methods. The difference in reaction temperature is highlighted as well as the relevance of the different heating techniques.

Chapter 3

3 MICROWAVE CAVITY THEORY

3.1 ELECTROMAGNETISM

Microwaves are a subset of the electromagnetic spectrum, like radio waves or visible light. The typical definition for microwaves is that they have a frequency between 0.3 GHz and 30 GHz (or wavelength between 1 m and 1 mm) [123]. A prominent figure in the early study of electromagnetism was James Clerk Maxwell, who developed a number of equations to quantify and understand electromagnetic fields and their interaction with matter.

3.1.1 MAXWELL'S EQUATIONS

These equations provide a broad understanding of how electric and magnetic fields behave and interact with each other. Many other useful equations in electrical engineering can be derived from Maxwell's. The four equations are shown in differential vector format in (3.1), (3.2), (3.3) and (3.4) [124][125].

$$\nabla \cdot \bar{D} = \rho \quad (3.1)$$

$$\nabla \cdot \bar{B} = 0 \quad (3.2)$$

$$\nabla \times \bar{E} = -\frac{\partial \bar{B}}{\partial t} \quad (3.3)$$

$$\nabla \times \bar{H} = J + \frac{\partial \bar{D}}{\partial t} \quad (3.4)$$

In these equations, D is electric flux density, B is the magnetic flux density, E is the electric field strength, H is the magnetic field strength, ρ is the electric charge density and J is the electric current density. Equation (3.1) describes the divergence of electric fields, which is dependent on

electric charge polarity, either positive or negative acting as a field source or sink. Equation (3.2) shows that magnetic monopoles cannot exist; magnetic fields exist between two poles. Equations (3.3) and (3.4) describe the induction of each field with the changing intensity of the opposite field, with the additional term J in (3.4), which shows a magnetic field can be generated by the presence of flowing current.

The flux densities and field intensities can be related to each other through two further equations, (3.5) and (3.6),

$$\bar{D} = \varepsilon_0 \bar{E} \quad (3.5)$$

$$\bar{B} = \mu_0 \bar{H} \quad (3.6)$$

where ε_0 and μ_0 are the permittivity and permeability of free space, respectively. These are constants that define how easily electromagnetic waves can travel in a vacuum and can be used to calculate the maximum speed of the waves, that is the speed of light. They can be scaled by the inclusion of relative permittivity and permeability terms to describe how waves behave in a material [126][127]. This will be further explained in later sections.

From these, a further derivation can be made to describe propagating waves. In a source-free region ($J=0$), by taking the curl ($\nabla \times$) of (3.3), substituting in (3.4) and using a vector identity (3.7) can be determined

$$\nabla^2 \bar{E} = \mu_0 \varepsilon_0 \frac{\partial^2 \bar{E}}{\partial t^2} \quad (3.7)$$

This is the vector wave equation describing the electric field in free space [128][129]. It can also be shown that the equation is identical for magnetic field, H . This equation describes the propagation of waves in space, time and the speed of propagation of the wave.

Maxwell's equations can be further modified to be more suitable and convenient for further calculations using some assumptions. Assuming a source-free region where all waves are sinusoidal and have a time

dependence based on their frequency of the form $e^{j\omega t}$, where j is the imaginary unit equal to $\sqrt{-1}$, ω is the angular frequency of the wave and time is t , the two curl-based equations (3.3) and (3.4) combined with the relationships (3.5) and (3.6) can be rewritten as

$$\nabla \times \bar{E} = -j\omega\mu_0\bar{H} \quad (3.8)$$

$$\nabla \times \bar{H} = j\omega\varepsilon_0\bar{E}. \quad (3.9)$$

These new equations allow the reformatting of the vector wave equation (3.7) to incorporate these assumptions as shown in (3.10).

$$\nabla^2 \bar{E} + \omega^2\mu_0\varepsilon_0\bar{E} = 0 \quad (3.10)$$

An identical equation exists for magnetic waves where E is substituted for H . This modified version of the wave equation allows the definition of a new constant called the wavenumber, k [128][129]. The wavenumber is defined such that

$$k^2 = \omega^2\mu_0\varepsilon_0 \therefore k = \omega\sqrt{\mu_0\varepsilon_0} \quad (3.11)$$

so it can be easily substituted into the second term of the wave equation (3.10). For general lossy mediums a complex propagation constant γ can be defined as a complex number consisting of an attenuation constant α and a phase constant β . This is shown in (3.12) for a medium with conductivity σ .

$$\gamma = \alpha + j\beta = jk\sqrt{1 - j\frac{\sigma}{k}\sqrt{\frac{\mu}{\varepsilon}}} = j\omega\sqrt{\mu\varepsilon}\sqrt{1 - j\frac{\sigma}{\omega\varepsilon}} \quad (3.12)$$

In this formulation, ε_0 and μ_0 are replaced by their complex versions ε and μ which contain a real part (subscript 1) and imaginary part (subscript 2) ($\varepsilon = \varepsilon_0(\varepsilon_1 - j\varepsilon_2)$ and $\mu = \mu_0(\mu_1 - j\mu_2)$). The imaginary part of each is what describes the losses in the medium. The attenuation constant describes how propagating waves lose energy as they travel in a lossy system and the phase constant relates the frequency, speed and phase relationships

of the wave. For a wave propagating in the +z direction the propagation factor of the wave can be described by the propagation constant in the form

$$e^{-\gamma z} = e^{-\alpha z} e^{-j\beta z}. \quad (3.13)$$

It can be seen that if a lossless transmission description is required, that is the wave does not attenuate and $\alpha = 0$, both (3.12) and (3.13) can be reduced to show $\gamma = j\beta = jk$ and $e^{-\gamma z} = e^{-j\beta z}$.

3.1.2 TEM, TE AND TM WAVES

Electromagnetic waves can take a number of forms and propagate in different ways. Transverse electromagnetic (TEM) waves can only propagate when supported by two separate conductors, such as in a coaxial cable. They are defined as having both electric and magnetic fields perpendicular (or transverse) to the direction of propagation of the wave [128][130]. For a wave travelling in the z-axis the electric and magnetic fields will only have components in the x and y axes and the components of the fields in the direction of propagation, E_z and H_z , are equal to zero.

Transverse electric (TE) and transverse magnetic (TM) waves occur when either the electric or magnetic field has a non-zero component in the same axis as the direction of propagation. Again, for a wave travelling in the z direction when there is a non-zero magnetic field component in the z direction ($H_z \neq 0$) it is only the electric field which is perpendicular (transverse) to the direction of travel and it is known as a TE wave. For TM waves, $E_z \neq 0$ and so the magnetic field is the transverse element. In a hollow waveguide, TEM waves cannot exist and so TE and TM waves are the only possible forms of propagation. Figure 3.1 shows two orientations of TEM waves (a and b) and examples of TM (c) and TE (d) waves where the z components are non-zero, and thus not perpendicular to the z-axis.

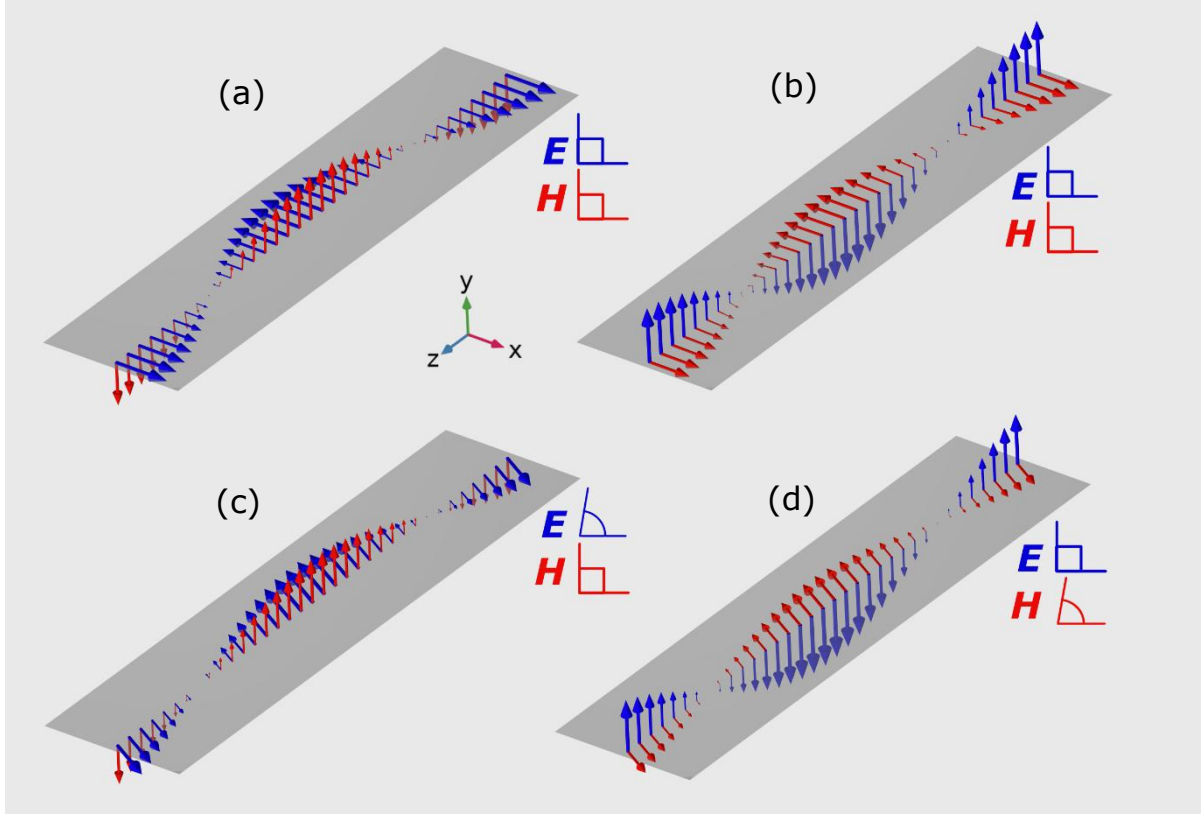


Figure 3.1 – Electric (blue) and Magnetic (red) field components of a wave travelling in the z direction showing TEM waves (a)(b), a TM wave (c) and a TE wave (d)

General solutions for Maxwell's equations can be developed for the cases of TEM, TE and TM waves. Beginning with the curl equations (3.8) and (3.9) and the associated assumptions of time dependence and a source-free region, they can be expanded and separated into their particular x, y and z components. For a vector $\vec{A}(x,y,z)$, the curl of $\vec{A}$ ($\nabla \times \vec{A}$) can be expanded as in (3.14).

$$\nabla \times \vec{A} = \begin{vmatrix} \hat{x} & \hat{y} & \hat{z} \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \\ A_x & A_y & A_z \end{vmatrix} = \left(\frac{\partial A_z}{\partial y} - \frac{\partial A_y}{\partial z} \right) \hat{x} + \left(\frac{\partial A_x}{\partial z} - \frac{\partial A_z}{\partial x} \right) \hat{y} + \left(\frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y} \right) \hat{z}. \quad (3.14)$$

Applying this expansion to (3.8) and (3.9) and splitting each equation into the three directional components with a propagation constant equal to $j\beta$ yields six equations as shown below, relating magnetic field components to changing electric field components and vice versa.

$$\frac{\partial E_z}{\partial y} + j\beta E_y = -j\omega\mu H_x \quad (3.15)$$

$$-j\beta E_x - \frac{\partial E_z}{\partial x} = -j\omega\mu H_y \quad (3.16)$$

$$\frac{\partial E_y}{\partial x} - \frac{\partial E_x}{\partial y} = -j\omega\mu H_z \quad (3.17)$$

$$\frac{\partial H_z}{\partial y} + j\beta H_y = j\omega\varepsilon E_x \quad (3.18)$$

$$-j\beta H_x - \frac{\partial H_z}{\partial x} = j\omega\varepsilon E_y \quad (3.19)$$

$$\frac{\partial H_y}{\partial x} - \frac{\partial H_x}{\partial y} = j\omega\varepsilon E_z \quad (3.20)$$

By equating components from pairs of equations these can be further manipulated to give equations for the x and y components of both electric and magnetic fields purely in terms of the z components. The process is shown below with the derivation of H_x from (3.15) and (3.19).

$$\begin{aligned} \frac{\frac{\partial E_z}{\partial y} + j\omega\mu H_x}{-j\beta} &= \frac{-j\beta H_x - \frac{\partial H_z}{\partial x}}{j\omega\varepsilon} \\ \omega\varepsilon \frac{\partial E_z}{\partial y} + j\omega^2\mu\varepsilon H_x &= j\beta^2 H_x + \beta \frac{\partial H_z}{\partial x} \\ j\omega^2\mu\varepsilon H_x - j\beta^2 H_x &= \beta \frac{\partial H_z}{\partial x} - \omega\varepsilon \frac{\partial E_z}{\partial y} \\ H_x(\omega^2\mu\varepsilon - \beta^2) &= \frac{1}{j}(\beta \frac{\partial H_z}{\partial x} - \omega\varepsilon \frac{\partial E_z}{\partial y}) \\ H_x &= \frac{-j}{k_c^2}(\beta \frac{\partial H_z}{\partial x} - \omega\varepsilon \frac{\partial E_z}{\partial y}) \end{aligned} \quad (3.21)$$

$$\text{where } k_c^2 = k^2 - \beta^2.$$

The same process can be applied to the other equations to provide equations for H_y , E_x and E_y .

$$H_y = \frac{-j}{k_c^2} \left(\beta \frac{\partial H_z}{\partial x} + \omega \varepsilon \frac{\partial E_z}{\partial y} \right) \quad (3.22)$$

$$E_x = \frac{-j}{k_c^2} \left(\omega \mu \frac{\partial H_z}{\partial x} + \beta \frac{\partial E_z}{\partial y} \right) \quad (3.23)$$

$$E_y = \frac{-j}{k_c^2} \left(-\omega \mu \frac{\partial H_z}{\partial x} + \beta \frac{\partial E_z}{\partial y} \right) \quad (3.24)$$

These equations are especially useful as they can be solved for TEM, TE and TM waves. TEM waves will not be pursued as the further work involved pertains to waveguides and resonant cavities, which do not support TEM waves. The TEM solutions can provide further insights into the voltage across two conductors, the current flow and general free space wave impedance.

3.1.3 CYLINDRICAL COORDINATES

The systems used in this work are based only on cylindrical waveguides and cavities. It is useful in this case to modify the coordinate system used from the standard Cartesian x, y, z to the cylindrical coordinate system r, θ, z which is shown in Figure 3.2 [131]. This means modifying the derived equations for the fields in the x and y directions to represent fields in the r and θ axes, where r is the axis originating at the centre and emanating outwards and θ is the rotational axis following the arc of the circle.

Modifying the equations in terms of x and y to cylindrical coordinates yields (3.25), (3.26), (3.27) and (3.28) for the magnetic and electric fields.

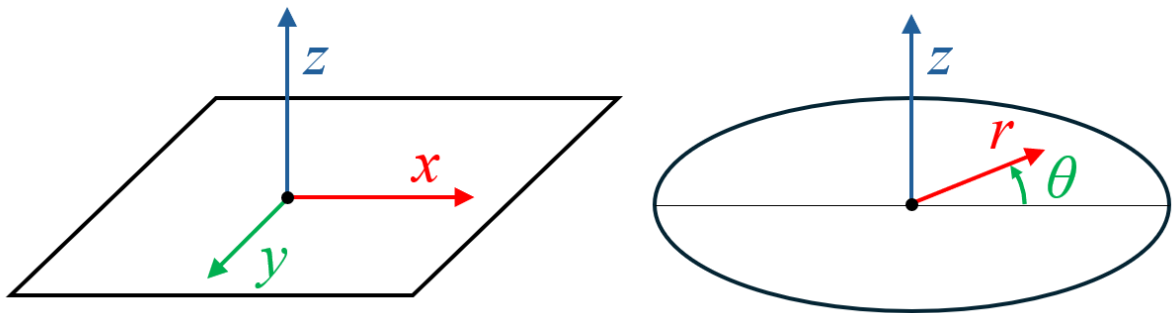


Figure 3.2 – Cartesian and cylindrical coordinate systems

$$H_r = \frac{-j}{k_c^2} \left(\beta \frac{\partial H_z}{\partial r} - \frac{\omega \varepsilon}{r} \frac{\partial E_z}{\partial \theta} \right) \quad (3.25)$$

$$H_\theta = \frac{-j}{k_c^2} \left(\frac{\beta}{r} \frac{\partial H_z}{\partial r} + \omega \varepsilon \frac{\partial E_z}{\partial \theta} \right) \quad (3.26)$$

$$E_r = \frac{-j}{k_c^2} \left(\frac{\omega \mu}{r} \frac{\partial H_z}{\partial r} + \beta \frac{\partial E_z}{\partial \theta} \right) \quad (3.27)$$

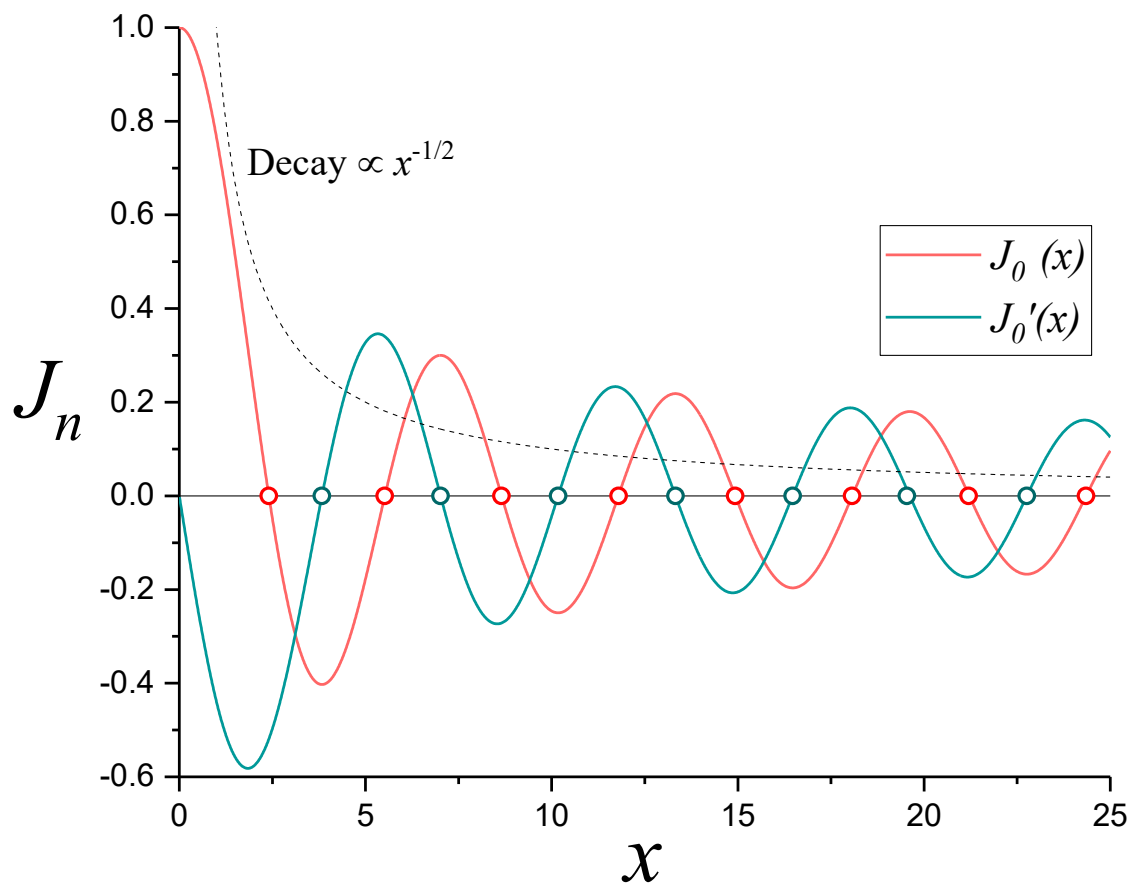
$$E_\theta = \frac{-j}{k_c^2} \left(-\omega \mu \frac{\partial H_z}{\partial r} + \frac{\beta}{r} \frac{\partial E_z}{\partial \theta} \right) \quad (3.28)$$

Along with redefining the working coordinate system it is necessary to introduce Bessel functions. These are functions based on solutions of a particular type of differential equation that are used for solutions to cylindrical or spherical problems [132]. They have a wide applicability to all sorts of subjects such as pressure, acoustics, seismology and importantly for this work, EM waves in a cylindrical waveguide [133][134][135][136][137].

For our purposes, the Bessel functions of the first kind and their derivatives are of interest. Using a standard x variable, these are often notated as $J_n(x)$ and $J_n'(x)$ respectively, where n refers to the order of the function designated by integer numbers. As Bessel functions are commonly used in many fields they often have prebuilt functions for visualising them. Shown in Figure 3.3 are the Bessel function and its derivative for the zeroth order. They resemble sinusoidal waves which decay proportional to $x^{-1/2}$. Also highlighted are the points where each function is equal to zero, or its roots where $J_n(x) = 0$. The value of x at this point is important for later solutions to equations. For $J_n(x)$ the roots will be designated as u_{mn} and for $J_n'(x)$ the roots will be designated as u'_{mn} . Similarly to the Bessel functions themselves, the roots are well documented and the first few are shown below for reference in Table 3-1.

Table 3-1 – Bessel function roots for J_n and J_n'

m	u_{m1}	u_{m2}	u_{m3}	u_{m4}	u'_{m1}	u'_{m2}	u'_{m3}	u'_{m4}
0	2.405	5.520	8.654	11.792	3.832	7.016	10.174	13.324
1	3.832	7.016	10.174	13.324	1.841	5.331	8.536	11.706
2	5.135	8.417	11.620	14.796	3.054	6.706	9.970	13.170
3	6.380	9.761	13.015	16.224	4.201	8.015	11.346	14.586

**Figure 3.3** – Zeroth order Bessel function and its derivative shown with approximate decay rate and roots up to $x = 25$.

For the purposes of understanding cylindrically constrained EM waves the roots u_{mn} are associated with the TM resonant modes and the roots of the derivative u'_{mn} are associated with the TE resonant modes. For both TM and TE modes of a waveguide with the condition that due to the conductive boundary the electric field's tangential component must be

equal to zero, it can be deduced that the root of the Bessel function must be equal to zero at the point where r is equal to the radius, a . This leads to the wave cutoff number k_c being defined as the Bessel root divided by the radius a . This is true for both TE and TM modes and is shown below.

$$k_c = \frac{u_{mn}}{a} \text{ for TM modes or, } = \frac{u'_{mn}}{a} \text{ for TE modes.} \quad (3.29)$$

This leads to a propagation constant of β equal to

$$\beta = \sqrt{k^2 - k_c^2} = \sqrt{k^2 - \left(\frac{u_{mn}}{a}\right)^2}, \quad (3.30)$$

and a cutoff frequency f_c equal to

$$f_c = \frac{u_{mn}}{2\pi a \sqrt{\mu\epsilon}}, \quad (3.31)$$

for TM modes where the same is true for TE modes, simply with u'_{mn} substituted in place of u_{mn} . The cutoff frequency of a cylindrical waveguide with fixed radius and materials is directly dependent on the Bessel function roots. The lowest frequency representing the dominant modes can be read directly from Table 3-1 as being the TM_{01} mode and the TE_{11} mode, as these are the lowest value Bessel function roots so when plugging in to (3.31) give us the lowest cutoff frequency.

3.2 RESONANT CAVITIES

The transfer of electrical power is typically performed by conduction through wires or transmission lines. This can become problematic when dealing with high power levels, which could be high enough to cause breakdown of structures like coaxial cables or create significant loss in the cable. A solution to this problem was to transmit EM waves through air and contain their radiation with a conductive boundary. The result is a waveguide, a hollow metal tube which can handle high power levels[128][138][139]. If a waveguide is terminated on its ends with similar highly conductive boundaries it can accommodate standing waves

and demonstrate resonance. This is the basis of a resonant cavity. Resonant cavities are incredibly useful tools that can act as power delivery systems to their contents or as highly sensitive detectors of material EM properties.

3.2.1 CYLINDRICAL CAVITY FREQUENCY

The resonant frequency of a cavity, or a general oscillating system, can be thought of as the frequency at which external energy transfer is most effective and can cause the greatest amplitude of oscillation within the system. At a resonant frequency the EM waves will interfere and create nodes and antinodes of standing waves, which appear to remain in place and create regions of well-defined electric and magnetic fields. The resonant frequencies of a cavity can be determined using its dimensions and by defining how many wavelengths i.e. standing wave nodes/antinodes are present in each axis.

As stated, a resonant cavity is effectively a waveguide which has been short-circuited at both ends to create a hollow cavity enclosed by highly conductive boundaries on all sides. In the case of cylindrical cavities this is in the form of a hollow metal tube. The introduction of new metal boundaries requires new boundary conditions where, as before the formulations of the fields in a waveguide structure required that at the walls the tangential electric field is equal to zero, it is now also true that the transverse electric field components are equal to zero at the conductive ends of the waveguide. In order to achieve this condition for a cylindrical cavity with radius a and a height h , a sinusoidal wave with argument βh will be equal to zero. Sine waves are equal to zero in general every half-wavelength at $0, \pi, 2\pi, \dots$ meaning βh will be equal to $p\pi$, where p is zero or a positive integer. Using (3.30), multiplying both sides by h and substituting βh for $p\pi$ it can be derived that the resonant frequency (f_{mnp}) of a cavity is

$$f_{mnp} = \frac{1}{2\pi\sqrt{\mu\epsilon}} \sqrt{\left(\frac{u_{mn}}{a}\right)^2 + \left(\frac{p\pi}{h}\right)^2}, \quad (3.32)$$

for TM modes with a simple substitution of the Bessel root for the derivative root as done in (3.30) to calculate for TE modes [128]. The subscript mnp attached to the resonant frequency indicates the resonant mode of the cavity with m and n the number of half-wavelengths in the cylindrical plane and p the number of half-wavelengths in the z -axis. For modes where $p = 0$, there is no variation of fields in the z -axis and (3.32) reduces to (3.31), being independent of the cavity height. Modes are typically referred to by their mnp integers, for example the TM_{010} mode or the TE_{111} mode.

3.2.2 TM AND TE MODES

As with waveguides, resonant cavities can be excited in a whole range of modes with different frequencies and field distributions. They are typically referred to by the type of propagating wave i.e. TE or TM as previously mentioned, and the mode integers mnp (sometimes also labelled as nmp) [128]. These integers can give an indication of how complex a mode's field distributions may be, with higher numbers and more non-zero terms generally indicating a more complex field pattern. Specifically, m refers to the number of half-wavelengths in the azimuthal direction as defined by θ in the cylindrical coordinate system, and n refers to the number of half-wavelengths in the radial direction, defined by r . When $m = 0$ there is no variation in the rotational portion of the cylinder and the fields are symmetrical around the circular plane and the fields in this plane are dependent on n . Similarly, when $p = 0$ there is no variation in the z -direction of the cavity and the field intensities are constant throughout any particular vertical cross section in the cavity. These points can be seen with the magnetic and electric field distributions displayed in Figure 3.4.

Some modes are more useful than others for particular tasks. Modes with strong and relatively uniform fields across a small vertical section of the cavity can be used for cavity perturbations to determine a material's permittivity and permeability. Taking note of the electric field at the centre of the TM_{010} , TM_{011} , TM_{020} and TM_{021} modes it can be seen to be relatively high and reasonably constant in the vertical plane. These modes are useful for performing cavity perturbations to determine a material's permittivity. The modes TM_{110} , TE_{011} , TE_{021} and TE_{012} show similar qualities for the magnetic field, making them suitable for determining the permeability of a material. If the objective is to heat the cavity contents a region of high intensity field is generally desirable.

When using higher order modes, the physical space occupied by the high-intensity regions is diminished and it can be more difficult to place a sample in the most effective position. This difficulty is compounded by the fact that introducing any other object into the cavity will disturb the field distributions from the idealised versions shown in Figure 3.4, again shifting or damping the high-intensity regions. Using the simplest mode possible is therefore preferable to maintain confidence in the sample positioning being optimal.

The TM_{010} mode is a popular choice for microwave heating experiments as it has perhaps the simplest field distribution of any cylindrical resonant mode, with only one half-wavelength in the radial axis and no rotational or vertical variation. This is exhibited as a magnetic field minimum in the centre of the cavity rising to a maximum just before the cylindrical walls, and an electric field which is zero at the cylindrical walls and rises to a maximum in the centre. The maxima regions are relatively large compared to the size of the overall cavity and with no vertical field variation, any sample placed throughout the entire height of the cavity should experience identical field exposure and therefore heating. As it has rotational symmetry, it is also easy to access the high magnetic field region with confidence at any point around the cavity by simply

measuring in from the cavity wall to where the point of maximum field should be.

3.2.2.1 MODE DEGENERACY

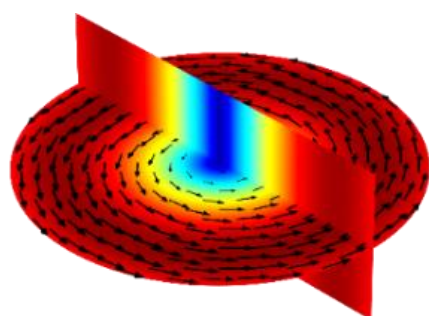
The frequency of a mode is dependent on its mnp integers and the dimensions of the cavity as shown in (3.32). Where the frequency of two modes are identical they exist in the same frequency-space and are known as degenerate modes [128][140][141]. Mode degeneracy is not desirable because if there is uncertainty about the actual mode you are using, the placement of your sample and the field distributions may not line up in the expected way. This can cause erroneous measurements or significantly hamper efforts to heat samples.

Some modes can be degenerate with a different orientation of the same mode. For example, the TM_{110} mode has two orientations that exist with a 90° separation, one of which is shown in Figure 3.4. This is sometimes referred to as orthogonal degeneracy.

Another type of degeneracy occurs between modes that are completely different. For a cavity with fixed height and radius the frequency is dependent on the value of p and the values of m and n , which correspond to a particular Bessel function root. Observing the values in Table 3-1 shows that the row for values of u_{mn} (TM modes) where $m = 1$ is identical to the row of values of u'_{mn} where $m = 0$. Referring back to (3.32), with fixed cavity dimensions, this shows that modes TM_{1np} are degenerate with modes TE_{0np} . For the modes of interest in this work this is relevant for the TE modes used, TE_{011} , TE_{021} , and TE_{012} . It is not applicable for the TM_{110} mode as the TE_{010} cannot exist. Splitting these degenerate modes will be discussed later alongside the construction of cavities through minor modification to cavity structures.

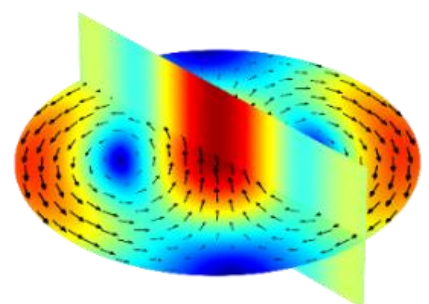
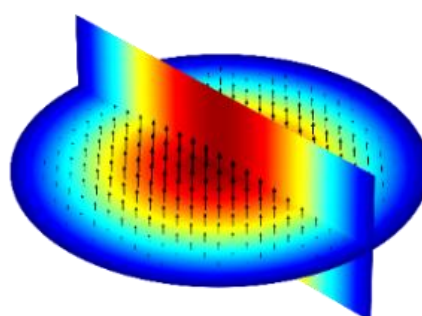
Magnetic Field Distributions

Electric Field Distributions



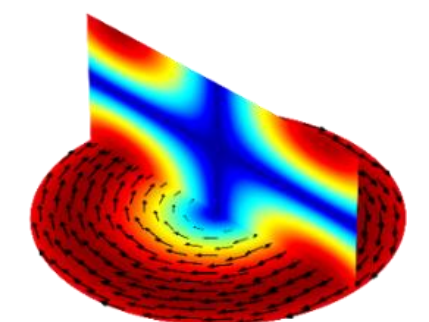
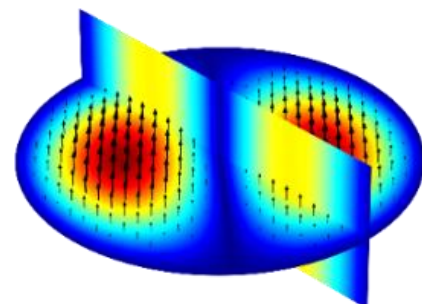
TM_{010}

2.342 GHz



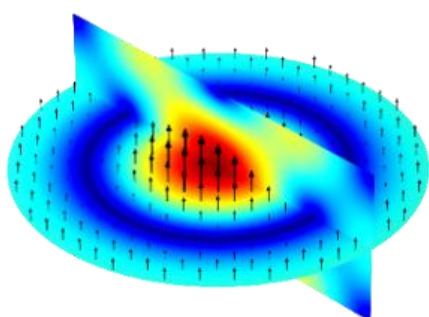
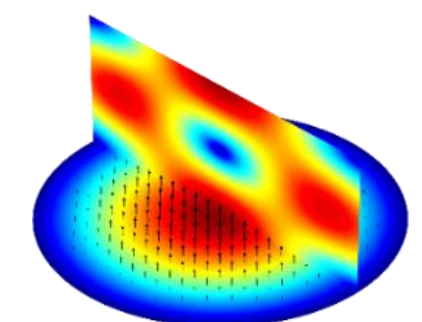
TM_{110}

3.731 GHz



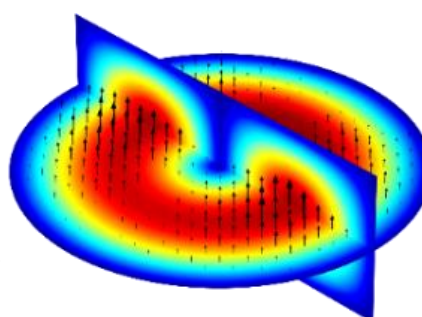
TM_{011}

4.419 GHz



TE_{011}

5.288 GHz



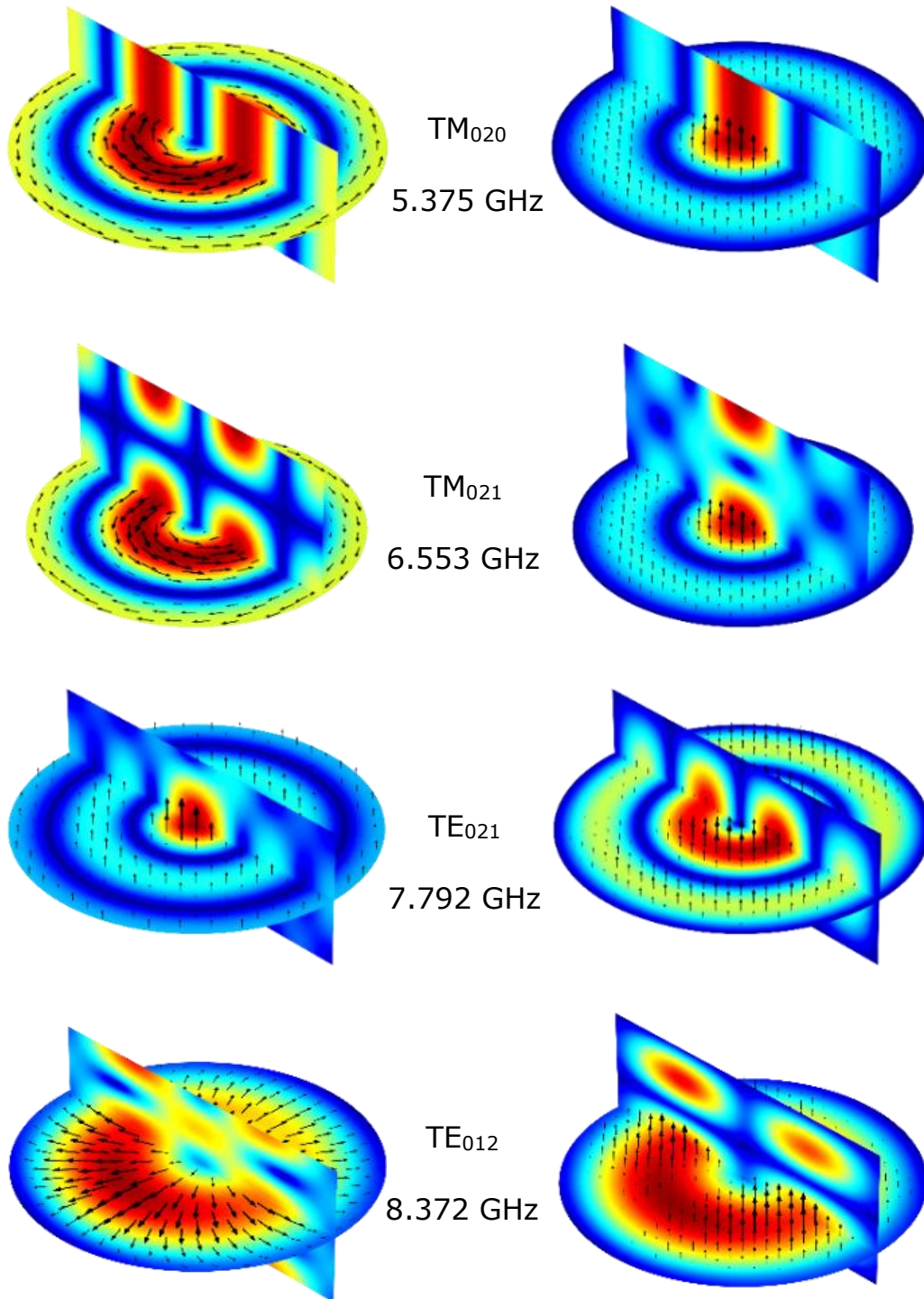


Figure 3.4 – Magnetic and electric field distributions of resonant modes of interest in this work for a cylindrical cavity with $a = 4.9$ cm and $h = 4.0$ cm. Arrows show field intensities in the cylindrical plane using the absolute value for the vertical z -component.

3.2.3 QUALITY FACTOR

A useful figure of merit used to quickly assess the quality of a resonator is the aptly named quality factor, often referred to simply as Q . In general, the Q of a resonator is a measure of how much energy it can store compared to how much energy it dissipates, or is lost in the resonant system [126][128]. This is true not only for resonant cavities but other more common resonant systems like pendulums, tuning forks and crystal oscillators [142] and can be expressed as in (3.33)

$$Q = \text{resonant frequency} \cdot \frac{\text{energy stored}}{\text{energy dissipated per second}} = \omega_0 \frac{W}{P_L}, \quad (3.33)$$

where W is the total energy stored and P_L is the energy loss per second or power dissipated. For electromagnetic cavity resonators, W consists of the total electrical energy stored (W_e) and the magnetic energy stored (W_m). The dissipated energy can also be split into the contributions from dissipation in the conducting cavity walls (P_c) and the dissipation in the cavity filling dielectric (P_d). This allows the splitting of the unloaded quality factor (Q_o) of the resonator into these two contributions as in (3.34)

$$\frac{1}{Q_o} = \frac{P_c + P_d}{\omega_0 W} = \frac{1}{Q_c} + \frac{1}{Q_d}, \quad (3.34)$$

where Q_c is the contribution to Q due to the cavity conducting walls, and Q_d is the contribution due to the lossy cavity dielectric. The contribution to Q from the dielectric filling material can be explained as the energy stored in the dielectric divided by the dissipated energy, or simply the real part of the permittivity (ϵ_1) divided by the imaginary part (ϵ_2). For an air-filled cavity $\epsilon_1 \approx 1.0005$ and ϵ_2 is so low that it is often approximated to zero. This means that Q_d tends to infinity, and the reciprocal tends to zero meaning the contribution to Q must only consider the losses in the cavity walls.

The values for Q_c can be derived from (3.34) as the time-average stored energy (W) divided by the power losses in the conducting walls (P_c), all multiplied by the (angular) resonant frequency (ω_0). Based on the wave equations defined in cylindrical form shown in (3.25), (3.26), (3.27) and (3.28), general equations for Q_c can be constructed for both TM and TE modes.

To calculate the time-averaged stored energy in the resonator either the electric or magnetic energy can be considered. For EM waves in a volume V , the stored electrical energy (W_e) is shown in (3.35),

$$W_e = \frac{\varepsilon}{4} \int_V |\bar{E}|^2 dV, \quad (3.35)$$

while similarly for the magnetic energy (W_m) shown in (3.36)

$$W_m = \frac{\mu}{4} \int_V |\bar{H}|^2 dV. \quad (3.36)$$

This means that we can simply take the square of the absolute value of the respective fields and integrate over the volume then multiply by the relevant constant to get the stored energy. Since the magnetic and electric energies at resonance are equal, we only have to choose one of these equations and multiply it by two to calculate W . If we consider the scenario for calculating the electrical energy where $W = 2W_e$, (3.35) can be expanded to give (3.37)

$$2W_e = \frac{\varepsilon}{2} \int_0^h \int_0^{2\pi} \int_0^a (|\bar{E}_r|^2 + |\bar{E}_\theta|^2 + |\bar{E}_z|^2) r dr d\theta dz, \quad (3.37)$$

where the same process can be done for the magnetic energy and (3.36) to yield a similar result.

To calculate the power lost in the conducting walls we initially consider the magnetic and electric fields at the surface of the conducting boundary. Through the use of identities and simplification (see Appendix 1) this can

be reduced to considering only the tangential magnetic fields (H_{tan}) right at the conductor boundary. The equation for P_c , is shown in (3.38)

$$P_c = \frac{R_s}{2} \int_S |\bar{H}_{tan}|^2 dS \quad (3.38)$$

where R_s is the surface resistance of the conductive material and defined as in (3.39)

$$R_s = \sqrt{\frac{\omega\mu}{2\sigma}}. \quad (3.39)$$

When considering the tangential fields, we must split a cylindrical cavity into the constituent shapes of the curved cavity wall and the two circular end plates. The fields that are tangential to the wall are H_z and H_θ and the fields that are tangential to the end plates are H_r and H_θ . The calculation can further be simplified by considering the fields at the wall must exist where the radial component r is equal to the cavity radius dimension a i.e. $r = a$ and the end plates are considered where the z component is equal to zero or the cavity height h i.e. $z = [0, h]$. As the plates are identical their contribution will also be identical so we only need to consider one and simply double the final value to account for both. Using these simplifications, (3.38) can be expanded to produce (3.40)

$$P_c = \frac{R_s}{2} \left[\int_0^h \int_0^{2\pi} (|H_z(r=a)|^2 + |H_\theta(r=a)|^2) a d\theta dz \dots \right. \\ \left. + 2 \int_0^{2\pi} \int_0^a (|H_r(z=0)|^2 + |H_\theta(z=0)|^2) r dr d\theta \right] \quad (3.40)$$

These equations can now be used to calculate Q_c for TM and TE modes.

3.2.3.1 Q FOR TE_{MNP} MODES

For TE_{mnp} modes the field equations can be written in terms of sinusoidal functions and Bessel functions as shown below in (3.41), (3.42), (3.43), (3.44), (3.45) and (3.46).

$$H_z = (A \sin m\theta + B \cos m\theta)J_n(k_c r)e^{-j\beta z} \quad (3.41)$$

$$H_r = \frac{-j\beta}{k_c} (A \sin m\theta + B \cos m\theta)J'_n(k_c r)e^{-j\beta z} \quad (3.42)$$

$$H_\theta = \frac{-j\beta m}{k_c^2 r} (A \cos m\theta - B \sin m\theta)J_n(k_c r)e^{-j\beta z} \quad (3.43)$$

$$E_z = 0 \quad (3.44)$$

$$E_r = \frac{-j\omega\mu m}{k_c^2 r} (A \cos m\theta - B \sin m\theta)J_n(k_c r)e^{-j\beta z} \quad (3.45)$$

$$E_\theta = \frac{j\omega\mu}{k_c} (A \sin m\theta + B \cos m\theta)J'_n(k_c r)e^{-j\beta z} \quad (3.46)$$

The wave impedance for TE modes is shown in (3.47)

$$Z_{TE} = \frac{\omega\mu}{\beta} = \frac{\eta k}{\beta} \text{ where } \eta = \sqrt{\frac{\mu}{\epsilon}} \quad (3.47)$$

where η is the intrinsic impedance of the wave propagation medium.

When applying these field equations, the magnetic fields are multiplied by H_0 and electric fields by $H_0\eta$.

To carry out the calculation for the stored energy, it makes sense to use the electric fields, as by definition $E_z = 0$, so we can discount it. The stored energy in TE_{mnp} modes is therefore

$$\begin{aligned} W &= \frac{\epsilon}{2} \int_0^h \int_0^{2\pi} \int_0^a \left(\frac{k^2 \eta^2 m^2 H_0^2}{k_c^4 r^2} \sin^2 m\theta \sin^2 \frac{p\pi z}{h} J_n^2(k_c r) \dots \right. \\ &\quad \left. + \frac{k^2 \eta^2 H_0^2}{k_c^2} \cos^2 m\theta \sin^2 \frac{p\pi z}{h} J_n'^2(k_c r) \right) r dr d\theta dz, \\ W &= \frac{\epsilon}{2} \frac{k^2 \eta^2 H_0^2}{k_c^2} \int_0^h \int_0^{2\pi} \int_0^a \left(\frac{m^2}{k_c^2 r^2} \sin^2 m\theta \sin^2 \frac{p\pi z}{h} J_n^2(k_c r) \dots \right. \\ &\quad \left. + \cos^2 m\theta \sin^2 \frac{p\pi z}{h} J_n'^2(k_c r) \right) r dr d\theta dz, \end{aligned}$$

where it can be noted for TE modes, p must be ≥ 1 , so the evaluation of $\sin^2$ and $\cos^2$ of $p\pi z/h$ from zero to h evaluates to $h/2$ and the evaluation

of $\sin^2$ and $\cos^2$ of $m\theta$ from zero to 2π results in π , meaning it can be reduced to

$$W = \frac{\varepsilon}{2} \frac{k^2 \eta^2 H_0^2}{k_c^2} \frac{h\pi}{2} \int_0^a \left(\frac{m^2}{k_c^2 r^2} J_n^2(k_c r) + J_n'^2(k_c r) \right) r dr,$$

where the remaining integral can be evaluated to

$$\frac{a^2}{2} \left(1 - \left[\frac{m}{u'_{mn}} \right]^2 \right) J_n^2(u'_{mn}),$$

leaving us with

$$W = \frac{\varepsilon}{2} \frac{k^2 \eta^2 H_0^2}{k_c^2} \frac{h\pi}{2} \frac{a^2}{2} \left(1 - \left[\frac{m}{u'_{mn}} \right]^2 \right) J_n^2(u'_{mn}),$$

which with simplification and substitution of (3.29) gives the final equation for stored energy in TE_{mnp} modes in a cylindrical cavity shown in (3.48)

$$W = \frac{\varepsilon k^2 \eta^2 H_0^2 a^4 h\pi}{8 u_{mn}'^2} \left(1 - \left[\frac{m}{u'_{mn}} \right]^2 \right) J_n^2(u'_{mn}). \quad (3.48)$$

Using the wave equations, we can also derive a similar term for P_c as shown below split into the wall and plate contributions, which can then be summated together later to give (3.49)

$$P_c(\text{walls}) = \frac{R_s}{2} \left[\int_0^h \int_0^{2\pi} \left(H_0^2 \cos^2 m\theta \sin^2 \frac{p\pi z}{h} J_n^2(u'_{mn}) + \frac{\beta^2 H_0^2 m^2}{k_c^4 a^2} \sin^2 m\theta \sin^2 \frac{p\pi z}{h} J_n^2(u'_{mn}) \right) a d\theta dz \right]$$

$$P_c(\text{walls}) = \frac{R_s}{2} H_0^2 \pi J_n^2(u'_{mn}) \frac{ha}{2} \left(1 + \left[\frac{\beta ma}{u_{mn}'^2} \right]^2 \right)$$

$$P_c(\text{plates}) = \frac{R_s}{2} \left[2 \int_0^a \int_0^{2\pi} \left(\frac{\beta^2 H_0^2}{k_c^2} \cos^2 m\theta J_n'^2(k_c r) + \frac{\beta^2 H_0^2 m^2}{k_c^4 r^2} \sin^2 m\theta J_n^2(k_c r) \right) r dr d\theta \right]$$

$$\begin{aligned}
 P_c(\text{plates}) &= \frac{R_S}{2} \left[2 \frac{\beta^2 H_0^2}{k_c^2} \pi \int_0^a \left(J_n'^2(k_c r) + \frac{m^2}{k_c^2 r^2} J_n^2(k_c r) \right) r dr d\theta \right] \\
 P_c(\text{plates}) &= \frac{R_S}{2} \frac{2\beta^2 H_0^2 \pi a^2}{k_c^2} \left(1 - \left[\frac{m}{u'_{mn}} \right]^2 \right) J_n^2(u'_{mn}) \\
 P_c(\text{plates}) &= \frac{R_S}{2} \frac{\beta^2 H_0^2 a^4 \pi J_n^2(u'_{mn})}{u'_{mn}{}^2} \left(1 - \left[\frac{m}{u'_{mn}} \right]^2 \right) \\
 P_c &= \frac{R_S}{2} H_0^2 \pi J_n^2(u'_{mn}) \left[\frac{ha}{2} \left(1 + \left[\frac{\beta ma}{u'_{mn}{}^2} \right]^2 \right) + \frac{\beta^2 a^4}{u'_{mn}{}^2} \left(1 - \left[\frac{m}{u'_{mn}} \right]^2 \right) \right]. \quad (3.49)
 \end{aligned}$$

The equation for Q_c can then be determined by substituting (3.48) and (3.49) into (3.34) to give (3.50)

$$\begin{aligned}
 Q_c &= \omega \frac{\frac{\varepsilon k^2 \eta^2 H_0^2 a^4 h \pi}{8 u'_{mn}{}^2} \left(1 - \left[\frac{m}{u'_{mn}} \right]^2 \right) J_n^2(u'_{mn})}{\frac{R_S}{2} H_0^2 \pi J_n^2(u'_{mn}) \left[\frac{ha}{2} \left(1 + \left[\frac{\beta ma}{u'_{mn}{}^2} \right]^2 \right) + \frac{\beta^2 a^4}{u'_{mn}{}^2} \left(1 - \left[\frac{m}{u'_{mn}} \right]^2 \right) \right]} \\
 Q_c &= \omega \frac{\frac{\varepsilon k^2 \eta^2 a^4 h}{8 u'_{mn}{}^2} \left(1 - \left[\frac{m}{u'_{mn}} \right]^2 \right)}{\frac{R_S}{2} \left[\frac{ha}{2} \left(1 + \left[\frac{\beta ma}{u'_{mn}{}^2} \right]^2 \right) + \frac{\beta^2 a^4}{u'_{mn}{}^2} \left(1 - \left[\frac{m}{u'_{mn}} \right]^2 \right) \right]} \\
 Q_c &= \omega \frac{\varepsilon k^2 \eta^2 a^4 h \left(1 - \left[\frac{m}{u'_{mn}} \right]^2 \right)}{4 R_S u'_{mn}{}^2 \left[\frac{ha}{2} \left(1 + \left[\frac{\beta ma}{u'_{mn}{}^2} \right]^2 \right) + \frac{\beta^2 a^4}{u'_{mn}{}^2} \left(1 - \left[\frac{m}{u'_{mn}} \right]^2 \right) \right]} \\
 Q_c &= \omega \frac{\varepsilon k^2 \eta^2 a^4 h \left(1 - \left[\frac{m}{u'_{mn}} \right]^2 \right)}{4 R_S \left[\frac{ha}{2} (u'_{mn}{}^2 + [\beta ma]^2) + \beta^2 a^4 \left(1 - \left[\frac{m}{u'_{mn}} \right]^2 \right) \right]}
 \end{aligned}$$

where we can use the relationships $\omega\mu = \eta k$, $\omega = 2\pi f$, $\beta = p\pi/h$ and the resonant frequency equation previously calculated in (3.32) to further simplify

$$\begin{aligned}
 Q_c &= \frac{\omega^3 \epsilon \mu^2 a^4 h \left(1 - \left[\frac{m}{u'_{mn}}\right]^2\right)}{4R_s \left[\frac{ha}{2} (u'_{mn}{}^2 + [\beta ma]^2) + \beta^2 a^4 \left(1 - \left[\frac{m}{u'_{mn}}\right]^2\right)\right]} \\
 Q_c &= \frac{\epsilon \mu^2 a^4 h \frac{1}{(\sqrt{\mu \epsilon})^3} \left(\sqrt{\left(\frac{u'_{mn}}{a}\right)^2 + \left(\frac{p\pi}{h}\right)^2}\right)^3 \left(1 - \left[\frac{m}{u'_{mn}}\right]^2\right)}{4R_s \left[\frac{ha}{2} (u'_{mn}{}^2 + [\beta ma]^2) + \beta^2 a^4 \left(1 - \left[\frac{m}{u'_{mn}}\right]^2\right)\right]} \\
 Q_c &= \frac{\eta a^4 h \left(\sqrt{\left(\frac{u'_{mn}}{a}\right)^2 + \left(\frac{p\pi}{h}\right)^2}\right)^3 \left(1 - \left[\frac{m}{u'_{mn}}\right]^2\right)}{4R_s \left[\frac{ha}{2} (u'_{mn}{}^2 + [\beta ma]^2) + \beta^2 a^4 \left(1 - \left[\frac{m}{u'_{mn}}\right]^2\right)\right]} \\
 Q_c &= \frac{\eta a h \left(\sqrt{(u'_{mn})^2 + \left(\frac{p\pi a}{h}\right)^2}\right)^3 \left(1 - \left[\frac{m}{u'_{mn}}\right]^2\right)}{4R_s \left[\frac{ha}{2} (u'_{mn}{}^2 + [\beta ma]^2) + \beta^2 a^4 \left(1 - \left[\frac{m}{u'_{mn}}\right]^2\right)\right]} \\
 Q_o \cong Q_c &= \frac{\sqrt{\sigma} h}{4\sqrt{\pi \epsilon} \sqrt{f} a} \frac{\left[\left(\sqrt{(u'_{mn})^2 + \left(\frac{p\pi a}{h}\right)^2}\right)^3 \left(1 - \left[\frac{m}{u'_{mn}}\right]^2\right)\right]}{\left[\frac{h}{2a} (u'_{mn}{}^2 + \left[\frac{p\pi ma}{h}\right]^2) + \left(\frac{p\pi a}{h}\right)^2 \left(1 - \left[\frac{m}{u'_{mn}}\right]^2\right)\right]} \quad (3.50)
 \end{aligned}$$

The final equation shown in (3.50) is valid for TE_{mnp} modes with $p \geq 1$. For a specific mnp mode configuration and given the associated Bessel root value, a cylindrical cavity of radius a , and height h , made of a conducting material with conductivity σ , will have an unloaded Q value approximately equal to that given by (3.50). The terms in brackets are dependent on the mode integers and the cavity dimensions only. For a highly conductive metal like aluminium the conductivity is of the order of 10^7 S/m [143] and does not deviate much over the span of a few gigahertz in frequency, meaning it can be effectively treated as constant. For identical cavities made with different materials the Q of a particular mode will be proportional to $\sqrt{\sigma}$, meaning very high conductivity materials can be used to make high- Q resonators, and the lower the conductivity, the lower the

Q across all modes. Lower conductivity will more significantly reduce the Q of high- Q modes, for example TE_{021} .

3.2.3.2 Q FOR TM_{MNP} MODES

For TM_{mnp} modes the field equations can be written in terms of sinusoidal functions and Bessel functions as shown below in (3.51), (3.52), (3.53), (3.54), (3.55) and (3.56).

$$H_z = 0 \quad (3.51)$$

$$H_r = \frac{j\omega\epsilon m}{k_c^2 r} (A \cos m\theta - B \sin m\theta) J_n(k_c r) e^{-j\beta z} \quad (3.52)$$

$$H_\theta = \frac{-j\omega\epsilon}{k_c} (A \sin m\theta + B \cos m\theta) J'_n(k_c r) e^{-j\beta z} \quad (3.53)$$

$$E_z = (A \sin m\theta + B \cos m\theta) J_n(k_c r) e^{-j\beta z} \quad (3.54)$$

$$E_r = \frac{-j\beta}{k_c} (A \sin m\theta + B \cos m\theta) J'_n(k_c r) e^{-j\beta z} \quad (3.55)$$

$$E_\theta = \frac{-j\beta m}{k_c^2 r} (A \cos m\theta - B \sin m\theta) J_n(k_c r) e^{-j\beta z} \quad (3.56)$$

The wave impedance for TM modes is shown in (3.57)

$$Z_{TM} = \frac{\beta}{\omega\epsilon} = \frac{\eta\beta}{k}. \quad (3.57)$$

When applying these field equations, the electric fields are multiplied by E_0 and magnetic fields by E_0/η .

To perform the calculation for stored energy we can again choose either the magnetic or electric fields as the energies are equal, and it makes sense to work with the magnetic fields as H_z is zero. The stored energy can be calculated using (3.37) with the magnetic fields instead as shown below

$$\begin{aligned}
 W &= \frac{\mu}{2} \int_0^h \int_0^{2\pi} \int_0^a \left(\frac{k^2 m^2 E_0^2}{\eta^2 k_c^4 r^2} \sin^2 m\theta \cos^2 \frac{p\pi z}{h} J_n^2(k_c r) \dots \right. \\
 &\quad \left. + \frac{k^2 E_0^2}{\eta^2 k_c^2} \cos^2 m\theta \cos^2 \frac{p\pi z}{h} J_n'^2(k_c r) \right) r dr d\theta dz, \\
 W &= \frac{\mu k^2 E_0^2}{2 \eta^2 k_c^2} \int_0^h \int_0^{2\pi} \int_0^a \left(\frac{m^2}{k_c^2 r^2} \sin^2 m\theta \cos^2 \frac{p\pi z}{h} J_n^2(k_c r) \dots \right. \\
 &\quad \left. + \cos^2 m\theta \cos^2 \frac{p\pi z}{h} J_n'^2(k_c r) \right) r dr d\theta dz,
 \end{aligned}$$

where as before $\sin^2$ and $\cos^2$ of $m\theta$ can be evaluated to π but the evaluation of $\cos^2 p\pi z/h$ must also be considered where $p = 0$. This leads to two variations of the equation for $p = 0$, where the cosine terms evaluate to h and for $p \geq 1$ where they evaluate to $h/2$.

$$\begin{aligned}
 W &= \frac{\mu k^2 E_0^2}{2 \eta^2 k_c^2} h\pi \int_0^a \left(\frac{m^2}{k_c^2 r^2} J_n^2(k_c r) + J_n'^2(k_c r) \right) r dr, \text{ for } p = 0 \\
 W &= \frac{\mu k^2 E_0^2}{2 \eta^2 k_c^2} \frac{h\pi}{2} \int_0^a \left(\frac{m^2}{k_c^2 r^2} J_n^2(k_c r) + J_n'^2(k_c r) \right) r dr, \text{ for } p \geq 1
 \end{aligned}$$

where the remaining integral can be evaluated to

$$\frac{u_{mn}^2}{2} J_n'^2(u_{mn}),$$

leaving us with

$$\begin{aligned}
 W &= \frac{\mu k^2 E_0^2}{2 \eta^2 k_c^2} h\pi \frac{u_{mn}^2}{2} J_n'^2(u_{mn}), \text{ for } p = 0 \\
 W &= \frac{\mu k^2 E_0^2}{2 \eta^2 k_c^2} \frac{h\pi}{2} \frac{u_{mn}^2}{2} J_n'^2(u_{mn}), \text{ for } p \geq 1
 \end{aligned}$$

which with simplification and substitution of (3.29) gives the final equation for stored energy in TM_{mnp} modes in a cylindrical cavity shown in (3.58)

$$W = \begin{cases} \frac{\mu k^2 E_0^2 h \pi a^2}{4 \eta^2} J_n'^2(u_{mn}), & p = 0 \\ \frac{\mu k^2 E_0^2 h \pi a^2}{8 \eta^2} J_n'^2(u_{mn}), & p \geq 1 \end{cases} \quad (3.58)$$

The power loss in the cavity walls can be calculated using the same process as performed for the TE modes, where the tangential magnetic fields are integrated over the curved wall surface and the two circular end plates as in (3.40).

$$\begin{aligned} P_c(\text{walls}) &= \frac{R_s}{2} \left[\int_0^h \int_0^{2\pi} \left(\frac{k^2 E_0^2}{\eta^2 k_c^2} \cos^2 m\theta \cos^2 \frac{p\pi z}{h} J_n'^2(u_{mn}) \right) a d\theta dz \right] \\ P_c(\text{walls}) &= \frac{R_s}{2} \left[\frac{k^2 E_0^2 \pi h a}{\eta^2} J_n'^2(u_{mn}) \right] \text{ for } p = 0 \\ P_c(\text{walls}) &= \frac{R_s}{2} \left[\frac{k^2 E_0^2 \pi h a}{2 \eta^2} J_n'^2(u_{mn}) \right] \text{ for } p \geq 1 \\ P_c(\text{plates}) &= \frac{R_s}{2} \left[2 \int_0^{2\pi} \int_0^a \left(\frac{k^2 m^2 E_0^2}{\eta^2 k_c^4 r^2} \sin^2 m\theta J_n^2(k_c r) \dots \right. \right. \\ &\quad \left. \left. + \frac{k^2 E_0^2}{\eta^2 k_c^2} \cos^2 m\theta J_n'^2(k_c r) \right) r dr d\theta \right] \\ P_c(\text{plates}) &= \frac{R_s}{2} \left[2 \frac{k^2 E_0^2 \pi}{\eta^2 k_c^2} \int_0^a \left(\frac{m^2}{k_c^2 r^2} J_n^2(k_c r) + J_n'^2(k_c r) \right) r dr \right] \\ P_c(\text{plates}) &= \frac{R_s}{2} \left[2 \frac{k^2 E_0^2 \pi}{\eta^2 k_c^2} \frac{u_{mn}^2}{2} J_n'^2(u_{mn}) \right] \\ P_c(\text{plates}) &= \frac{R_s}{2} \left[\frac{k^2 E_0^2 \pi a^2}{\eta^2} J_n'^2(u_{mn}) \right] \\ P_c &= \begin{cases} \frac{R_s}{2} \frac{k^2 E_0^2 \pi}{\eta^2 u_{mn}^2} J_n'^2(u_{mn}) \left[1 + \frac{h}{a} \right], & p = 0 \\ \frac{R_s}{2} \frac{k^2 E_0^2 \pi}{\eta^2 u_{mn}^2} J_n'^2(u_{mn}) \left[1 + \frac{h}{2a} \right], & p \geq 1 \end{cases} \quad (3.59) \end{aligned}$$

The equation for Q_c can then be determined by substituting (3.58) and (3.59) into (3.34) to give (3.50)

$$Q_c = \omega \frac{\frac{\mu k^2 E_0^2 h \pi}{4 \eta^2 u_{mn}^2} J_n'^2(u_{mn})}{\frac{R_s}{2} \frac{k^2 E_0^2 \pi}{\eta^2 u_{mn}^2} J_n'^2(u_{mn}) \left[1 + \frac{h}{a}\right]}$$

$$Q_c = \omega \frac{\mu a}{2 R_s \left[\frac{a}{h} + 1\right]}, p = 0$$

$$Q_c = \omega \frac{\mu a}{2 R_s \left[2 \frac{a}{h} + 1\right]}, p \geq 1$$

where we can use the resonant frequency equation previously calculated in (3.32) and the surface resistance equation from (3.39) to further simplify to yield the final equation for the unloaded Q of TM_{mnp} modes of a cylindrical cavity in (3.60).

$$Q_o \cong Q_c = \frac{\frac{\sqrt{\sigma}}{2\sqrt{\epsilon\pi}\sqrt{f}} \frac{u_{mn}}{\left[\frac{a}{h} + 1\right]}, \quad p = 0}{\frac{\sqrt{\sigma}}{2\sqrt{\epsilon\pi}\sqrt{f}} \frac{\sqrt{(u_{mn})^2 + \left(\frac{p\pi a}{h}\right)^2}}{\left[2 \frac{a}{h} + 1\right]}, \quad p \geq 1} \quad (3.60)$$

As with the Q for TE_{mnp} modes, (3.60) can be seen to be dependent on the conductivity of the cavity material, the resonant frequency, the mode integers and associated Bessel roots, and the cavity dimensions. If the Q values of various TE and TM modes are plotted against a varying conductivity in the region of 10^7 S/m as in Figure 3.5, we can see the dependence of all modes on the material conductivity. The modes that are naturally higher in Q are much more affected by changes in conductivity.

A term that appears frequently in calculations for Q is the ratio of the cavity dimensions, the radius divided by the height. If the same modes plotted for Figure 3.5 are used and their Q values plotted instead against the radius-to-height ratio we can observe more interesting mode-specific dependence that is not general for all modes. This is shown in Figure 3.6 for a fixed conductivity of $2.5 \cdot 10^7$ S/m. It can be seen that for some modes Q is maximised for particular cavity dimension ratios, for example

the TE_{011} and TE_{012} modes have a maximum Q for cavities with radius approximately half the height. For the shown TM modes, they have maximum Q for cavities with very low a/h ratio, and they decrease non-linearly as the ratio increases.

The frequency of different modes is also dependent on the cavity dimensions. Plotting the frequency of selected modes against the cavity dimension ratio reveals a reciprocal relationship; very low cavity dimension ratios produce very high frequencies which stabilise for very high cavity dimension ratios. This is shown in Figure 3.7, where the different rates of change for frequencies of different modes are apparent. This is important when designing a cavity as good separation of modes is important for avoiding degenerate modes with more chaotic or unpredictable field distributions. A more thorough consideration of this

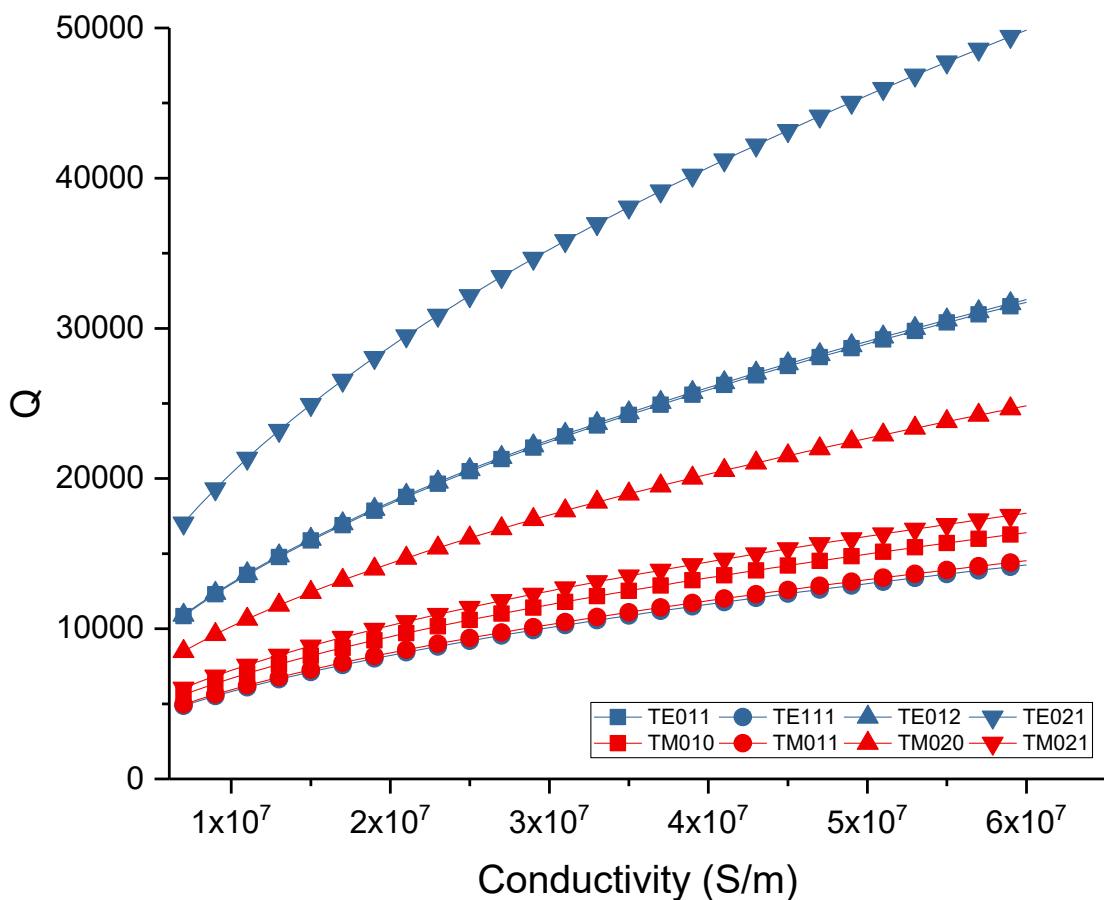


Figure 3.5 – Q of various TE and TM modes with varied conductivity

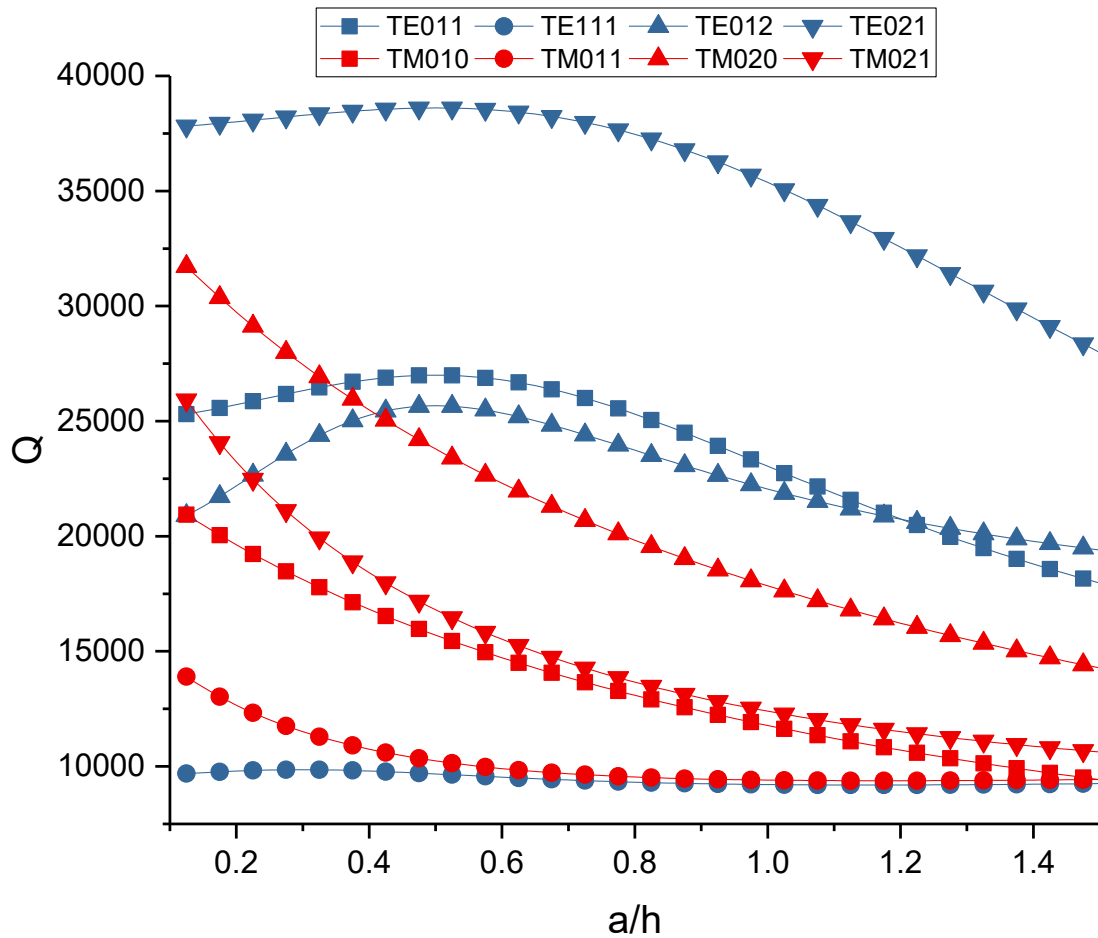


Figure 3.6 – Q for various TE and TM modes against cavity dimension ratio a/h , by varying a

can be done for all potential modes and an appropriate set of cavity dimensions chosen, depending on the desired operating modes or applications.

3.2.4 BANDWIDTH

When considering the resonant frequency of a cavity resonator, or in general a resonant network, it might be thought of as a single frequency which the system resonates and functions at. For real systems this is not exactly the case as such a system would have no room for slight deviations in frequency and would not be practical to use. In fact, the resonant frequency and the frequencies immediately surrounding it provide a usable range within which to operate, and this range is referred to as the bandwidth [144][145]. A narrow bandwidth resonator will be

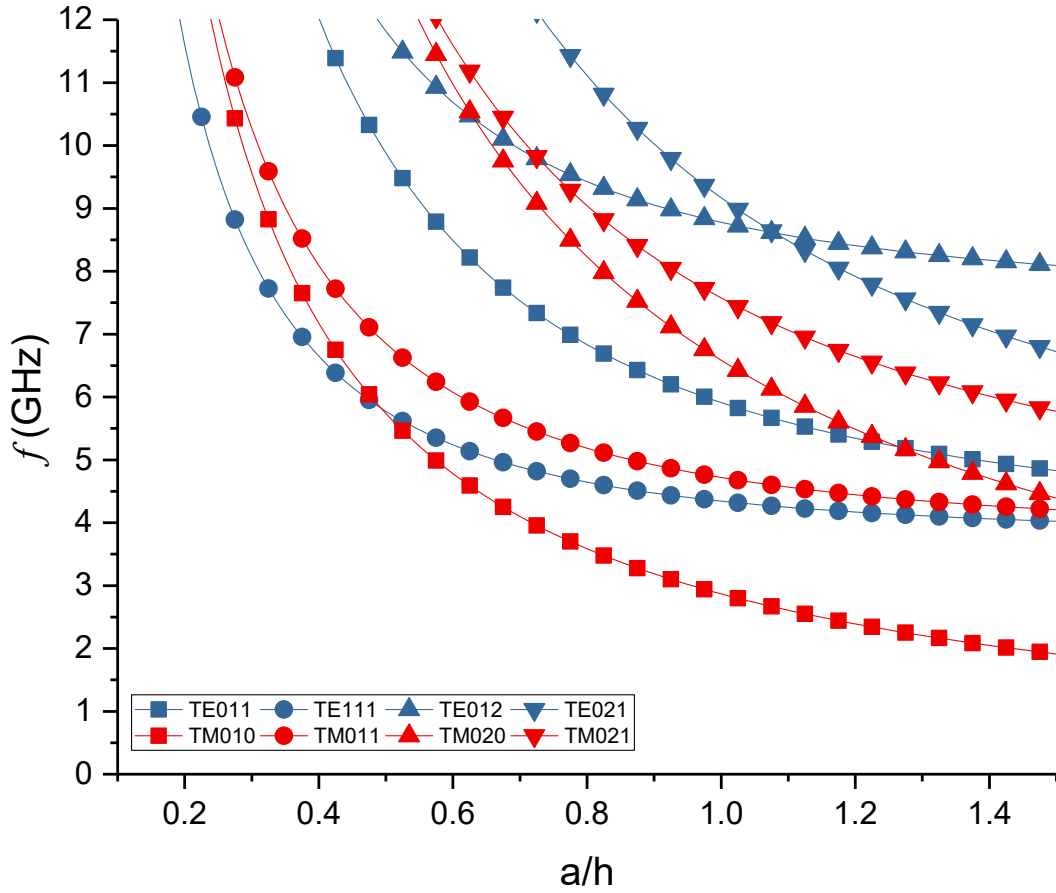


Figure 3.7 – Resonant frequency of various TE and TM modes against the cavity dimension ratio a/h

useful over a small window of frequencies but will often be higher in Q with an increased frequency selectivity, with the opposite being true for wider bandwidths.

If we consider a resonator to have an equivalent circuit model made of passive components R , L and C as in Figure 3.8, operating at a frequency ω , then its input impedance Z_{in} is the summation of the contribution from all three components as shown in (3.61) [128][146]

$$Z_{in} = R + j\omega L - \frac{1}{j\omega C}. \quad (3.61)$$

At resonance, the stored magnetic and electric energies are equal, here represented by the inductor and capacitor. This means the input impedance is equal to the resistance R .

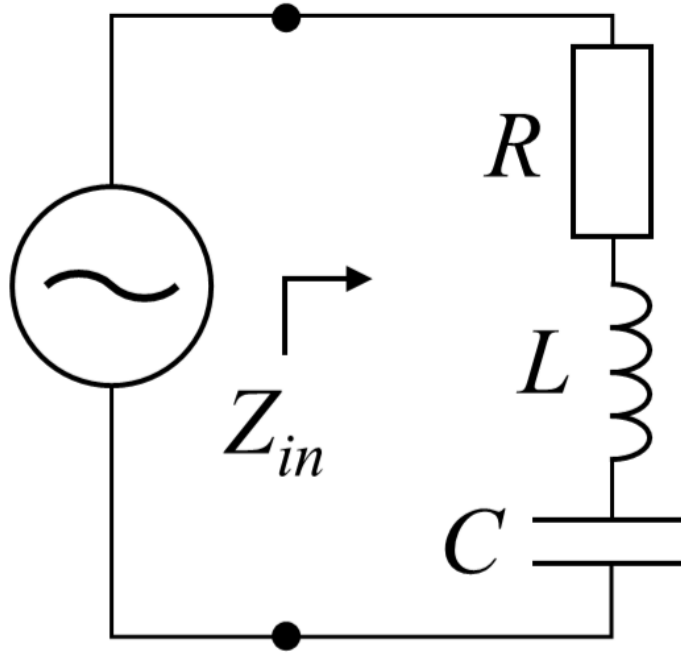


Figure 3.8 – Lumped element RLC representation of a resonator

If we consider the region around the original resonant frequency ω_0 , where it has only been shifted by a small amount $\Delta\omega$, meaning $\omega = \omega_0 + \Delta\omega$ the input impedance can be rewritten as being approximately equal to (3.62)

$$Z_{in} \cong R + j \frac{2RQ_o\Delta\omega}{\omega_0}. \quad (3.62)$$

This can then be used to relate the Q and bandwidth (BW) of the resonator. The boundaries of the bandwidth are application dependent but commonly the points at which the power delivered to the circuit is half of its maximum value are used. The maximum power occurs at resonance where Z_{in} is equal to R , so the half power points occur where $|Z_{in}|^2 = 2R^2$. The small variation in frequency is applied to both sides of the resonant frequency to obtain the full bandwidth, meaning the fractional frequency change $\Delta\omega/\omega_0$ is equal to half the bandwidth i.e. $BW/2$. Applying these conditions to (3.62) gives (3.63)

$$|R + jRQ_oBW|^2 = 2R^2. \quad (3.63)$$

which then gives the relationship between Q and BW as (3.64) [128].

$$BW = \frac{1}{Q_o} \quad (3.64)$$

This relationship is incredibly useful for real-world applications including coupling and perturbation measurements. The bandwidth is often easily measurable given it represents simply a difference of two frequencies. This also highlights the inverse relationship and trade-off between the Q and BW as mentioned previously; resonators with very high quality factor will have narrow bandwidths.

3.2.5 S-PARAMETERS

When working with resonant cavities the scattering parameters or S -parameters are useful tools in assessing the quality of connections, power reflection and delivery and taking microwave measurements. S -parameters associate the voltages incident and returning to ports in a system. This could be ports on a vector network analyser (VNA) which often have four ports, or simply the single output port of an amplifier system which will only have one S -parameter based on the delivered and reflected power to that port. The general form of an S -parameter is shown in (3.65) [128][147]

$$S_{AB} = \frac{V_A^-}{V_B^+} \quad (3.65)$$

where A and B identify the ports and the V^- indicates the voltage of the reflected wave and V^+ indicates the voltage of the forward travelling or incident wave. For an n -port network, there will be n^2 S -parameters to account for interactions between all ports including reflection, transmission and crosstalk or interference. Only one- or two-port networks will be considered further. As S -parameters are ratios they are unitless but are often measured in decibels (dB) which can have different values depending on if the measurement is that of power or voltage. For a power ratio P_R , or a voltage ratio V_R the S -parameter in dB is equal to $10\log(P_R)$ or $10\log(V_R^2) = 20\log(V_R)$. Of particular interest are the forward voltage gain S_{21} , the transmission coefficient from an input port (usually

designated port 1) to an output port (usually designated port 2), and S_{11} , the input port reflection coefficient for a network terminated in Z_o .

3.2.5.1 S_{11} , REFLECTION COEFFICIENT

S_{11} is the reflection coefficient of a system which gives an indication of how much reflected signal is returning as a proportion of the original incident signal. This shows how well matched the system is, with an S_{11} of zero meaning no reflections or a perfect match, and an S_{11} of 1 meaning mismatch and total reflection. When S_{11} is displayed in the logarithmic dB scale zero dB means total reflection and increasingly negative values represent less reflection. A measurement of -3 dB means 50 % of power is being reflected, -20 dB means 1 % of power is reflected and -30 dB means only 0.1 % of power is reflected.

When displayed graphically over a range of frequencies the reflection coefficient of a resonant cavity around a resonant frequency will display an inverted Lorentzian curve, with sharper dips indicating higher Q . This allows measurements to be taken of resonant frequency and Q for a particular mode and even perturbation measurements can be performed using only the S_{11} value. A sharper S_{11} curve can be obtained with increased coupling strength which for cavity heating applications is desirable, but for precise perturbation measurements a two-port system is more often employed with the transmission coefficient being the more important quantity as it typically has a greater signal-to-noise ratio, allowing for accurate measurements of even weak signals.

3.2.5.2 S_{21} , TRANSMISSION COEFFICIENT

The transmission coefficient of a two-port system is often referred to as S_{21} and represents the proportion of an EM wave transmitted from the incident port to the output, or second port. This is particularly useful for performing microwave cavity perturbation measurements where measurements of the S_{21} can be made and the centre frequency and 3 dB bandwidth are observed and recorded. The 3 dB bandwidth is the

bandwidth between the points on the curve which are 3 dB below the peak value, representing a 50 % power reduction. Explicit calibration is not required for these perturbation measurements as they rely on relative measurements rather than the absolute values of transmission or reflection coefficient. However, port symmetry is important for perturbation measurements as the changes measured are often incredibly small; port asymmetry can significantly affect the precision of perturbation measurements. A basic diagram showing the signal flows in a two-port system connected to a device under test (DUT) is included in Figure 3.9.

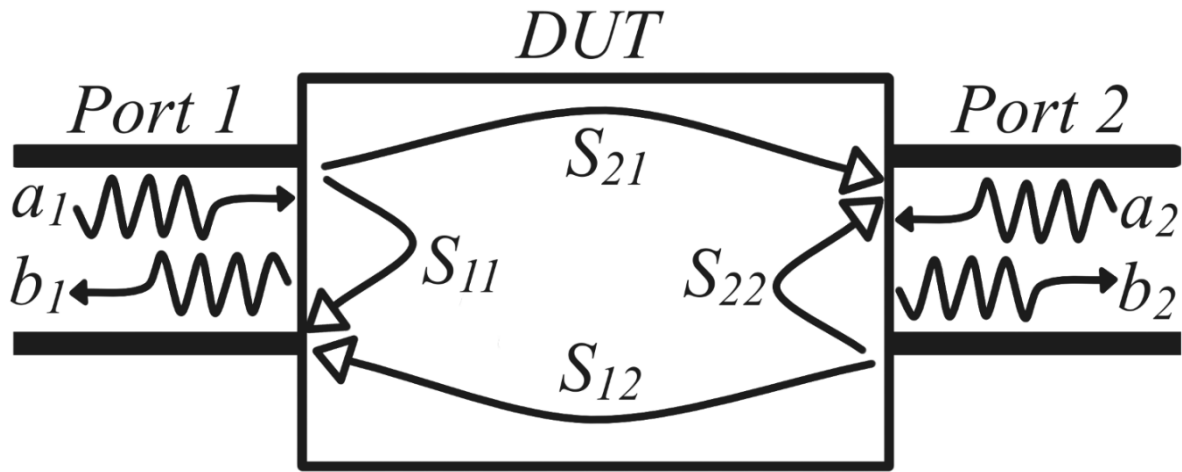


Figure 3.9 – Signal flow diagram illustrating the approximate physical origins of S-parameters

Measuring these quantities for an empty cavity and then adding in a material that slightly perturbs the fields causes small changes in the fields, the resonant frequency and the bandwidth. The small changes it causes can be used to calculate the electromagnetic qualities of the material, namely the complex permeability and permittivity. This will be explained in greater detail in Chapter 4 which discusses this procedure and calculation for experimental examples.

Shown in Figure 3.10 are two curves of simulated S_{21} for a resonant cavity around 2.5495 GHz. This cavity is coupled using two recessed coaxial probes and the sample is measured vertically through the centre of the cavity in the TM_{010} resonant mode i.e. the electric field. The

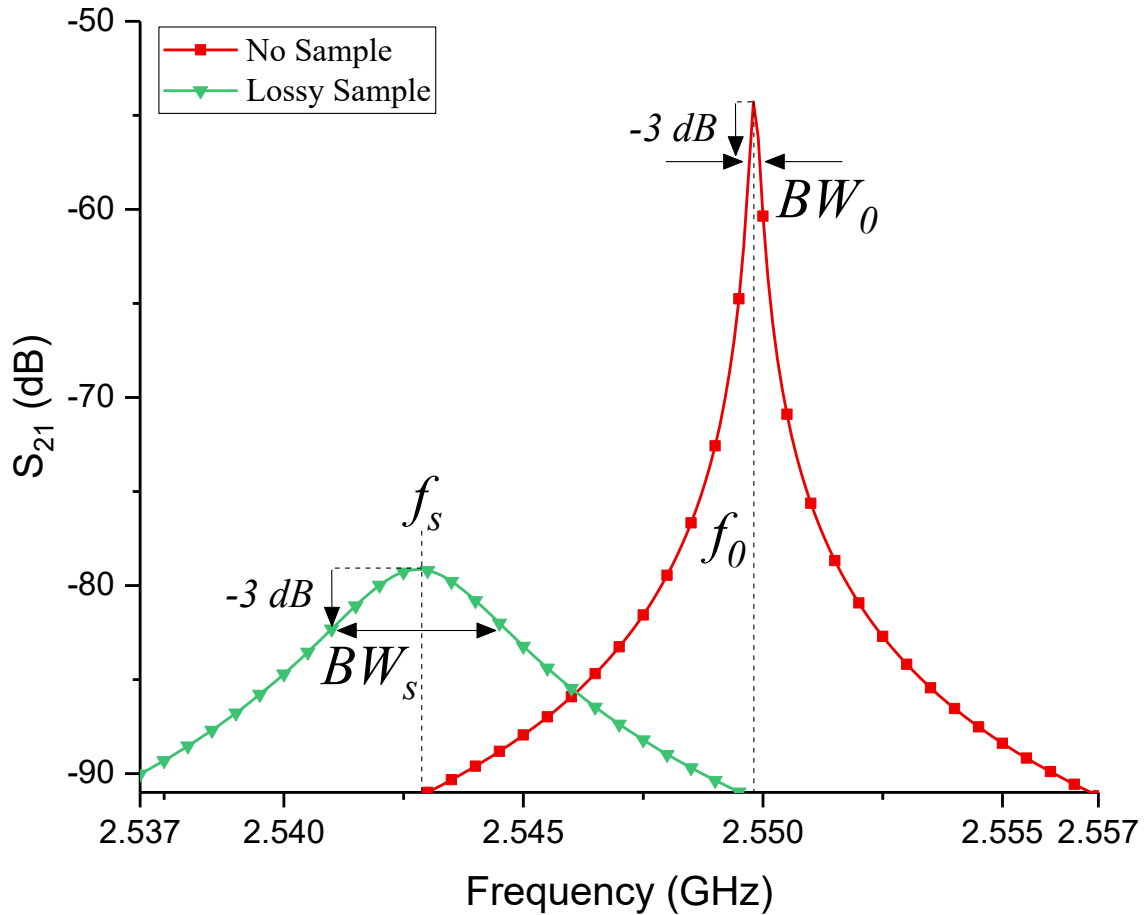


Figure 3.10 – S_{21} response of a simulated cavity in the electric field of the TM_{010} resonant mode. Two curves are shown to represent the unperturbed state and the presence of an electrically lossy sample

changing response is indicative of a material with non-zero dielectric loss. The sharper, taller curve on the right shows the response of the cavity when no sample is present, representing the unperturbed state. The other shallower curve shows the cavity response when an electrically lossy sample is introduced. This simulated cavity is very weakly coupled as indicated by the extremely low values for S_{21} in the range of -55 to -80 dB, which allows for high sensitivity to changes in the cavity volume. This is preferable in cavity perturbation measurements. A key limitation to note here is the accuracy of the magnitude and phase of S_{21} measurements. For the particular VNA used here and many similar VNAs the uncertainty in these measurements will begin to increase exponentially as it approaches the noise floor of the instrument; at an S_{21}

of -100 dB the uncertainty may be at or approaching 10 dB, making the measurements highly unreliable.

The real part of the material's permittivity (or permeability if using the magnetic field) causes the resonant frequency to decrease, translating it to the left at a new centre frequency of f_s . The second part of the complex permittivity indicates how lossy the material is in response to electric field exposure, and on the plot causes the broadening of the Lorentzian peak and subsequently the 3 dB bandwidth. This decreases the resonator Q . These changes in frequency and Q can be used to calculate the complex permittivity or permeability of an unknown material, or those of an established material for comparison to previous experiments and literature.

3.3 CONCLUSIONS

In this chapter the concept of cavity resonance has been discussed, beginning at Maxwell's equations for electromagnetism. These equations are developed to be applicable for both TE and TM waves and subsequently the TE and TM resonant modes created by a cavity's boundary conditions. These equations are made applicable to cylindrical systems using cylindrical coordinates and Bessel functions. These systems are the core use case in this work with a number of cylindrical cavities used later for characterisation and microwave heating applications.

Two key quantities related to a resonant cavity's operation are discussed in the resonant frequency and the quality factor, Q . The equation for cylindrical cavity resonant frequency is shown which relates the cavity radius and height to its mnp mode integers. A select number of simulated TM and TE mode distributions are shown for both the magnetic and electric fields within a cavity. These distributions are important to be aware of when designing or using resonant cavities as the locations within the cavity where each field is at a maximum or a minimum can be crucial to effectively use the cavity. The fields can have symmetries dependent

on the mode integers which can be useful to exploit. Some modes are more suitable for heating or characterisation, often with suitable high intensity field regions at the centre of the cavity which is easy to identify when operating the cavity. Some higher order modes can be much more complex but can still be useful especially if they are insensitive to perturbations which makes them well-suited to function as a reference mode.

The Q of a resonator is discussed at a fundamental level with reference to the energy in the system. While the equation for cavity frequency is a relatively straightforward calculation, based on cavity dimensions, Bessel roots and some constant factors, the cavity Q requires a more detailed examination to fully appreciate. The expressions for Q for both TM and TE modes are more complex, involving the cavity material's conductivity, the resonant frequency and like the frequency, the cavity dimensions. The Q of various TE and TM modes is shown for varied cavity dimension ratios and material conductivity which significantly change the expected Q of the resonator and therefore how well it may operate as a measurement cavity or for heating applications.

Concluding this chapter are discussions of the bandwidth and S -parameters, which are the readily available measurement tools we have to interact with a cavity. Measurement of S -parameters and resonant signal bandwidth with microwave instruments like a VNA allow the assessment of cavity performance or the ability to perform processes like cavity perturbation. From a typical VNA response a resonant frequency can be observed and recorded. Along with the bandwidth measurements this allows calculation of Q . Using appropriate data logging software these qualities can be automatically recorded over extended periods of time meaning calculations of material permeability and permittivity can be made in response to other external factors, such as material temperature.

Chapter 4

4 MICROWAVE CAVITY PERTURBATION

4.1 ELECTROMAGNETIC MATERIAL QUALITIES

Materials interact with EM fields differently depending on their properties much like with other phenomena such as thermodynamics, chemical reactions or mechanical integrity. As electromagnetic fields consist of both a magnetic and electric component there are two properties used to describe materials' interactions with each. These are the permeability which describes interactions with magnetic fields and permittivity which describes interactions with electric fields.

These quantities are often described as a single number, however when they are examined more closely, they can be more accurately defined as complex numbers, consisting of both a real and imaginary part [128][148]. The real part of each quantity describes how much the magnetic or electric fields are permitted to enter the material, and hence the magnetic or electric energy storage capability. The complex or imaginary part of each term describes the dissipated magnetic or electric energy in the material and hence represents the electromagnetic losses in response to a magnetic or electric field. This more complete description of these properties allows deeper analysis of the electromagnetic energy storage and losses exhibited by a material, comparisons between materials and the ability to assess materials' frequency or temperature-dependent electromagnetic responses. This is particularly useful for characterising how well a material is heated by electromagnetic interactions or how well it electrically insulates for example.

4.1.1 PERMEABILITY

The permeability of free space has been previously defined in (3.6) as the scalar relationship between the magnetic flux density and magnetic field strength. This is true for fields in free space but when working with field interactions with real materials the actual permeability (μ) is more convenient to describe as a multiplication of the permeability of free space (μ_0) and a relative term (μ_r) which is shown in (4.1)

$$\mu = \mu_0 \mu_r \quad (4.1)$$

As we are typically not concerned with the actual values of permeability in Henries per meter (H/m) it is common practice to simply refer to the relative part, a unitless value which is often a number between one and a few thousand for typical materials. This makes direct comparison of material properties simple.

Complex permeability can be defined as the combination of two parts. These are the commonly used real part (μ_1 sometimes also labelled μ') and the imaginary part (μ_2 sometimes also labelled μ''). Together these terms form part of the relative complex permeability as shown in (4.2)

$$\mu_r = \mu_1 - j\mu_2 \quad (4.2)$$

where μ_1 represents how much energy can be stored by the material in response to applied magnetic fields and μ_2 represents the dissipated energy in the material in response to an applied magnetic field. High values of μ_1 represent a material which can hold a lot of stored magnetic potential energy such as iron, while a value of one represents no additional energy storage relative to a vacuum. A material with $\mu_2 = 0$ is magnetically lossless with any non-zero value meaning a material which dissipates magnetic energy, often in the form of heat. For kHz or MHz frequencies values for μ_2 can be in the region of tens of thousands [149] but for microwave frequencies in the GHz range these values may not even exceed one. However, this can still produce significant heat

dissipation, depending on other factors such as applied field strength and material mass.

4.1.2 PERMITTIVITY

Permittivity is a similar quantity to permeability but concerns electric fields and materials' interactions with them. As with permeability, permittivity is defined relative to a constant which represents the permittivity of free space, ϵ_0 , which is shown in (3.5). Shown in (4.3) is the relationship between permittivity (ϵ), the permittivity of free space (ϵ_0) and relative permittivity (ϵ_r).

$$\epsilon = \epsilon_0 \epsilon_r \quad (4.3)$$

Similarly to permeability, the relative permittivity is often quoted and reported in works rather than the actual value of permittivity in Farads per meter (F/m) and the relative complex permittivity can be split into two components as in (4.4)

$$\epsilon_r = \epsilon_1 - j\epsilon_2 \quad (4.4)$$

where ϵ_1 (sometimes also ϵ') represents how much energy can be stored by the material in response to applied electric fields and ϵ_2 (sometimes also ϵ'') represents the dissipated energy in the material in response to an applied electric field. ϵ_1 is commonly reported for many materials and is often also called the dielectric constant [97][150].

The mechanisms of dielectric loss are different to those for magnetic loss and although many materials experience relatively low losses at GHz frequencies, far fewer materials exhibit magnetic losses. This is very useful when considering materials for their capacity to heat by microwave exposure. One of the main drivers for dielectric heating at these frequencies is the electronic polarisation of molecules. Many common materials like water have uneven distribution of charge across the molecule [151], and these polar molecules can be rotated by a high

frequency alternating electric field, which can lead to a significant heating effect. Magnetic loss mechanisms around GHz frequencies are typically driven by domain wall and natural ferromagnetic resonant effects [93][97], which occur in far fewer materials. This means heating via magnetic mechanisms can be much more selective in nature than commonly used microwave dielectric heating methods.

Many materials have been extensively dielectrically characterised, especially those which are very low loss like quartz, silica, mica and TeflonTM (PTFE) [152][153][154][155], which are extensively used in existing microwave applications.

4.1.3 LOSS TANGENT

Another common way that the permeability or permittivity of a material is reported is through the loss tangent. This is simply the imaginary part of permeability divided by the real part to give the magnetic loss tangent and the same for the electric loss tangent as shown in (4.5).

$$\tan \delta_m = \frac{\mu_2}{\mu_1}, \quad \tan \delta_e = \frac{\varepsilon_2}{\varepsilon_1}. \quad (4.5)$$

The loss tangent is useful for at-a-glance comparisons of the relative losses of materials in either electric or magnetic fields. Given the loss tangent is the ratio of the energy dissipated to the energy stored it could be considered similar to the interpretation of Q for resonators as in (3.33), where the reciprocal of the loss tangent could represent the quality of a very low loss material. For example, a fused quartz sample with a loss tangent $\tan \delta_e$ of $0.06 \cdot 10^{-3}$ would have loss-quality factor of over 16,600, showing it is a very low loss material.

It is important to note that permeability, permittivity and therefore loss tangent, are frequency and temperature dependent [148][149][156]. Some materials may not exhibit strong relationships but over large frequency or temperature ranges there are typically wide ranges of complex permeability and permittivity. Some materials may have

drastically different quantities even over very small frequency ranges. When considering measured or reported values for permeability or permittivity they should be associated either with a particular temperature and frequency, or a range of each. Other material properties can affect how a material heats, or given their changes could indicate how a material has changed such as density, chemical composition and structure e.g. crystal lattice structure, and these factors should also be considered.

4.2 CAVITY PERTURBATION TECHNIQUE

Measuring the electromagnetic qualities of a material is an important and difficult task. A popular method for doing so is the use of a resonant cavity to measure the changes in the EM fields caused by inserting a small quantity of material. This method is suitable for frequencies in the range of around 1-10 GHz, that is microwave frequencies and is particularly useful for accurate measurements of relatively low loss materials. This is known as the microwave cavity perturbation (MCP) method [128][157][158][159].

Resonant cavities are very sensitive to changes in their shape and filling material, and this high sensitivity is what allows the accurate measurement of permittivity and permeability. Recording the resonant frequency and bandwidth, or Q , when a material is present in a cavity allows accurate calculation of the complex permittivity and permeability terms. As well as the high sensitivity, the MCP method is non-contact, non-destructive and can be done in real-time to observe changes in the material composition, such as those induced by temperature changes.

The major limitations of the MCP technique are related to the sample size and preparations. Samples must be very small so as not to significantly perturb the field distributions. Measurement of uniform samples is ideal but this can be difficult when measuring powders for example, which must be prepared to minimise air gaps, voids, or clumping to provide the

most accurate measurements. Samples with unusual shapes may need specialised cavity designs to measure, or be prepared in a way to alter their shapes to reduce the effect of polarisation. To overcome some of these difficulties a number of assumptions and approximations are made which are discussed below.

4.2.1 ASSUMPTIONS AND APPROXIMATIONS

When performing MCP there are a number of considerations to be made about the sample material and the fields inside the cavity that make the calculations feasible [160]. As the perturbation of a cavity is sensitive to the material properties and the shape changes, to obtain measurements of the material properties the impact of any shape perturbation must be minimised. This is achieved by shrinking the shape of the material into a small rod that extends through the entire length of the cavity parallel to the field, thus minimising the perturbation contribution from the sample shape and its depolarisation or demagnetising factor.

Minimising the actual material volume is also important as a key assumption made in MCP is that the field distribution is not significantly different as compared to the unperturbed state. This reduces the changes in the system to only be a small change in electric or magnetic field strength and thus a small change in frequency and bandwidth, caused primarily by the sample permittivity and permeability.

Another useful assumption is made based on the sample placement in the resonant EM fields. When measuring these quantities, it is much simpler to measure one at a time. This is done by choosing points within the resonant cavity where one field (electric or magnetic) is at a maximum and the other is at a minimum and can be considered to be approximately zero for the purposes of calculation. The field of interest is also assumed to be constant across the entire length of the sample.

4.2.2 MCP EQUATIONS

An equation for the MCP technique can be derived from Maxwell's equations [124][125] that includes the electric and magnetic field changes based on the material perturbation of permittivity ($\Delta\epsilon$) and permeability ($\Delta\mu$) [128][161][162]. This is shown in (4.6)

$$\frac{\omega - \omega_0}{\omega} = \frac{- \int_{V_0} (\Delta\epsilon \cdot \bar{E} \cdot \bar{E}_0^* + \Delta\mu \cdot \bar{H} \cdot \bar{H}_0^*) dv}{\int_{V_0} (\epsilon \cdot \bar{E} \cdot \bar{E}_0^* + \mu \cdot \bar{H} \cdot \bar{H}_0^*) dv}. \quad (4.6)$$

where ω_0 is (angular) resonant frequency of the unperturbed cavity, ω is the resonant frequency of the perturbed cavity, $\bar{E}_0^*$ and $\bar{H}_0^*$ are the complex conjugates of the electric and magnetic fields of the original unperturbed cavity and $\bar{E}$ and $\bar{H}$ are the electric and magnetic fields of the perturbed cavity, with the integration over the volume of the cavity V_0 . Typically the perturbed frequency of the cavity is lower than the unperturbed frequency, representing a negative shift.

Using the discussed assumption that the material perturbation is small and thus the difference in field strength between the original and perturbed states is minimal, the perturbed fields can be approximated to be equal to the original fields. Given the frequency change is also small the denominator of ω can also be approximated to ω_0 . This enables (4.6) to be simplified to (4.7)

$$\frac{\omega - \omega_0}{\omega_0} \cong \frac{- \int_{V_0} (\Delta\epsilon \cdot |\bar{E}_0|^2 + \Delta\mu \cdot |\bar{H}_0|^2) dv}{\int_{V_0} (\epsilon \cdot |\bar{E}_0|^2 + \mu \cdot |\bar{H}_0|^2) dv}. \quad (4.7)$$

which relates a fractional difference in resonant frequency to a relative change in material permittivity and permeability. By choosing measurement points in the cavity where either the electric field or magnetic field is approximately zero the related terms can be ignored and either the permeability or permittivity measured by the sole contributions from the relevant field.

Employing the above assumptions and simplifications, practical equations for the direct calculation of complex permeability and permittivity can be derived, with the real parts based on frequency shift and the imaginary parts based on observed changes in Q or bandwidth [39][96][163]. The equation for μ_1 is shown in (4.8)

$$\mu_1 = 2 \frac{f_0 - f_s}{f_0} \frac{V_C}{V_S} G_{\mu-mnp} + 1 \quad (4.8)$$

where f_0 and f_s are the unperturbed frequency and frequency with sample present respectively. V_C and V_S are the volume of the cavity and the sample and $G_{\mu-mnp}$ is the mode-specific cavity filling constant, associated with the cavity and sample volumes, the cavity resonant mode and the magnetic field strength in both the cavity and the sample. This will be discussed later with the cavity construction and simulation.

A similar equation can be derived for μ_2 and is shown in (4.9)

$$\mu_2 = \left(\frac{1}{Q_S} - \frac{1}{Q_0} \right) \frac{V_C}{V_S} G_{\mu-mnp} \quad (4.9)$$

where the unperturbed and perturbed values of Q ; Q_0 and Q_S are used instead of frequency.

Similar equations exist for the calculation of complex permittivity values and are shown in (4.10) and (4.11)

$$\varepsilon_1 = 2 \frac{f_0 - f_s}{f_0} \frac{V_C}{V_S} G_{\varepsilon-mnp} + 1 \quad (4.10)$$

$$\varepsilon_2 = \left(\frac{1}{Q_S} - \frac{1}{Q_0} \right) \frac{V_C}{V_S} G_{\varepsilon-mnp} \quad (4.11)$$

using $G_{\varepsilon-mnp}$ instead of $G_{\mu-mnp}$, which is the same scaling factor but calculated based on the electric field instead of magnetic field.

A diagram representative of the expected S_{21} VNA (vector network analyser) response for different types of sample is shown in Figure 4.1 over a span of 20 MHz. This shows the unperturbed cavity response on the top right in red with a sharp narrow peak at a particular resonant frequency f_0 . If a lossless sample is introduced which has a higher real

permittivity or permeability than air i.e. >1 then it would appear like the yellow trace on the top left. This shows a negative frequency shift proportional to the measured real permeability or permittivity of the sample, but with no significant change in the sharpness of the peak. This illustrates the lossless nature of this sample as the bandwidth and therefore the Q are unchanged which means the sample exhibits no dielectric or magnetic loss, depending on the measurement mode. The blue trace on the bottom right illustrates a reasonable lossy sample but with a real part or permeability or permittivity equal to 1. This trace shows no frequency shift but a significant flattening of the peak, meaning an increased bandwidth, lower Q , and higher loss. The green trace represents a more realistic scenario of a sample which has both a real permeability/permittivity greater than one and a significant loss. In this

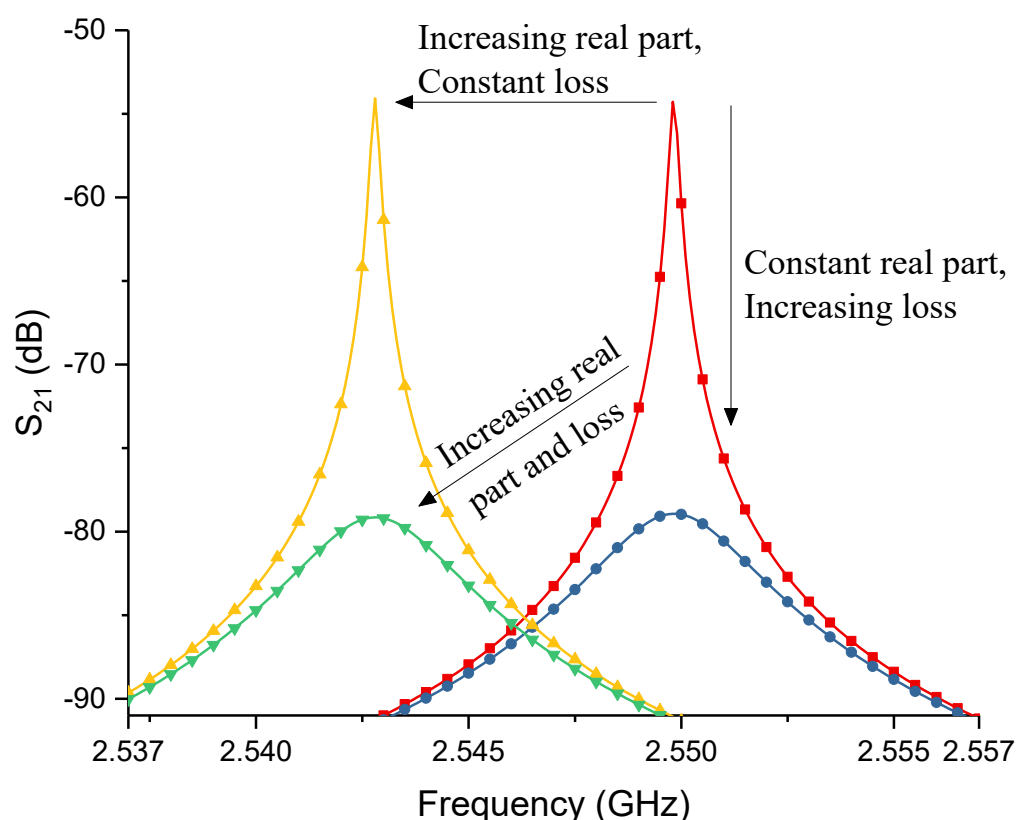


Figure 4.1 – Simulated S_{21} responses for an empty cavity (red), samples with increased real permittivity/permeability (yellow), increased imaginary permittivity/permeability i.e. loss (blue) and more realistic samples with both components (green)

situation a sample will cause a perturbation by both shifting the resonant frequency and flattening the curve. Measuring these differences allows the use of the equations (4.8), (4.9), (4.10) and (4.11) to calculate the desired values.

4.3 CAVITY DESIGN AND CONSTRUCTION

There are many types of resonant structures including coplanar waveguides, microstrip rings, dielectric-filled resonators and cavity resonators [164][165][166], which can be further described by their shape, for example rectangular, spherical or cylindrical. Hollow cavities are employed here for the MCP procedure in part due to their high sensitivity to small changes in material properties. This is because like waveguides, they can maintain high energy densities which in turn leads to high Q factor as compared to other methods. Cylindrical cavities are used throughout this work both for material characterisation and microwave heating applications as they have many axially symmetrical modes that are convenient to work with.

Two existing cylindrical cavities were used for MCP measurements, one designed for dielectric measurements of permittivity designated ϵ -Cav and the other designed for magnetic measurements of permeability designated μ -Cav. These are similar in design with slight differences in shape. The primary difference in construction of these cavities is that μ -Cav has a hole cut into its top and bottom plates which from the perspective of the cavity interior forms a recess which disrupts the surface currents. This disruption also affects the resonant frequency and combats particular mode degeneracies by slightly separating their resonant frequencies.

4.3.1 CONSTRUCTION OF μ -CAV

This cavity is a cylindrical cavity with a radius a of 47.5 mm and height h of 40.0 mm with one piece of aluminium forming the walls and base with

a flanged portion at the top for bolts to fasten to the top plate to the bottom part. The top is simply a flat aluminium plate with eight holes around its edge to thread steel bolts that allow fastening of the two main pieces together. Both the top plate and bottom part have a circular hole cut at their centre with radius a_r of 13 mm, the top hole having a depth of 7 mm and the bottom having a depth of 10 mm. These holes are covered by separate aluminium pieces with the same thickness as the cavity walls that protrude out from the hollow cavity interior. These parts have a central hole drilled through them with a radius a_s of 2.5 mm to allow thin sample tubes to be inserted into the cavity. To connect external systems to the cavity for measurement and monitoring two SMA short-circuited coaxial loop antennas are situated on the top plate. This cavity only has one external join between the top plate and the bottom dish part which helps to maintain high quality factor for the TM modes by minimising

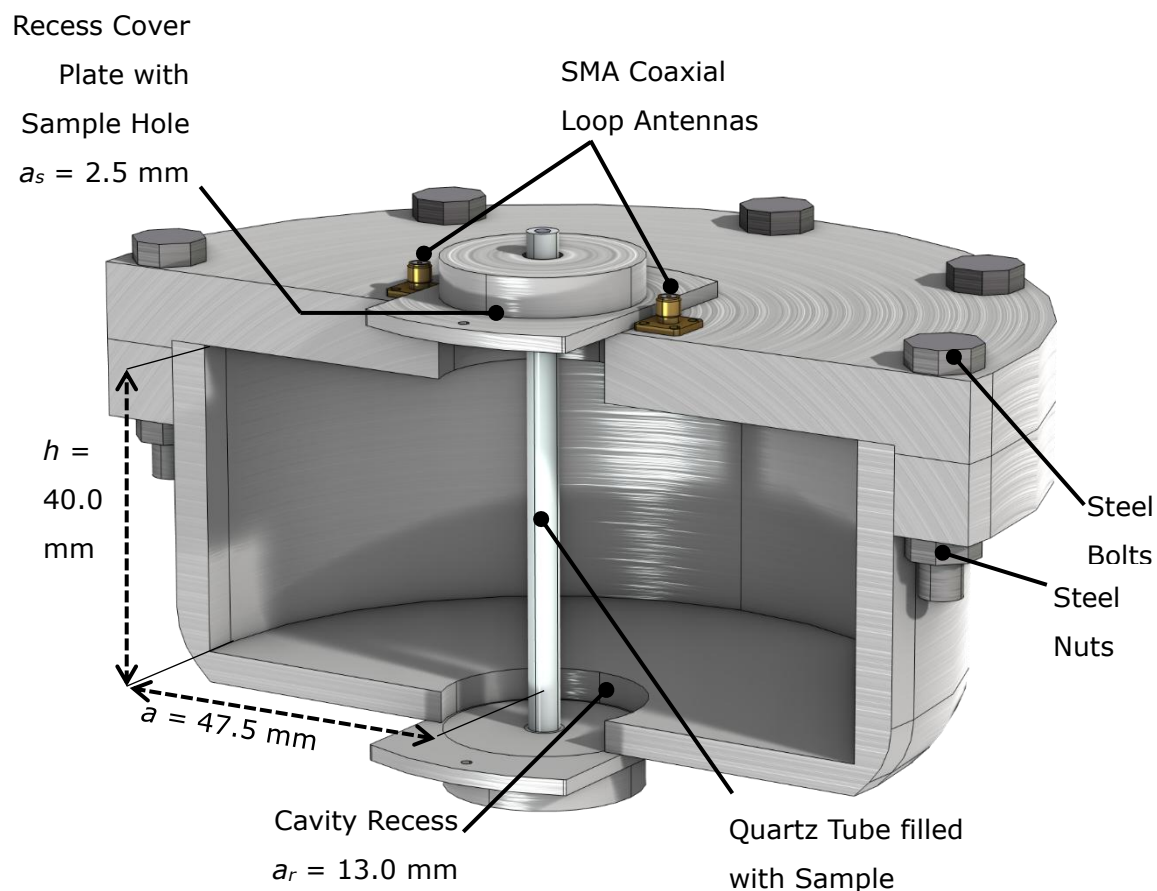


Figure 4.2 – Internal cutaway of μ -Cav shown with a sample present

potential interruption to circulating surface currents. A cutaway of the cavity is shown in Figure 4.2

4.3.2 CONSTRUCTION OF ϵ -CAV

This cavity is a cylindrical cavity with a radius a of 46.0 mm and height h of 40.0 mm. Unlike μ -Cav this cavity is constructed from three separate pieces of aluminium; a short section of tube with the radius and height dimensions mentioned and two plates with grooved inlays to fit on either end of the tube section, forming a tight connection. Eight steel bolts are threaded through both the end plates to hold them securely to the tube and form the resonant cavity. A sample hole with radius a_s of 2.375 mm is drilled through the centre of both end plates to allow thin sample tubes to be inserted into the cavity. To connect external systems to the cavity for measurement and monitoring two SMA open-circuited coaxial probe antennas are situated on the top plate. This cavity only has two external joins between the top and bottom plates and central tube part. A cutaway of the cavity is shown in Figure 4.3

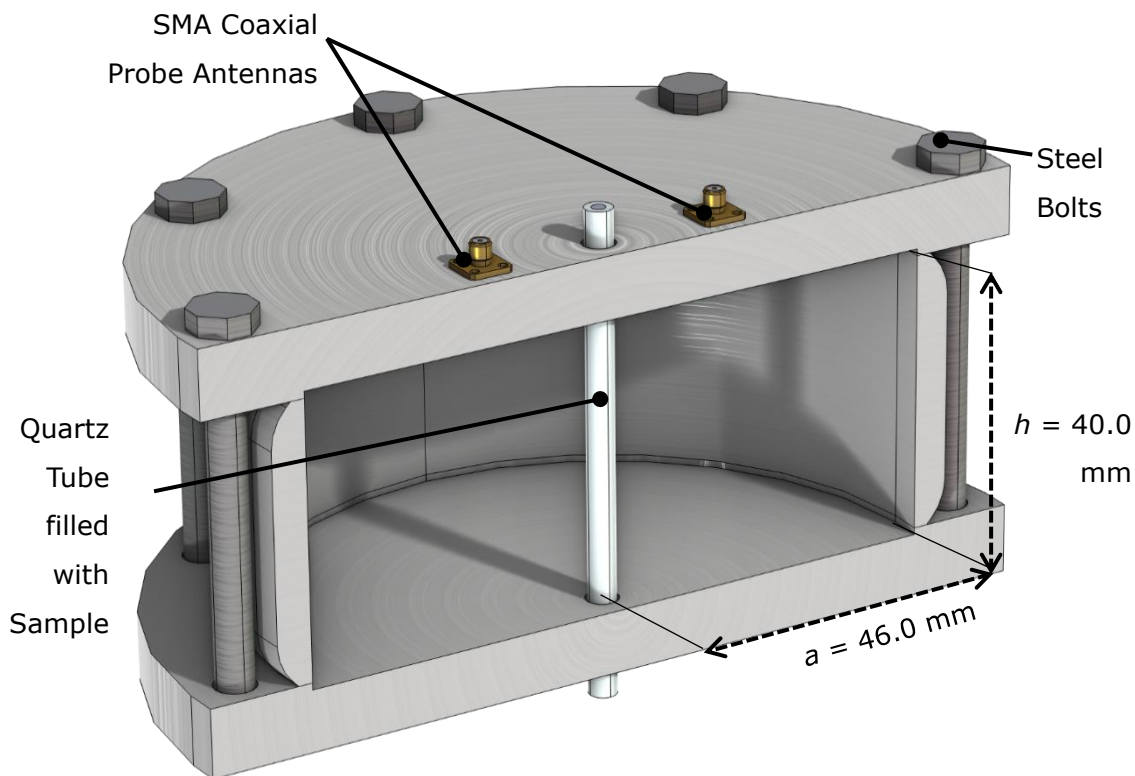


Figure 4.3 – Internal cutaway of ϵ -Cav shown with a sample present

4.3.1 FREQUENCY OF RESONANT MODES

To perform MCP measurements it is important to be aware of the expected resonant frequency of intended modes. There are many possible modes a resonant cavity can operate in and especially for higher order modes, there can often be overlap (degeneracy) or clustering of many resonant frequencies in a small frequency range. The frequencies of the modes utilised for MCP can be calculated using (3.32) and further approximated using simulation. Finite element modelling software COMSOL Multiphysics is used to simulate the cavities by creating a model based on cavity dimensions and performing eigenfrequency evaluations around the expected frequencies. These frequencies are shown in Table 4-1 and Table 4-2 along with the measured frequencies recorded using the actual empty cavities.

Table 4-1 – Values for f_{mnp} for modes used in μ -Cav

<i>Mode</i>	<i>Analytical (GHz)</i>	<i>Simulated (GHz)</i>	<i>Measured (GHz)</i>
TM ₁₁₀	3.8490	3.7907	3.7864
TE ₀₁₁	5.3719	5.3629	5.3570
TE ₀₂₁	7.9816	7.9537	7.9432
TE ₀₁₂	8.4254	8.3993	8.3874
TM ₃₁₀	6.4089	6.4063	6.5196
TM ₅₁₀	8.8110	8.8127	9.0717

Table 4-2 – Values for f_{mnp} for modes used in ε -Cav

<i>Mode</i>	<i>Analytical (GHz)</i>	<i>Simulated (GHz)</i>	<i>Measured (GHz)</i>
TM ₀₁₀	2.4944	2.4947	2.5010
TM ₀₁₁	4.5017	4.5019	4.5771
TM ₀₂₀	5.7258	5.7274	5.7325
TM ₀₂₁	6.8431	6.8459	6.8962
TM ₃₁₀	6.6179	6.6179	6.6220
TM ₅₁₀	9.0983	9.0991	9.1026

The modes listed include four measurement modes used for each cavity and two higher order modes, TM_{310} and TM_{510} which are used later as reference modes for corrections to permeability and permittivity calculations. These modes are chosen for their insensitivity to samples inserted into the cavity, that is their field distribution changes in response to the sample are negligible. They are therefore useful for recording changes that affect the entire cavity and all its operating modes, such as the ambient temperature.

Most of the recorded frequencies agree with the expected values based on the analytical and simulated values, with deviations typically around 10s of MHz or less. The difference in the measured values for the reference modes in μ -Cav are the largest with around 250 MHz being the greatest for TM_{510} . These reference modes are confirmed during acquisition by observing their insensitivity to introduced materials. Also of note for μ -Cav is that the simulated values differ more significantly from the analytical values as compared to ε -Cav. This is because the simulation takes into account the top and bottom recesses, which increase the effective cavity volume, and thus decrease frequency marginally.

4.3.2 QUALITY FACTOR OF RESONANT MODES

As with resonant frequencies, the quality factor expected of each mode is also important as this is used in the calculation of the complex permeability and permittivity of materials. Employing the same strategy as used for calculating the resonant frequencies, the Q can be calculated analytically using (3.50) and (3.60) and simulated to further refine the values, and finally measured directly with the real cavities. The values are reported below in Table 4-3 and Table 4-4 assuming a conductivity of the machine-grade aluminium (6082-T6) of approximately $2 \cdot 10^7$ S/m [168].

Table 4-3 – Values for Q for modes used in μ -Cav

<i>Mode</i>	<i>Analytical</i>	<i>Simulated</i>	<i>Measured</i>
TM ₁₁₀	11973	9530	8865
TE ₀₁₁	18538	18243	20888
TE ₀₂₁	28943	28008	32734
TE ₀₁₂	18558	18048	20065

Table 4-4 – Values for Q for modes used in ε -Cav

<i>Mode</i>	<i>Analytical</i>	<i>Simulated</i>	<i>Measured</i>
TM ₀₁₀	9497	9488	10401
TM ₀₁₁	8312	8298	8968
TM ₀₂₀	14389	14363	15169
TM ₀₂₁	10249	10241	10200

The difference between analytical and measured values suggests a slight underestimation of the aluminium conductivity of approximately 5-8 % indicating a more accurate conductivity value closer to $2.2 \cdot 10^7$ S/m. The differences for values associated with μ -Cav are greater than those for ε -Cav because the analytical approach does not factor in the modified cavity geometry and assumes a perfectly cylindrical cavity. This is most apparent for the TM₁₁₀ mode which has a difference of more than 3000 between the analytical and measured values. This is because the recesses are designed to interfere directly with this degenerate mode; its fields are consequently the most affected by their addition resulting in a significant shift in Q and frequency.

The simulated value here is much closer to the measured value as it does incorporate these large recesses. A simulated plot of both the magnetic and electric field distributions for this mode are included in Figure 4.4. The fields are not significantly affected by the inclusion of the recesses but at a glance it appears the intensity has dropped. This is in part due to the sharp corners formed at the recess-cavity join which create regions of higher field strength. Simulation of this resonant mode confirms a shift of frequency and Q from the idealised basic cylinder version, which is in agreement with the analytical results for TM_{110} from Table 4-1 and Table 4-3, becoming closer to the measured values for the same mode i.e. frequency shift from 3.8490 GHz to 3.7907 GHz and Q shift from 11973 to 9530.

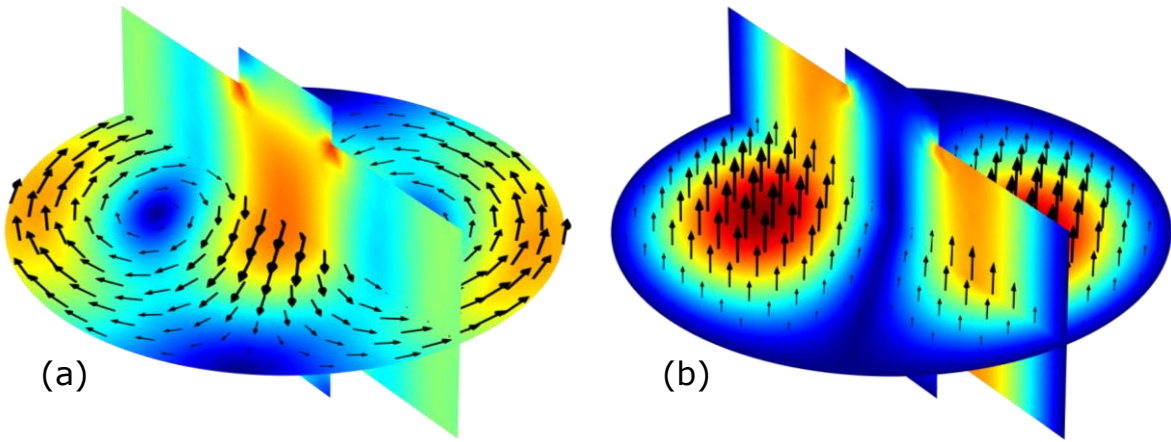


Figure 4.4 – Magnetic (a) and electric (b) field distributions for TM_{110} of μ -Cav with the additional top and bottom recesses included

4.3.3 MODE SCALING FACTOR, G_{MNP}

The mode scaling factor is a representation of the relationship between relevant fields present in the sample and those fields in the entire cavity volume. It is a ratio of the field in the cavity as compared to the sample field strength and can be calculated based on the volume integration of the field strength as shown in (4.12) for $G_{\mu-mnp}$

$$G_{\mu-mnp} = \frac{\int_{V_c} |\bar{H}_0|^2 dv}{\int_{V_s} (\bar{H}_0 \cdot \bar{H}_s) dv}. \quad (4.12)$$

where H_0 is the magnetic field strength in the unperturbed cavity, H_s is the magnetic field strength in the sample, V_c is the cavity volume and V_s is the sample volume. A similar calculation can be performed for $G_{\varepsilon-mnp}$ with the focus on electric field instead as shown in (4.13)

$$G_{\varepsilon-mnp} = \frac{\int_{V_c} |\vec{E}_0|^2 dv}{\int_{V_s} (\vec{E}_0 \cdot \vec{E}_s) dv}. \quad (4.13)$$

These equations typically produce a number between zero and one for the most useful measurement modes, with lower numbers indicating higher sensitivity to the sample under measurement.

Finite element modelling (FEM) software such as COMSOL Multiphysics is particularly useful for assessing these quantities as cavity models with varying degrees of detail can be constructed for analysis. Simulations were constructed of μ -Cav and ε -Cav in COMSOL with samples of set permeability and permittivity modelled as solid rods running the entire height of the cavities at the cavity centre. By performing the volume integration of the relevant fields according to (4.12) and (4.13) values of G_{mnp} can be calculated. These values are shown in Table 4-5 and Table 4-6 along with previous simulations performed for these same cavities in another work [96]. Also included in these tables are measured values using the actual cavities previously performed using a metal rod perturbation for μ -Cav and a rod of a well-characterised low-loss dielectric material, PTFE [96]. Differences in simulated values can be attributed to different levels of detail used in simulations for cavity construction and meshing.

Table 4-5 – Values for $G_{\mu-mnp}$ for measurement modes used in μ -Cav

<i>Mode</i>	<i>Simulated</i>	<i>Simulated [96]</i>	<i>Measured [96]</i>
TM ₁₁₀	0.408	0.414	0.388 ± 0.008
TE ₀₁₁	0.273	0.285	0.285 ± 0.001
TE ₀₂₁	0.095	0.105	0.107 ± 0.001
TE ₀₁₂	0.462	0.490	0.494 ± 0.003

Table 4-6 – Values for $G_{\varepsilon-mnp}$ for measurement modes used in ε -Cav

<i>Mode</i>	<i>Simulated</i>	<i>Simulated [96]</i>	<i>Measured [96]</i>
TM ₀₁₀	0.288	0.290	0.294 ± 0.002
TM ₀₁₁	0.991	0.995	0.962 ± 0.006
TM ₀₂₀	0.121	0.125	0.124 ± 0.001
TM ₀₂₁	0.185	0.191	0.183 ± 0.001

Measured values for G_{mnp} are used in calculations as these measurements were performed for these specific characterisation cavities. The simulated values differ from the measured values, typically by no more than $\pm 5\%$ however the measured values more accurately represent the real-life operation and construction of the cavities. This includes the cavity material which may have impurities in the metal or imperfections in the cavity shape, for example small pits or grooves in the cavity walls, or the necessary joins between separate metal parts. These small deviations from the semi-idealised model are often far too small to precisely model with a reasonable mesh size in FEM software, and doing so would be an exceptionally time consuming and computationally intensive task.

4.4 MATERIALS AND EQUIPMENT

4.4.1 SAMPLE MATERIALS

Perturbation measurements are performed on two types of iron oxide which are common materials, with reasonable costs compared to other rarer elements such as cobalt, nickel or neodymium [169][170][171]. Iron is an abundant material with a wide variety of applications, and this includes its other forms, like oxides. Fe₃O₄ or iron (II,III) oxide is commonly referred to as magnetite. It occurs naturally as an ore forming a strong black powder when processed which has established applications as a pigment [172], as an iron source and notably for its magnetic qualities. One particularly notable use of magnetite is in magnetic resonance imaging (MRI) as a contrast agent for diagnosis of many

diseases, including cancers [173][174]. As it has already demonstrated useful applications, magnetite is a prime candidate for further investigation and characterisation at microwave frequencies as this may illuminate new opportunities for its applicability and further advance our understanding of it.

Another common iron oxide is Fe_2O_3 , iron (III) oxide, specifically the α -phase referred to as haematite (also hematite). Like magnetite this occurs commonly as an ore material but presents as a red or dark orange powder when processed. It was widely used historically as a pigment but garnered fewer notable recent applications apart from the production of iron and steel [175]. It is known to be very weakly magnetic so its usefulness may not be as apparent as magnetite, but it is still important to characterise its microwave responses as there could be as yet unidentified properties. It is also useful to characterise alongside magnetite as a similar material for comparison.

Powders of magnetite and haematite were purchased from Sigma-Aldrich. Magnetite (310069) has an average particle diameter less than five microns with at least 95 % purity and haematite (310050) also has average particle diameters of less than five microns with a purity equal to or greater than 96 %. To perform the perturbations a number of other pieces of equipment are required. These are detailed below.

4.4.2 SAMPLE TUBING

For these measurements the powders cannot be placed in the cavities without support. To contain powders for MCP measurements a very low-loss microwave material must be used so as not to interfere significantly with the fields and thus the measurements. Fused quartz is the common choice for most microwave applications that require a low loss container to be inserted into a cavity. It is a non-magnetic material with very low dielectric loss value in the region of 10^{-5} for microwave frequencies i.e. single-digit GHz values. Thin-walled capillary tubes are obtained from CM

Scientific with an internal diameter of $2.0 \text{ mm} \pm 0.20 \text{ mm}$ and an outer diameter of $2.40 \text{ mm} \pm 0.24 \text{ mm}$.

4.4.3 VECTOR NETWORK ANALYSER

To capture the S_{21} response across a broad range of frequencies a vector network analyser is used. This is a high-precision benchtop system that can measure S -parameters for a variety of systems, including resonant cavities. A Keysight N5232A PNA-L (300 kHz- 20 GHz) is used to record S_{21} from the cavity. It is connected to each cavity via high-quality coaxial RF cables screwed into the SMA ports on the top plates of μ -Cav and ε -Cav.

4.4.4 OVEN

During the MCP measurements the temperature is very important, having a significant impact on material properties and the expansion of the metal cavity itself. As a result, a method of temperature control is to place the entire cavity with the sample into an oven. The oven can be heated steadily to ensure all the contents are at the same temperature, with the temperature measured using a resistance temperature detector (RTD) affixed to the cavity exterior. The rationale behind this approach will be explained in more detail in a later section. The oven used is a Memmert UF 30 Plus with a hole cut into the side to allow cable access.

4.4.5 SOFTWARE DATA CAPTURE

The data from the VNA is recorded using a purpose-built program developed by a previous member of the CHFE research group at Cardiff [176]. This software captures the S_{21} data at specified intervals, performs curve fitting and saves the data to text files for further analysis. This software can collect data from a number of measurement modes simultaneously, meaning during one data acquisition session, frequencies and Q (by measuring the 3 dB bandwidth) across a wide range can be collected.

Additionally, the software will record the temperature given by the RTD, which given a slow enough heating rate can be assumed to be equivalent to the temperature of the sample under measurement. Typical heating rates used in the following experiments are less than 0.5 °C/min. Using magnetite as an example, we can estimate the time taken for heat to flow through the least thermally conductive path; the sample tube walls and into the centre of the sample. Thermal diffusivity, α , is related to thermal conductivity, k , density, ρ , and specific heat capacity, c_p , as in (4.14)

$$\alpha = \frac{k}{\rho c_p} \quad (4.14)$$

and given a conservative thermal conductivity of magnetite of 3.5 W/m·K, density of magnetite of approximately $5.19 \cdot 10^{-3}$ g/mm³, and specific heat capacity of around 730 J/kg·K, the thermal diffusivity can be calculated at around 0.92 mm²/s. As an insulator, quartz has a similarly low thermal diffusivity of 0.94 mm²/s. If we further round these values down and use 0.90 mm²/s for both materials, and assume a 10 mm travel distance, which is much more than the diameter of the sample and measurement tubes combined, we can use the relationship between distance, d , diffusivity and time, t illustrated in (4.15) to calculate the time taken for heat to travel.

$$t = \frac{d^2}{\alpha} \quad (4.15)$$

With these values the time taken is around 111 seconds i.e. less than two minutes. Using all these conservative estimates indicates a maximum heating rate of 0.54 °C/min to ensure thermal equilibrium between sample and cavity. The PC running the data acquisition software can also directly control the heating program of the oven including set temperatures, heating ramps and cooling. Heating rates well below the maximum conservative calculation are used which also means the number of measurement points around each temperature point can provide highly graduated values.

4.5 METHODOLOGY

4.5.1 TEMPERATURE CONTROL METHOD

The cavity perturbation technique is very sensitive, and this means that even very small changes in the shape of the cavity or the composition of its materials can significantly alter the frequency and bandwidth and make measurements unreliable. Thermal expansion of the cavity metal must therefore be taken into account, and at a minimum the temperature of the cavity should be recorded during measurements. Ideally the temperature should be controlled as to avoid swings in ambient temperature that could alter measurements.

As it is also desirable to study the permeability and permittivity of samples over a range of temperatures the solution chosen was to contain the cavity and sample together in an oven and perform measurements in situ. This allows control of the temperature of all contents and the heating to elevated temperatures but does present a new problem in that the cavity will be heated to hundreds of degrees above room temperature so the fluctuations due to temperature will not be ambient changes of perhaps a few tenths of degree and so the thermal expansion will be substantial. This requires a correction method, which for frequency is reasonably straightforward, but for Q is much more complicated.

This temperature control and correction method has been conceptualised and tested by a number of previous researchers and students at Cardiff with a number of works published on the topic [96][176][177][178]. It has been shown that the temperature dependence of resonant frequency has a linear relationship with the cavity dimensions and therefore the thermal expansion coefficient of the metal used for the cavity walls. The commonly reported value for aluminium is -23 to $-25 \cdot 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ [179], with a measured value performed on the actual cavities of $-22.8 \cdot 10^{-6} \text{ }^{\circ}\text{C}^{-1}$. The difference can be attributed to small impurities present in the machine-grade aluminium alloy used.

This linear relationship is proportional for all modes which allows the use of a higher order mode, acting as a reference to be able to correct for common temperature changes happening to all modes during heating. For the cavities used here, μ -Cav and ε -Cav, two modes are chosen as potential reference modes to ensure one is always available and account for unforeseen errors. These are TM_{310} and TM_{510} , which are two examples of whispering gallery modes which exhibit minimal electric and magnetic field strength at their centre [96][177][180][181]. This is particularly useful as a reference mode here because they are, unlike the chosen measurement modes, highly insensitive to samples presented at the cavity centre. This decouples the influence of the measured sample from the influence of the temperature on the thermal expansion.

To use one of these modes to correct a frequency measurement, (4.16) is used

$$f_{s,TC}(t) = \left(\frac{f_M(t) - f_M(0)}{f_M(0)} - \frac{f_R(t) - f_R(0)}{f_R(0)} \right) f_M(0) + f_M(0). \quad (4.16)$$

where at any time t during the measurement the temperature-corrected frequency due to the sample $f_{s,TC}$, is the product of the difference between fractional frequency shifts of the measurement mode f_M and the reference mode f_R , and the measured frequency at $t = 0$ $f_M(0)$, with the final addition of that same frequency. The difference of fractional frequencies between the measurement mode and reference mode removes the influence of the thermal expansion while the multiplication by the original measurement frequency scales the fractional difference back to the original size. The addition of the original measurement frequency translates the corrected frequency back to the original range of the measurement mode. The resultant frequency can then be used in the MCP equations (4.8) and (4.10) to calculate the real parts of permeability and permittivity of a sample through a continuous range of temperatures without the deformation caused by the cavity thermal expansion.

The relationship between temperature and bandwidth, and thus Q , is much more complicated than the temperature-dependence of frequency. Resonator Q is dependent on conductivity, frequency and cavity dimensions, which are all themselves temperature dependent. This complexity is reflected in the relative complexity of analytical equations derived for Q as in (3.50) and (3.60) compared to the equation for cavity frequency in (3.32). If these were the only considerations it would make the Q -temperature relationship more complicated but not unreasonable to calculate, however, another key element that is affected by temperature changes is the coupling structures. Changes in these already small structures can cause substantial changes and will impact the coupling itself and the resultant field distributions. To fully account for these changes would require significant time and effort and so has been excluded as it deviates too far from the core investigations of this thesis.

These relationships between measured frequency, Q , and temperature are illustrated in Figure 4.5. In Figure 4.5(a) the frequency deviation from the frequency at time $t = 0$ is displayed for three frequencies over a temperature ramp. These are a measurement frequency, a reference mode frequency and a temperature-corrected version of the

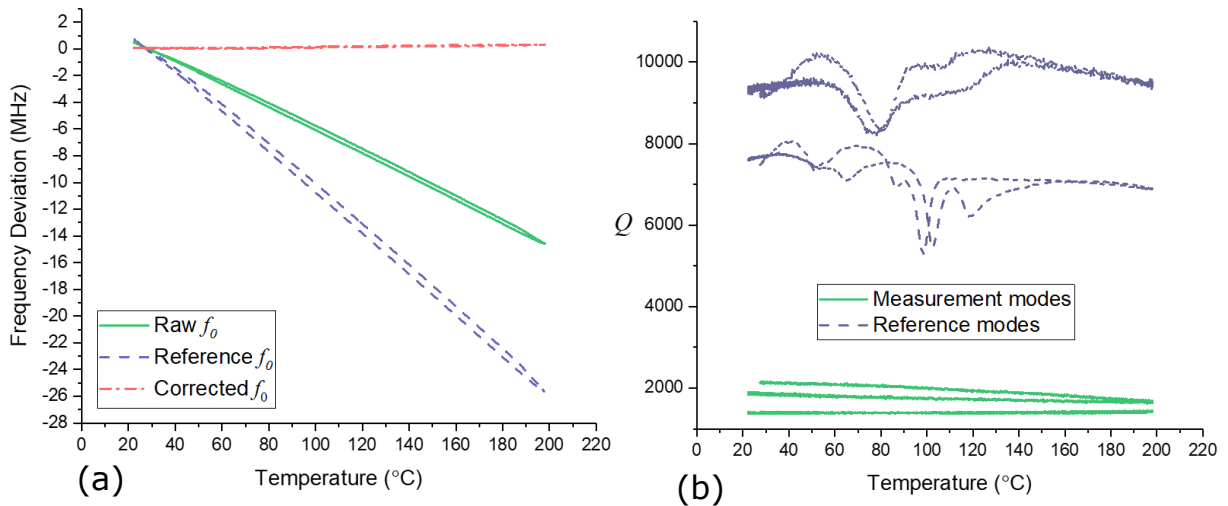


Figure 4.5 – Frequency deviation over temperature from frequency at $t = 0$ (a) for a measurement mode, a reference mode and the measurement mode with temperature correction applied. Q over the temperature ramp (b) for two measurement modes and the two reference modes

measurement mode with (4.16) applied. This shows the linear relationship between frequency and temperature apparent for both measurement and reference modes due to the thermal expansion of the cavity. The raw frequency and reference frequency are inserted into (4.16) as f_M and f_R respectively, and the output f_S , is the displayed corrected frequency. In contrast, Figure 4.5(b) shows the raw Q values for two measurement modes and the two reference modes, TM₃₁₀ and TM₅₁₀. As the temperature ramps up to the maximum and cools the measurement modes show steady changes driven by the sample behaviour, however the reference modes show inconsistent and erratic variations. This demonstrates the complicated nature of bandwidth with elevated temperature that prevents using the higher-order reference modes to correct measurements as is done with frequency.

An alternative method to measuring high-temperature MCP samples is to heat them externally and then manoeuvre them into the cavity quickly to measure the characteristics at the set temperature. To perform this method additional equipment would be required to heat the sample and move it, likely using stepper motors, into the correct position in the cavity for each test. One advantage of this method is that the cavity remains at room temperature so temperature correction methods would not be necessary. Although higher temperatures could be measured using the external heating method the high thermal gradients and rapid cooling would make the true temperature of the sample at the time of measurement unreliable. Using the integrated heating method means the cavity, air and all other contents in close proximity to the sample are at the same or a very similar temperature, minimising thermal gradients across the sample and any rapid cooling that would happen. This method was chosen based on the accuracy of temperature measurements and availability of parts and equipment for this method versus the cost and delay required to realise the alternative approach.

4.5.2 MCP PROCEDURE

4.5.2.1 SAMPLE PREPARATION

The MCP procedure begins with preparing the samples into appropriate containers for insertion into the measurement cavities. For powders, this involves funnelling small amounts into a quartz capillary tube with a sealed end and taking time to attempt to settle the powder using vibrating tools, like an electric toothbrush, placed against the quartz tube. Settling the powder is an important step as assumptions made previously regarding the sample shape use the model of a solid rod of the substance. To achieve this with a powder it would require compression of the powder which would be difficult in the fragile capillary tubes and may alter the powder's electromagnetic characteristics by forcing grains together. The powder should remain as much in its original physical state as possible while minimising air gaps and voids within the tube to allow accurate calculation of sample mass and provide the most accurate calculation of effective permeability and permittivity of the powder in the state it will be used in. An empty tube is prepared alongside any sample-filled tubes to use as a reference in the VNA measurements.

The approximate packing density or volume fill factor of both magnetite and haematite powders is estimated using their reported density, measured mass and volume calculations of the quartz tubes used. The packing density η , is calculated using (4.17)[182],

$$\eta = \frac{1}{\pi r_q^2} \frac{m}{h_s \rho} \quad (4.17)$$

where r_q is the internal radius of the quartz tube in mm, m is the mass of the sample powder in g, h_s is the height of the settled powder in the tube in mm and ρ is the powder density in g/mm³. Density values used for magnetite were 5.17·10⁻³ g/mm³ and 5.24·10⁻³ g/mm³ for haematite. r_q is 1.0 mm ±10 %. Measured and calculated values are shown in Table 4-7 – Packing density of measured powders

with η reported as a percentage. The reported values align with those reported in similar MCP experimentation [183].

Table 4-7 – Packing density of measured powders

<i>Powder</i>	<i>m (g)</i>	<i>h_s (mm)</i>	<i>η (%)</i>
Magnetite	0.233	75	19.13
Haematite	0.278	85	19.87

4.5.2.2 CAVITY SETUP

The cavity in use is connected to the ports of the VNA while empty and a frequency sweep of S_{21} is performed across the range of frequencies used; here this is from 1-12 GHz. Within this sweep the measured response can be compared against expected resonant frequencies of both the measurement and reference modes. Once confirmed, these modes can be entered into the data capture software to record the frequency and Q with a desired time interval. Reference measurements are made using the empty cavity while connected to the RTD for both μ -Cav and ε -Cav before each of their respective experiments were conducted. The same measurements are also performed with an empty quartz tube inserted into the cavity sample hole.

The sample-filled tube can then be slowly inserted into the cavity and the S_{21} responses observed. By inserting slowly, the gradual frequency and bandwidth shift can be observed to check the sample is not too lossy to measure. This would be observed as a severe flattening of the resonant peak to the point where no peak was discernible. Once the sample is inserted completely the cavity can be placed into the oven. A programme for the oven heating can be prepared to include an initial holding region to stabilise the temperature of all oven contents, followed by a heating region over multiple hours to a maximum value. This value is held for a short time again to ensure uniformity among all contents and the temperature then reduced back to the start temperature over a similar time scale to the heating region.

Once the cavity is in the oven with the heating program set the data capture program can be set up to save all the data over the whole heating and cooling session. This data can then be extracted and used in calculations, including the frequency-temperature correction method as shown in (4.16). This process can be reperformed for any other samples and the cavity replaced if necessary. A schematic diagram of the MCP equipment setup is shown in Figure 4.6 to illustrate the physical connections, data collection and output of the system.

As previously mentioned, two cavities are used for measuring both permeability and permittivity of materials. μ -Cav and ε -Cav each have four chosen measurement modes for measuring these values respectively, using regions of relatively constant field through the cavity centre; magnetic field regions at the centre are used in μ -Cav and electric field regions at the centre are used in ε -Cav. The relevant modes used for each cavity are outlined in Figure 3.4, Table 4-1, and Table 4-2. These provide limits for frequencies investigated here.

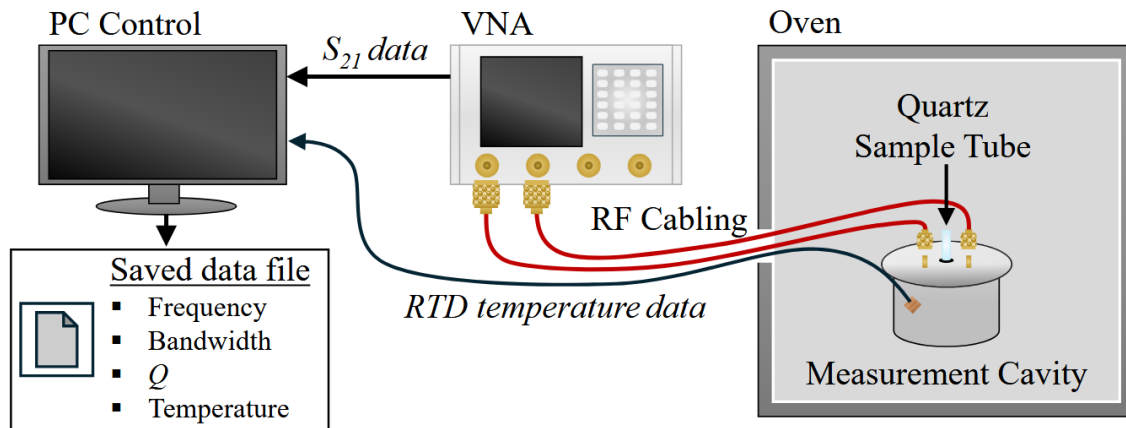


Figure 4.6 – Schematic diagram of MCP equipment connections including measurement cavity, oven, VNA and PC control systems

4.6 RESULTS - MEASURING MAGNETITE AND HAEMATITE

Both magnetite and haematite powders have their complex permeability and permittivity measured using the MCP methods described with both μ -Cav and ε -Cav. Modes and therefore measurement frequencies are selected for their suitability for measurement and their isolation from other potentially interfering neighbouring modes. This means the number of frequency points is limited across all measurements. These measurements could be reperformed using different size cavities to access similarly well-isolated modes at different frequencies, but this was not available due to time constraints. Measurements are performed using an oven to control and increase the temperature to be able to observe the temperature-dependent behaviours that may be exhibited by these materials. Measurements are also performed using resonant modes across gigahertz frequencies spanning around 2.5 to 8.4 GHz. This allows a limited look at any prominent frequency dependence displayed by the permeability or permittivity. Given the focus of this thesis has been on the magnetic field interactions, permeability will be discussed first.

4.6.1 ROOM TEMPERATURE MEASUREMENTS

4.6.1.1 PERMEABILITY

Magnetite and haematite powders are measured at room temperature by maintaining the oven and its contents at a controlled room-temperature value of 25 °C. The real and imaginary parts of permeability are shown in Figure 4.7 and Figure 4.8 respectively, calculated using (4.8) and (4.9). No correction is applied here as the correction method utilised performs adjustments relative to the initial values of frequency.

In Figure 4.7 the real permeability of magnetite can be seen to range between 1.5 and 0.9, with a distinct negative frequency dependence. This is in agreement with other work measuring similar values and frequency dependence over this frequency range [96][98]. Values of μ_1 only slightly above one indicate a limited capacity for magnetic energy storage at microwave frequencies. Magnetite displays a downward trend in μ_1 as frequency increases, highlighting the significant drop in magnetic energy storage capacity at GHz frequencies. This could be because at these frequencies the magnetic mechanisms such as rotation of domains simply cannot keep up with the speed of the alternating field, storing less and less energy. Another possible explanation is that this displays the tail end of a broadband natural ferromagnetic resonance that is present in magnetite [96]. This is suspected as at the higher measurement frequencies >8 GHz the permeability falls below one. This represents a positive frequency shift rather than the typically expected negative one

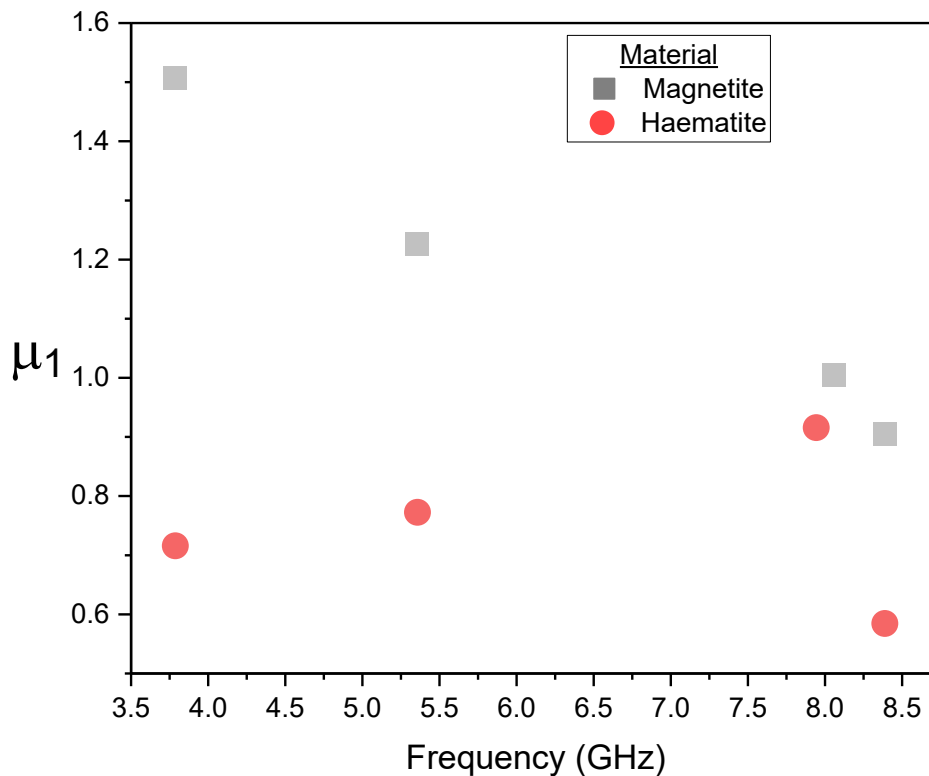


Figure 4.7 – Real part of permeability for magnetite and haematite at room temperature, 3.7-8.4 GHz

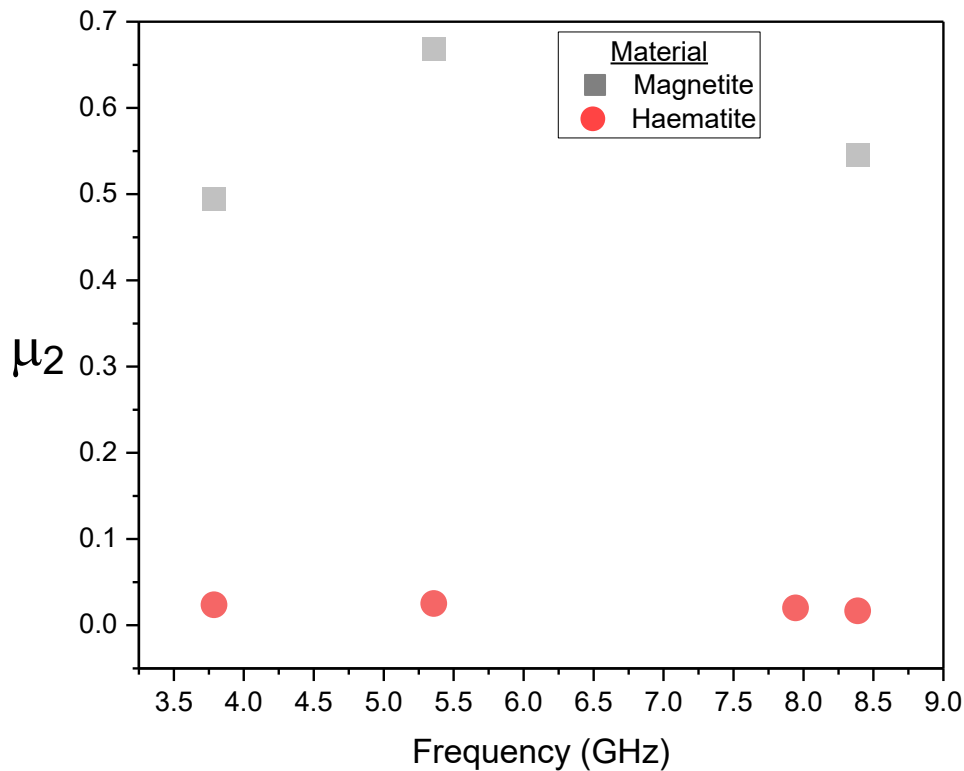


Figure 4.8 – Imaginary part of permeability for magnetite and haematite at room temperature, 3.7-8.4 GHz

and displays apparent negative magnetic energy storage which could be interpreted as a small, induced field opposing the applied measurement field.

The haematite permeability is also interesting as it displays values less than one across all the measurement frequencies. This aligns with commonly understood behaviour of haematite as a weakly antiferromagnetic or canted ferromagnetic material. Haematite also displays a similar behaviour to magnetite at the higher measurement frequencies where a negative frequency dependence could be inferred. This is very difficult to say conclusively as there is simply not enough data points and the frequency shift of the third haematite data point (approximately $f = 8$ GHz) is slightly different to the established frequency of the desired measurement mode of $f = 7.943$ GHz. This may indicate that an error has occurred with data capture, and the wrong mode is being measured here. It is possible that the density of resonant modes at these frequencies contributed to this.

The imaginary part of the permeability is shown in Figure 4.8. This shows the relative magnetic losses in each of the materials. No discernible frequency dependence can be observed for either the magnetite or haematite. Measurements from other sources suggest we may lack the required density of data points dispersed across frequency to see the ferromagnetic resonant peak at approximately 3 GHz [96][98]. Magnetite displays values between 0.50 and 0.67, which although small indicate that raw magnetite powder would certainly heat in response to a microwave magnetic field applied at any of the measured frequencies [98]. An erroneous value for the TE₀₂₁ mode (7.943 GHz) was excluded for magnetite measurements due to an error in data capture.

Haematite values show a significant difference in their magnetic behaviour as compared to magnetite as they have very small values for μ_2 with the greatest value no more than 0.025. These values indicate haematite may exhibit a limited heating response to a microwave magnetic field, suggesting it would lack effectiveness as a magnetically driven microwave susceptor [184].

4.6.1.2 PERMITTIVITY

The real and imaginary parts of permittivity are shown in Figure 4.9 and Figure 4.10 respectively, calculated using (4.10) and (4.11) with temperature held at 25 °C in the oven. As before, no correction is applied here as the correction method utilised performs adjustments relative to the initial values of frequency.

The real part of permittivity displayed in Figure 4.9 shows magnetite values of between 7.2 and 7.5 across the whole frequency range. There is minimal deviation and no apparent frequency dependence. This agrees with existing literature values of around 6 to 8 [98]. These values fall in an intermediate range between common microwave insulator materials like polytetrafluoroethylene (PTFE) ($\epsilon_1 \approx 2.1$) and materials with a higher electrical energy storage capability such as gallium arsenide (GaAs) ($\epsilon_1 \approx$

13.0) commonly used in microwave integrated circuits [171]. Haematite shows permittivity significantly lower than magnetite in the range of 3.1 to 4.2, which is in line with literature given the relative density of the powders used here [184]. There is a slight negative frequency correlation as the permittivity tails off towards higher frequencies suggesting it would behave more like an insulator, especially at higher frequencies.

In Figure 4.10 the imaginary part of permittivity is displayed for magnetite and haematite, showing a similar comparative relationship for dielectric loss as for magnetic loss. Magnetite displays loss values between 0.37 and 0.50 which suggest it will heat in response to an applied microwave electric field, but not as effectively as it would for a similar intensity magnetic field. This is significant as it displays magnetite's potential to be heated more effectively by magnetic fields, or even by a combination of both magnetic and electric fields. The loss values for haematite, like for its magnetic loss are very low with values

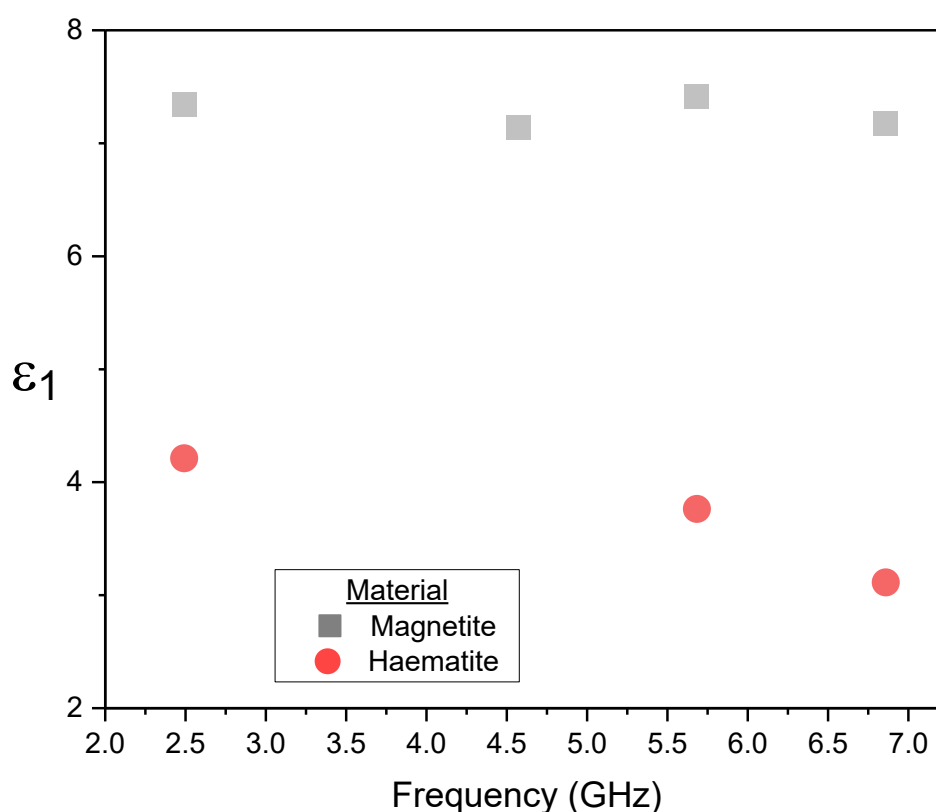


Figure 4.9 – Real part of permittivity for magnetite and haematite at room temperature, 2.5-6.9 GHz

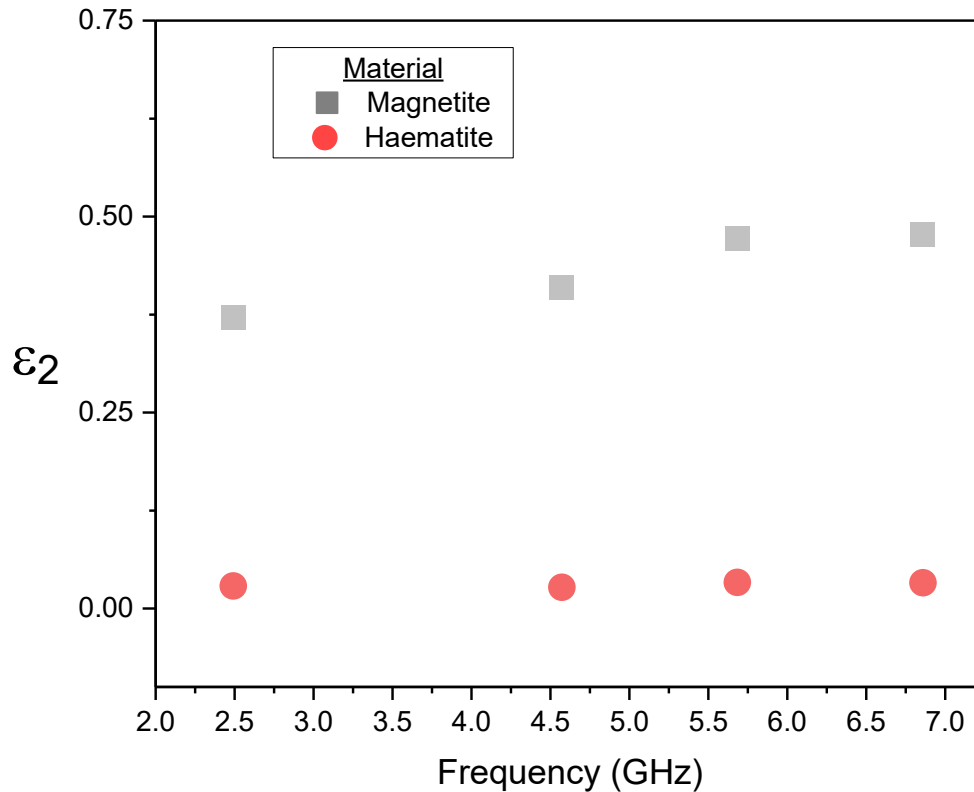


Figure 4.10 – Imaginary part of permittivity for magnetite and haematite at room temperature, 2.5-6.9 GHz

less than 0.033 across all frequencies. No noticeable frequency correlation is present. These values portray haematite to act more as a dielectric and magnetic insulator at these frequencies. These values are in alignment with established sources [96][98][184].

4.6.1.3 QUARTZ

During room temperature measurements data is collected with an unperturbed cavity and when perturbed only by a quartz sample tube. This allows calculation of the permittivity and permeability of the quartz tube itself. This is not the primary focus of these measurements but serves as an additional test of the accuracy of the measurement methods. Fused quartz is a prevalent material in microwave engineering applications for its very low loss values and as such is well understood and characterised in the literature.

Shown below are two figures showing the calculated complex permeability and permittivity of the quartz tubing used in these experiments. Their values should have minimal impact on the measurements of interest as the measured frequencies and bandwidths used as the baseline are those recorded with the quartz tubing present. This eliminates the influence of the quartz tube on the measurement and effectively measures only the difference, which is the sample material.

Figure 4.11 shows real permeability values of very close to one, as we would expect for a nonmagnetic material, with calculated values between 1.01 and 1.05. Complex permeability shows values mostly on the order of 10^{-5} for all frequencies other than 3.8 GHz (TM_{110}), which is around $4 \cdot 10^{-4}$. These values are in line with what would be expected for quartz, with very little capability for magnetic energy storage or loss. Figure 4.12 shows real permittivity values of between 3.98 and 3.83 with a decreasing correlation at increased frequencies. Imaginary permittivity values are on the scale of 10^{-4} with some values closer to 10^{-5} . This aligns

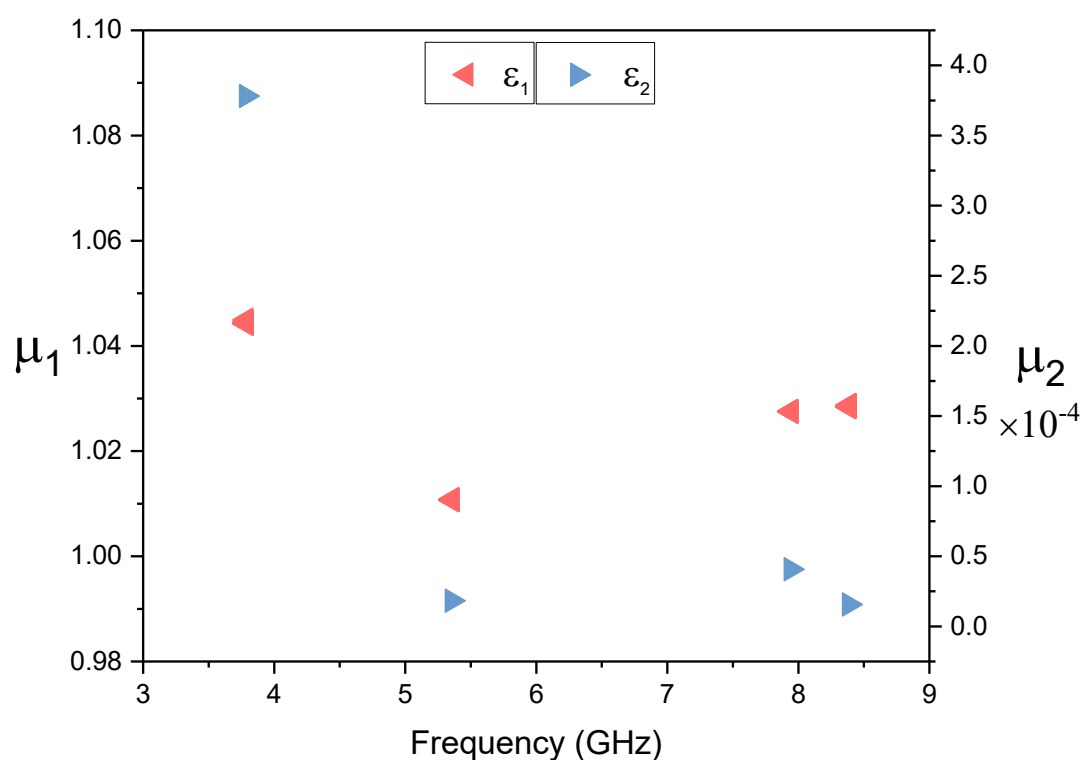


Figure 4.11 – Real and imaginary permeability values for quartz capillary tubing, 3.7-8.4 GHz

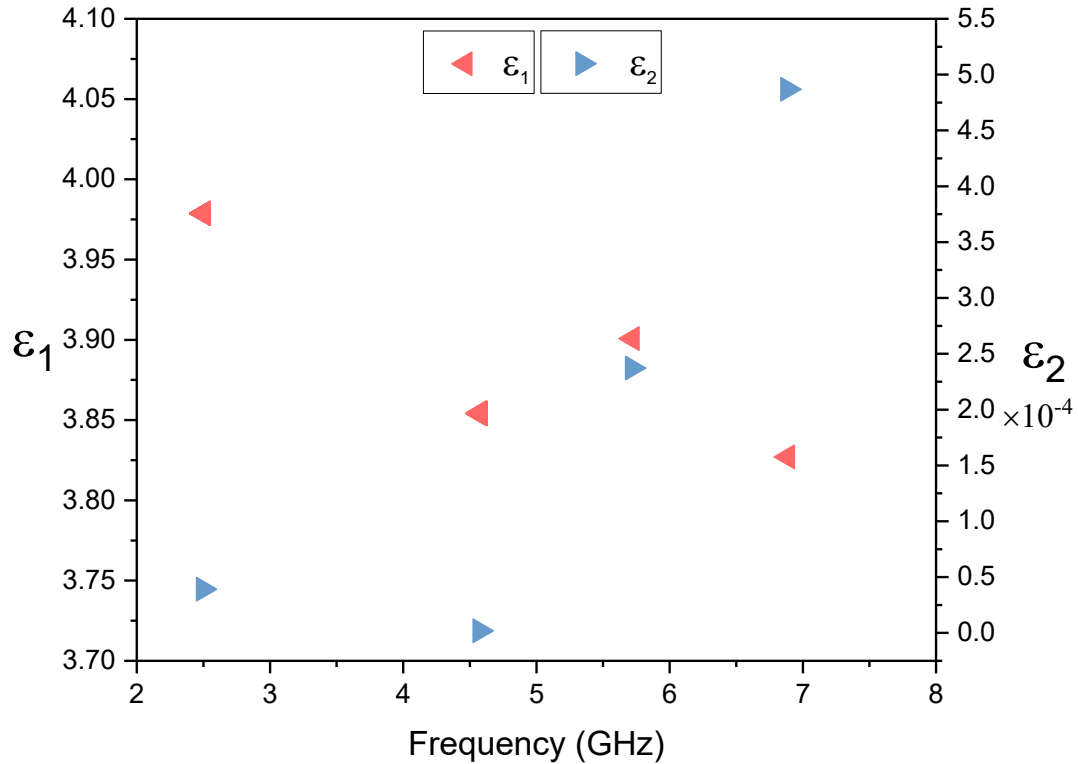


Figure 4.12 – Real and imaginary permittivity values of quartz capillary tubing, 2.5-6.9 GHz

well with reported values for quartz of around 3.8 and 10^{-5} [152], although we would expect the loss to decrease rather than increase with increasing frequency.

Small variations in these measured values are to be expected due to errors in frequency and bandwidth measurement, imperfections in the cavity material or shape, variations in the volume of the quartz sample used from the stated diameter values and assumptions made in the modelling and formulations of equations. This also applies for measurements of the materials of interest, magnetite and haematite. Despite this, these measurements can still be seen to be highly accurate and useful in characterising materials' electromagnetic qualities.

4.6.2 ELEVATED TEMPERATURES

The permeability and permittivity of magnetite and haematite are assessed up to 198 °C by slowly increasing the temperature of the oven from a hold state of 25 °C to 198 °C over 8 hours with a heating rate of

approximately 0.36 °C/min. The chosen temperature is a limitation of the available high-temperature RF cables available during experimentation, which were rated to 200 °C. The temperature is then decreased at a similar rate back to room temperature. By using this slow heating rate, it ensures the temperature reading from the RTD attached to the cavity exterior can be assumed to be equivalent to the sample itself. Along with the slow heating and cooling rates of the oven, the temperatures are held at 25 °C for 10 minutes or more at the end of the experiment to ensure the sample has completely cooled.

Assessing the permeability and permittivity of samples in situ while being heated provides valuable information about the temperature dependence of these qualities and allows observation of any changes as they happen. These changes may be missed if a more traditional approach of pre-heating or annealing samples was used; if samples were to be assessed at 50 °C, 100 °C and 150 °C it could miss interesting information in between these values.

4.6.2.1 PERMEABILITY

The permeability of magnetite and haematite powders were assessed up to 198 °C and back down to room temperature. The real part of permeability is shown in Figure 4.13 for both materials and all four measurement frequencies, with magnetite in black and haematite in red.

The magnetite shows relatively flat curves with initial and final values of similar magnitude, ranging between 0.80 and 1.51. Both 3.786 GHz and 5.356 GHz show a small decrease of approximately 0.25 in μ_1 at high temperatures while 7.943 GHz shows an increase of around 0.1. 8.387 GHz displays a relatively flat curve indicating a lack of temperature dependence at the operating frequency of 8.38 GHz. All frequencies except 7.943 GHz show some hysteresis in the permeability curves which end slightly lower than the initial values in each case. This provides the first indication that the magnetite has been chemically changed by the

applied heat, likely beginning the oxidation phase change to $\gamma\text{-Fe}_2\text{O}_3$ in the presence of air in the sealed tubes.

In contrast, the permeability of haematite shows little to no hysteresis across all frequencies with very flat curves that end exactly at their initial values. This shows haematite has not been changed by the heating process and the real permeability is generally temperature independent. Notably for haematite the real values of permeability are all consistently below one. This indicates the haematite is weakly antiferromagnetic, as was the case for the room temperature measurements.

The imaginary part of permeability is shown in Figure 4.14 with values shown for magnetite and haematite for three of the four utilised measurement frequencies. The data captured for 7.943 GHz was erroneous and excluded from the plot.

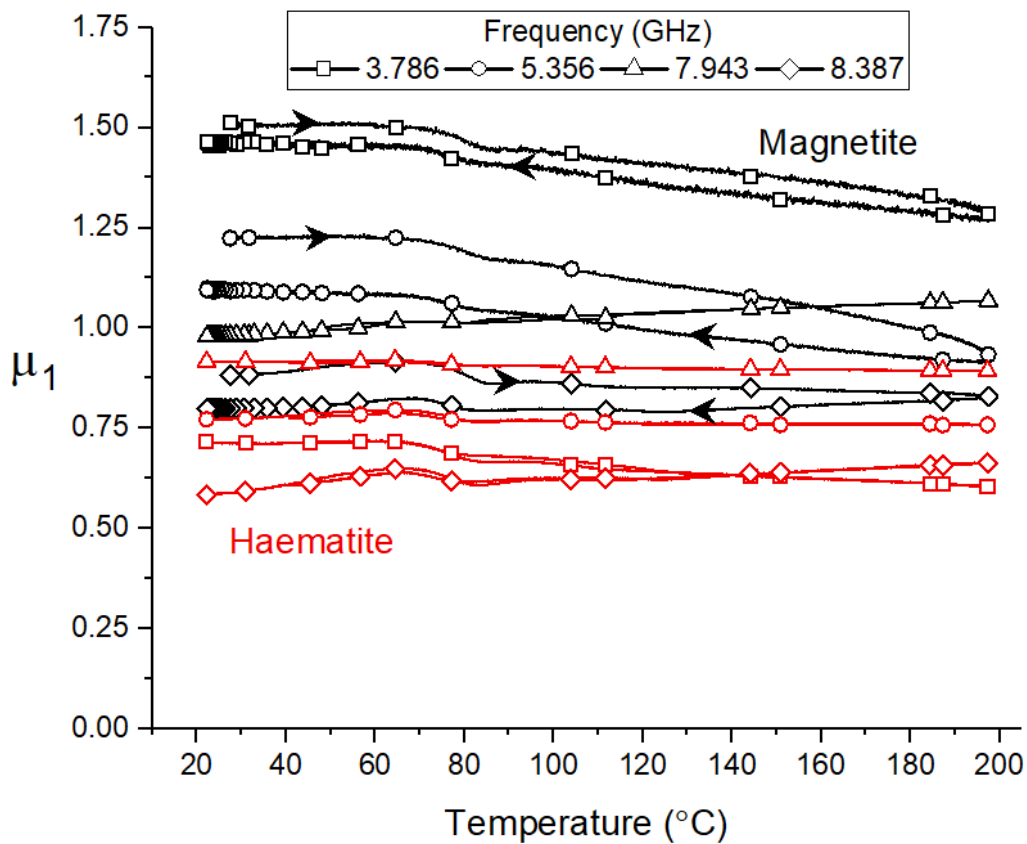


Figure 4.13 – Real part of permeability for magnetite and haematite from 25 $^{\circ}\text{C}$ to 198 $^{\circ}\text{C}$

Magnetite shows values between 0.34 and 0.69 over the entire temperature range. The three measurement frequencies shown display different behaviour as the magnetite is heated. At 3.786 GHz values start at around 0.49 and increase to approximately 0.65 at maximum temperature. Upon cooling the permeability reduces to a value of 0.58. The 5.356 GHz frequency shows a flat curve which begins and ends at around 0.67 and reduces only to 0.66 at maximum temperature. Measured values for 8.387 GHz begin at 0.55 which decreases to 0.34 at maximum temperature and then when cooling increases toward a value of 0.45.

Two frequencies display a large hysteresis and significant temperature dependence, although in opposite directions, while the other is relatively temperature independent. The reason for the different directions is likely a result of the broadband ferromagnetic resonance of magnetite which

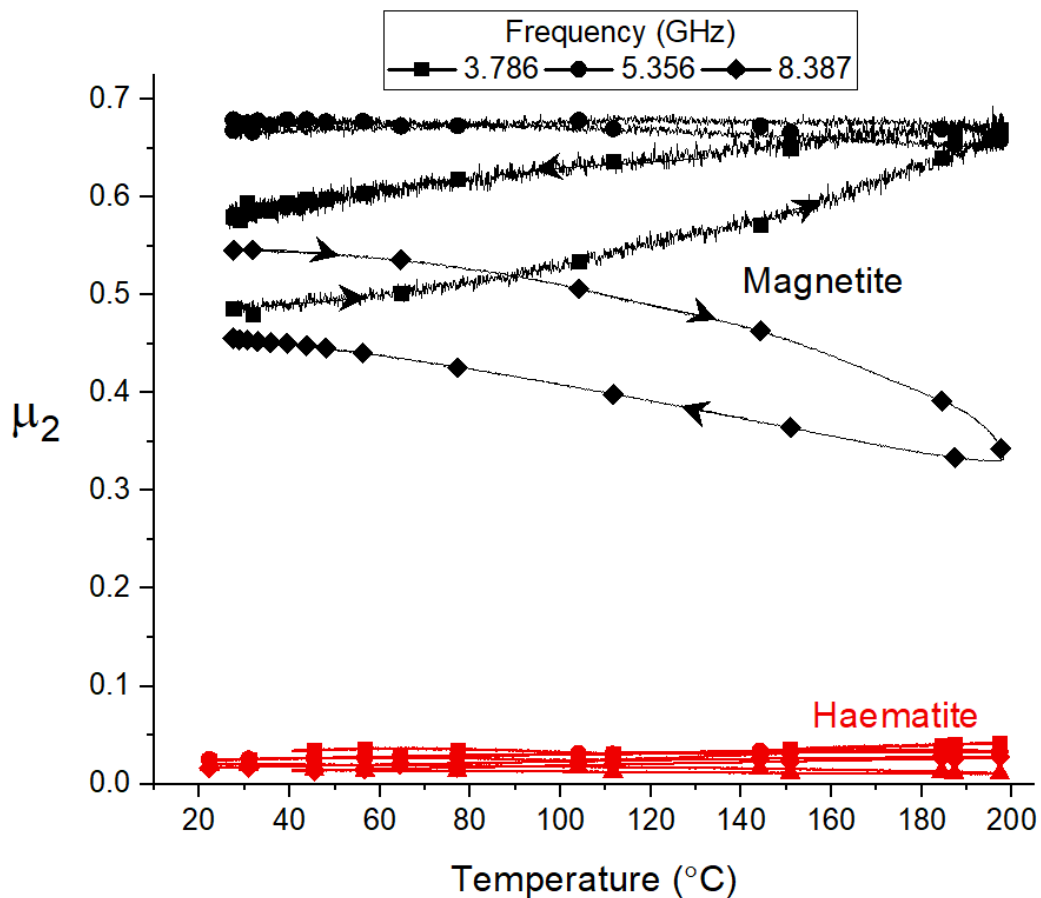


Figure 4.14 – Imaginary part of permeability for magnetite and haematite from 25 °C to 198 °C

can appear to reduce in peak frequency with increased temperature, leading the higher frequency measurement points to reduce and the lower values to appear to increase [96]. These curves again suggest magnetite has been partially oxidised by the heating up to 198 °C.

Haematite powder shows much less interesting results as all the curves remain very low, showing no significant hysteresis while not increasing above 0.05 even at 198 °C. This shows, like the room temperature measurements, that haematite is not very magnetically lossy and that this does not change while being heated up to 198 °C.

Some measurements exhibit high degrees of noise, for example in the imaginary part of permeability measured at 3.786 GHz. This is likely due to the insertion loss levels approaching the noise floor of the VNA near these frequencies, meaning more of the background noise is visible among the measurement values.

4.6.2.2 PERMITTIVITY

Similarly, the permittivity of both powders is assessed over the temperature from 25 °C to 198 °C. Figure 4.15 shows the real part of permittivity for both powders, data for TM_{011} (~ 4.57 GHz) has been excluded due to errors. The asterisk denotes the starting points for magnetite powder. Magnetite displays permittivity values between 5.5 and 6.0 at room temperature prior to any heat treatment. As heating begins all frequencies show a small dip in values, occurring between 60 and 110 °C, after which the permittivity begins to more rapidly increase until 180 °C. Near the maximum temperature the heating rate decreases slightly and the temperature is held at the maximum before decreasing again, and this produces a “bulb” shape for each curve near maximum temperature. When cooling below 180 °C back to room temperature the permittivity follows a much more linear-style relationship with temperature, settling at values between 3.60 and 5.20.

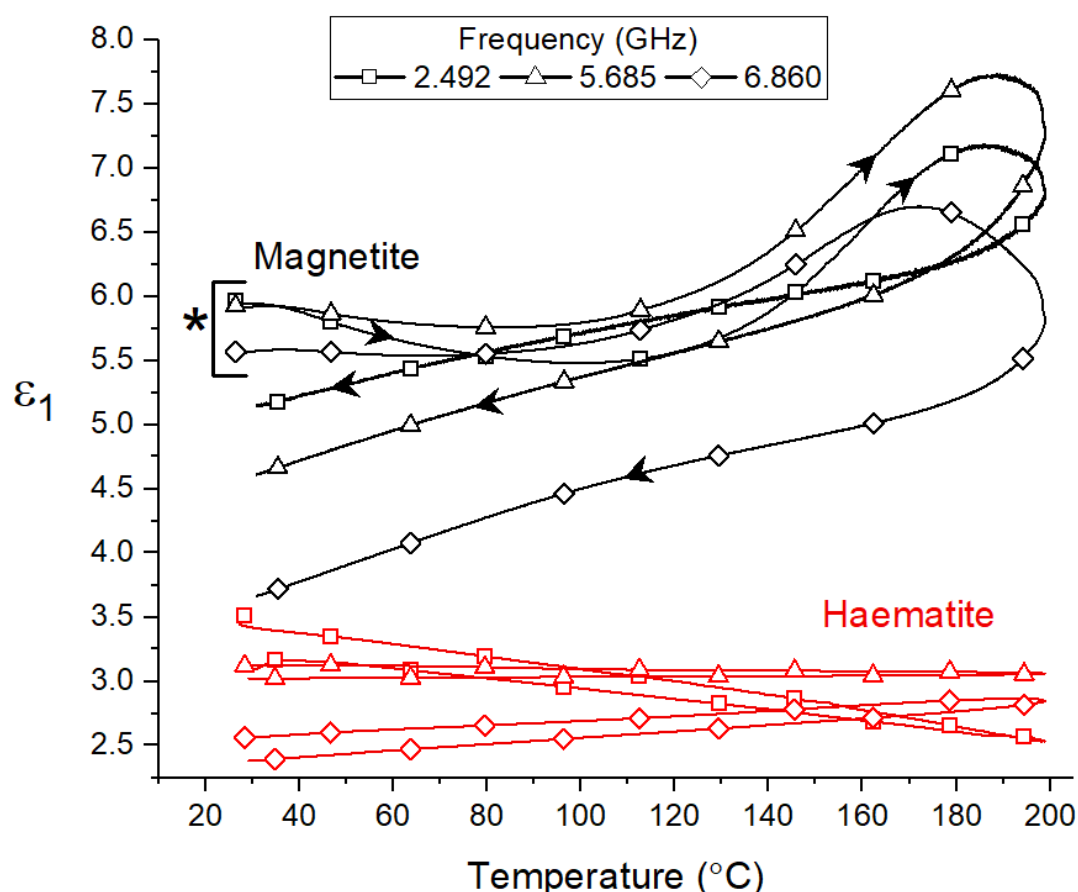


Figure 4.15 – Real part of permittivity for magnetite and haematite from 25 $^{\circ}\text{C}$ to 198 $^{\circ}\text{C}$

There are a number of interesting observations that can be made from this plot. Firstly, the dip in permittivity initially observed could be due to minimal water content in the powder. Water is a material with a very high permittivity so even a small moisture content could have a significant impact on measured permittivity. When heating above 60 $^{\circ}\text{C}$ this water may begin to evaporate and thus the permittivity reduces up until >100 $^{\circ}\text{C}$ where all the water which has not evaporated will be boiled away.

From this point up until 170-180 $^{\circ}\text{C}$ the permittivity increases but afterwards decreases even with increased temperature. When being held at the maximum temperature the permittivity continues to decrease as shown by the downward movement of each line. Upon cooling the traces all show similar linear behaviour with no more unusual deviations. These points indicate a chemical change is occurring in the magnetite that is strongly suspected to be a different polymorph of Fe_2O_3 , that is $\gamma\text{-Fe}_2\text{O}_3$ or

maghemite. While this has the same chemical formula as haematite it has a similar crystal structure and magnetic properties to magnetite, typically quoted as having a brownish hue to the powder. This transition has been observed indirectly through annealing of magnetite previously [96] with this data showing a transition in action. In this transition Fe^{2+} cations are oxidised to Fe^{3+} ones, which are believed to have lower contributions to the dielectric polarisation mechanism, therefore decreasing the relative permittivity [96][98].

The permittivity of haematite initially ranges from 2.3 to 3.5 and shows little temperature-dependent behaviour across the range studied, the most prominent being a negative correlation in the TM_{010} frequency with values reducing from 3.5 to 2.5. There is little to no hysteresis observed in the haematite curves and no unusual behaviour as was observed with the magnetite. This suggests no chemical or material change has taken place as the permittivity values return very closely to the initial measured values.

The imaginary part of permittivity is shown in Figure 4.16. Again, magnetite displays interesting temperature-related behaviour with values starting near 0.30 and ending near 0.95 with peaks up to 2.65. The asterisk denotes the start of the heating procedure where values across all frequencies are tightly spaced around 0.35. As observed with the real permittivity there is an initial dip dropping to 0.1-0.2 until 110-120 °C where a rapid increase begins. This reaches peaks between 1.70 and 2.65 indicating a significantly dielectrically lossy material with loss tangents in the region of 0.3. When cooling the temperature relationship stops being exponential in nature and becomes more linear as the values reduce to a grouping between 0.8 and just over 1.0.

These behaviours align with observations made of the real permittivity. It seems as though water is initially being driven off by the heating as the loss reduces. When the transition begins to maghemite it is much more pronounced for the imaginary permittivity as the values shoot up rapidly

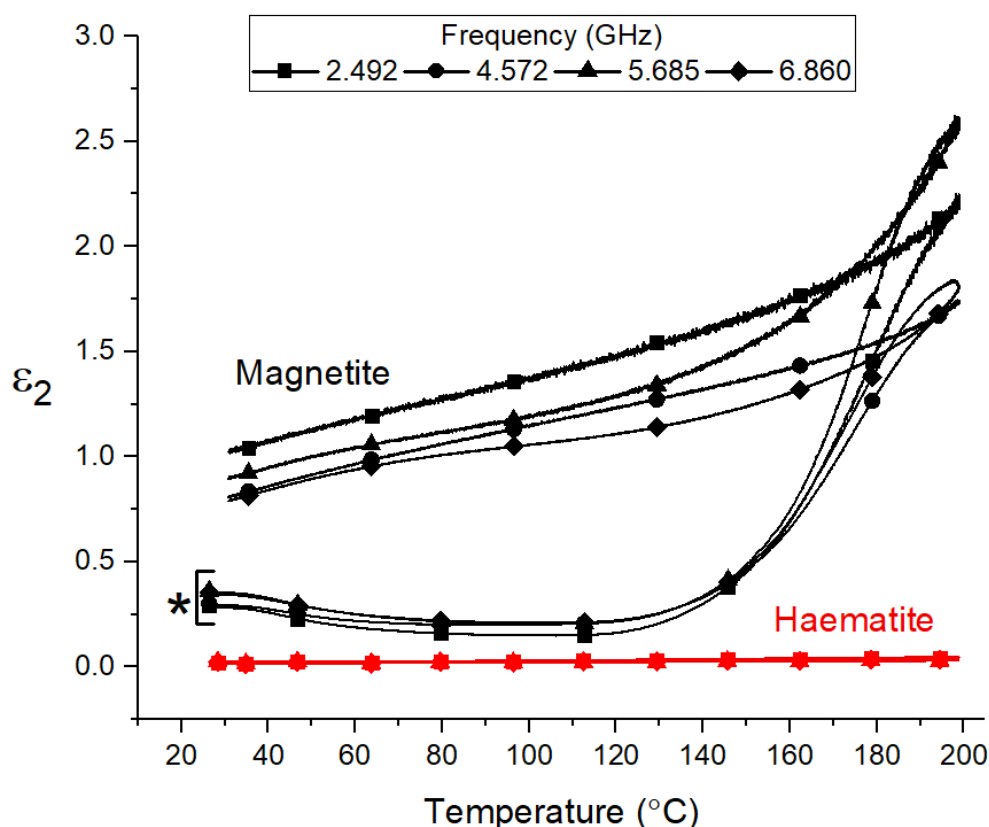


Figure 4.16 – Imaginary part of permittivity for magnetite and haematite from 25 °C to 198 °C. Asterisk denotes initial values.

and the final values are significantly different from the initial ones, showing a material change has taken place. The maghemite appears to be significantly more dielectrically lossy than magnetite even when cooled back to room temperature.

Haematite shows almost zero dielectric loss across all temperatures and frequencies studied. Although it is not possible to see on the graph, the haematite has values for imaginary permittivity of around 0.025, rising to 0.035 at maximum temperature that decreases to 0.015 when returning to room temperature. These values indicate a relatively low loss material with loss tangents of no more than around 0.01. This suggests that haematite will not heat effectively through microwave electric field heating.

4.6.3 FREQUENCY RANGE

As a number of frequency points over a range of a few gigahertz have been used to accumulate data while heating samples, it is also possible to present this data with relation to the frequency of the resonant mode. This may give some insight into any frequency-dependent behaviours displayed by the powders both generally and through the heating process. Due to the constraints of choosing suitable resonant modes to measure both the permeability and permittivity of the substances, there are only three or four x-axis data points. This makes it unlikely we can draw any definitive conclusions from the data presented in this way, although we may see correlations that warrant further investigation or discussion.

Given the relatively low values for both complex permeability and permittivity for haematite it is considered an unsuitable candidate for effective microwave heating applications. It is therefore excluded from further study in this section to more closely focus on the more interesting material of magnetite.

4.6.3.1 PERMEABILITY

The permeability of the magnetite pre- and post-heating was assessed against frequency. As the magnetite has been assumed to have transitioned, at least partially to maghemite it is labelled as maghemite in the plot in Figure 4.17. This compares both the real and imaginary permeability of magnetite and maghemite over the frequency range, with the real part on the left y-axis and imaginary part on the right y-axis.

From this plot we can conclude that the real permeability of magnetite has a frequency dependent component, showing a negative correlation over the span 3.7-8.4 GHz. The real part of permeability is highest at lower frequencies (> 1.5 at 3.78 GHz) and lowest at the highest frequency measured (< 0.91 at 8.78 GHz) showing a somewhat linear decrease with frequency. The maghemite is very similar across all frequencies showing the same trend but with slightly lower values,

typically a reduction of 0.5 to 0.15. This is similar to reported values in literature, showing real permeability often dropping below 1 at mid-range and high microwave frequencies with a steep negative gradient from peaks around 1.5-2.0 [98].

The imaginary permeability could be frequency independent, having no apparent association over these frequencies and showing variation in both directions with increased frequency. The imaginary permeability could also be exhibiting a peak at or around 5.4 GHz. Other work on this subject has observed this [98] broad peak of imaginary permeability. It is suspected, given the packing density and size of particles used we may be observing a similar phenomenon. Very small particles may exhibit a single domain and so the expected resonant peak due to domain wall rotation around 50 MHz will not be present, and the higher frequency peak (> 3 GHz) due to rotation of magnetic moments will dominate.

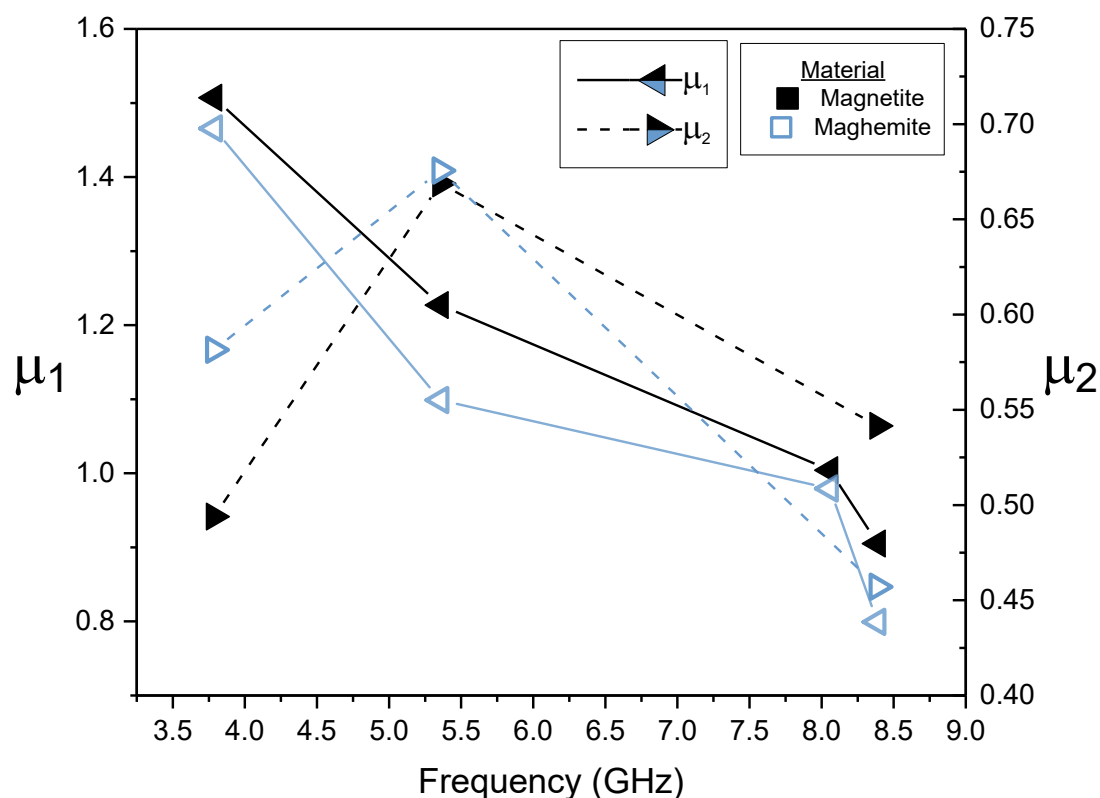


Figure 4.17 – Complex permeability of magnetite and suspected maghemite powders

It is important to keep in mind these measurements are constrained by limited data points and limited frequency scope. If there is some frequency effect to be observed as indicated by Figure 4.17 it may be an example of broadband natural resonance of magnetite, and we may only be seeing a small portion of correlated data, which may or may not be confirmed with more investigation.

4.6.3.2 PERMITTIVITY

The permittivity is also assessed against frequency for magnetite at room temperature and after heating to 200 °C and being allowed to cool back to room temperature. Both the real permittivity and the imaginary permittivity are shown in Figure 4.18, with the real part on the left axis and the imaginary part on the right axis. The asterisk denotes an excluded erroneous data point for the TM₀₁₁ mode (~4.5 GHz).

Initially the real permittivity shows no frequency dependence with values around 6.0 across all frequencies. Post-heating values for the permittivity are decreased across the whole frequency range by around 0.75-1, with the most prominent difference visible at the highest measured frequency of 6.86 GHz. At this frequency the real permittivity has decreased by more than 1.9 from 5.56 to 3.66. This is indicative of the sharp drop in dielectric constant observed for magnetite transitioning to maghemite when heated to 200 °C with a non-inert atmosphere [96] which is not present when magnetite is heated in an inert environment to at least 285 °C [185].

There is a slight downward trend in real permittivity of maghemite with increased frequency but it is difficult to draw firm conclusions based on the data available. This could be because the oxidation of Fe²⁺ to Fe³⁺ cations, reducing the effective polarisation impact, which is much more prominent with increased frequency where the polarisation mechanisms

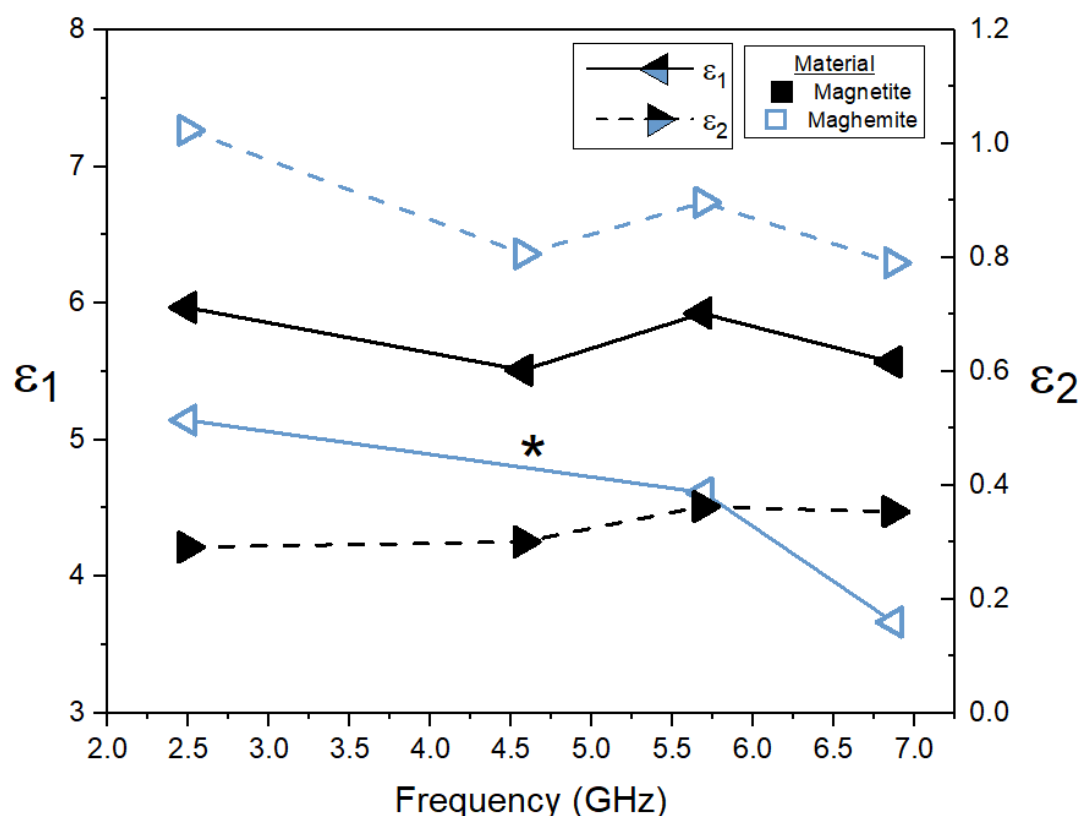


Figure 4.18 – Complex permittivity of magnetite and suspected maghemite powders. The asterisk denotes excluded data for the TM_{011} mode (~ 4.5 GHz)

becomes less dominant compared to other mechanisms such as atomic and electronic polarisation.

The imaginary part of relative permittivity shows initial values for room-temperature magnetite of around 0.30-0.35, which is in line with expected values for this range of packing density (relative density) of around 19-20 % [98]. There is little to no frequency dependence observed across these values with a slight increase over the approximate 5 GHz frequency range. We may expect to see some increase in loss at these frequencies and higher (>10 GHz), but this is highly dependent on particle size and packing density [98]. These loss values are low but are not characteristic of a low-loss material; magnetite could certainly be heated with this level of dielectric loss expected across all frequencies as evidenced by other work [9].

After heating and cooling, the maghemite shows significantly increased dielectric loss with values for imaginary permittivity between 0.8 and 1.0

with a slight negative frequency dependence. This agrees with values of other work where annealed Fe_3O_4 is measured using similar techniques to those used here [96]. Interestingly this work measured dielectric loss to peak at 200 °C near 1.0 and then rapidly decrease above this temperature to near zero at 300 °C. The initial room temperature to 200 °C measurements performed agree with the results presented here. The proposed explanation for this peak is the partial oxidation of the Fe_3O_4 to a much less lossy $\gamma\text{-Fe}_2\text{O}_3$. The significant difference between the dielectric loss of both materials and their physical mixture means that when a critical percentage of the volume of the lossy magnetite is oxidised to maghemite a significant increase in loss is observed.

Combining the results of post-200 °C heating of magnetite for permeability and permittivity presents an interesting opportunity for microwave heating scenarios. If magnetite powder could be heated to 200 °C in air to partially oxidise it and create a critical-volume mixture of magnetite and maghemite, it could potentially be both significantly magnetically lossy (> 0.67 at around 3.5 GHz) and also exhibit significant dielectric loss (> 0.9 at around 2.5 GHz). This mixture material could be a highly effective absorber of magnetic and electric field energy around common microwave frequencies e.g. 2.45 GHz, allowing highly effective energy transfer utilising both fields.

4.7 CONCLUSIONS

This chapter has discussed the application of the microwave cavity perturbation method to measure complex permeability and permittivity of powder materials. The assumptions and approximations used to make this method practically applicable were mentioned, including small sample quantities that experience constant field strength across their length, and do not significantly distort the field distributions of the relevant mode.

The microwave characterisation of magnetite and haematite powders has shown the complex permeability and permittivity at room temperature, up

to 200 °C, and across GHz frequencies. These powders were shown to exhibit moderate dielectric constants between 3 and 4 for haematite, and around 7.25 for magnetite. Dielectric loss values for both powders showed haematite to be low loss with around 0.02 across all frequencies suggesting minimal heating in response to microwave electric fields. Magnetite had a significant dielectric loss of between 0.37 and 0.5, suggesting that it could be compatible as an electrically stimulated catalyst. This agrees with other works that have utilised magnetite's electric heating capabilities [9].

Real permeability values of magnetite displayed some frequency dependence, with a negative correlation between frequency and permeability. Values were as high as 1.5 for low microwave frequencies that decreased to below 1 (approx. 0.9) for higher frequencies. This suggests magnetite may be exhibiting a form of natural resonance, being able to form a magnetic field in opposition to the applied one, making permeability values of below 1 possible. Haematite did not display any visible frequency dependence but its permeability was consistently below 1. This displays the weakly antiferromagnetic behaviour of haematite.

Magnetic loss values for magnetite and haematite were also significantly different. Haematite showed very low non-zero values much like its dielectric loss, suggesting minimal magnetic heating would be possible. Magnetite showed significant initial magnetic loss with values between 0.5 and 0.7. suggesting a strong heating response would be achieved in a microwave magnetic field. These measurements create an image of magnetite as an effective microwave absorber, both with the electric and magnetic fields. High magnetic loss values indicate the potential for a highly selective catalyst. Haematite was shown to be a poor microwave absorber that may heat in microwave EM fields but not particularly effectively.

Assessment of these values at elevated temperatures up to 200 °C showed significant changes in the magnetite. This was most visible in the

plots of real and imaginary permittivity. Dielectric loss of magnetite decreased during initial heating, which was theorised to be the drying of powder and driving off of highly lossy water. After 120 °C the loss began to increase rapidly and continued to rise until the maximum temperature, only decreasing once cooling had begun. This showed the (partial) transition of magnetite to maghemite, a different polymorph of Fe_2O_3 . The maghemite showed lower dielectric constant, higher dielectric loss and similar complex permeability values across most frequencies. Maghemite may also be a viable microwave magnetic susceptor that could warrant more thorough investigation.

Chapter 5

5 MONO-MODE MICROWAVE HEATING

5.1 WHY MICROWAVES?

In the previous chapter the results of MCP measurements on magnetite and haematite powders indicated a strong potential for magnetite to heat via magnetically driven microwave heating. This also demonstrated agreement with existing studies utilising magnetite's ability to effectively absorb energy from microwave electric fields [9][23][35][76][78][104]. This relationship is tested by applying microwave power using mono-mode resonant cavities. This is a very similar approach to the MCP measurements but with a significant difference being the power introduced into the cavity. In MCP measurement cavities the incident power is incredibly small on the order of fractions of microwatts or less than -30 dBm; just enough to create the electromagnetic fields and measure very small changes. When heating materials these tiny power levels will not have enough energy to produce meaningful temperature change so typical levels between 1-100s of Watts are used (30-50+ dBm) [17][18][19][20]. Although these power levels are still small and comparable with some common home appliances such as TVs, fans, or old incandescent light bulbs [110], in the context of microwave application they can contribute significant energy to materials and produce substantial temperature changes, depending on the sample size and cavity system used.

Microwave heating is widely used in interdisciplinary works in fields such as catalysis, bioscience, manufacturing, materials science, physics and medical engineering. [9][18][186][187][188][189][190] [192].

Microwave heating is often chosen over conventional methods due to its

different mechanism of heating. Conventional heating using an oven or furnace typically heats an element, which can either heat a material directly through conduction or heat a cavity full of air (or another fluid) to heat the desired substance through convection. Microwaves are inherently different in that they heat via radiation; microwaves are absorbed within the material, heating volumetrically. This absorption is what is being measured when the imaginary part of microwave permeability and permittivity is discussed.

Microwaves have another advantage in their selectivity. As previously discussed, materials will have different values of permeability and permittivity and so will absorb microwave energy to varying degrees. Materials with very low loss values (such as quartz) are effectively transparent to microwave radiation whereas materials with high loss values will absorb a lot of microwave energy. By carefully choosing materials based on these values the microwave energy can be selectively applied to certain target materials while avoiding wasting energy heating up others. This is useful for applications like catalysis where a sensibly chosen catalyst material can absorb a high proportion of the available energy, heating rapidly and efficiently. This is particularly applicable for magnetically lossy materials, of which there are far fewer than electrically lossy ones.

5.1.1 SELECTIVE HEATING AND SKIN DEPTH

The difference between conventional and microwave heating, and the selective nature of microwave magnetic field heating is shown schematically in Figure 5.1. This illustrates the mechanics of conventional heating, which must heat particles primarily through conduction and convection, initially from the particle exterior. Microwave heating mechanisms allow particles to be heated volumetrically given the particle is similar in radius or smaller than the skin depth of the material at the given EM frequency. Given microwave frequencies are in the region of 10^9

Hz and the discussion is limited to good conductors or electrical semiconductor materials with resistivities generally lower than $10^1 \Omega \cdot \text{m}$ a simplified skin depth calculation can be used to gauge what size a particle of material will need to be to heat volumetrically and avoid or diminish the skin effect. This relationship is shown in (5.1)

$$\delta = \sqrt{\frac{2\rho}{\omega\mu}}, \quad (5.1)$$

where δ is the skin depth, ρ is the electrical resistivity, ω is the angular frequency also equal to $2\pi f$, and μ is the permeability of the material equal to the relative permeability of the material multiplied by the permeability of free space. Given the resistivity of magnetite is in the region of 10^{-3} to $10^{-5} \Omega \cdot \text{m}$ [191], the heating frequency is around 2.45 GHz and the relative permeability of magnetite in this region is approximately 1.5, the skin depth can be estimated to be between 26 and 260 μm . This provides the approximate distance into the particles that EM waves can permeate before being diminished to $1/e$ or around 37 % of their initial value. If particles are comparable in size to the skin depth or significantly smaller than it, they will absorb EM energy throughout their volume.

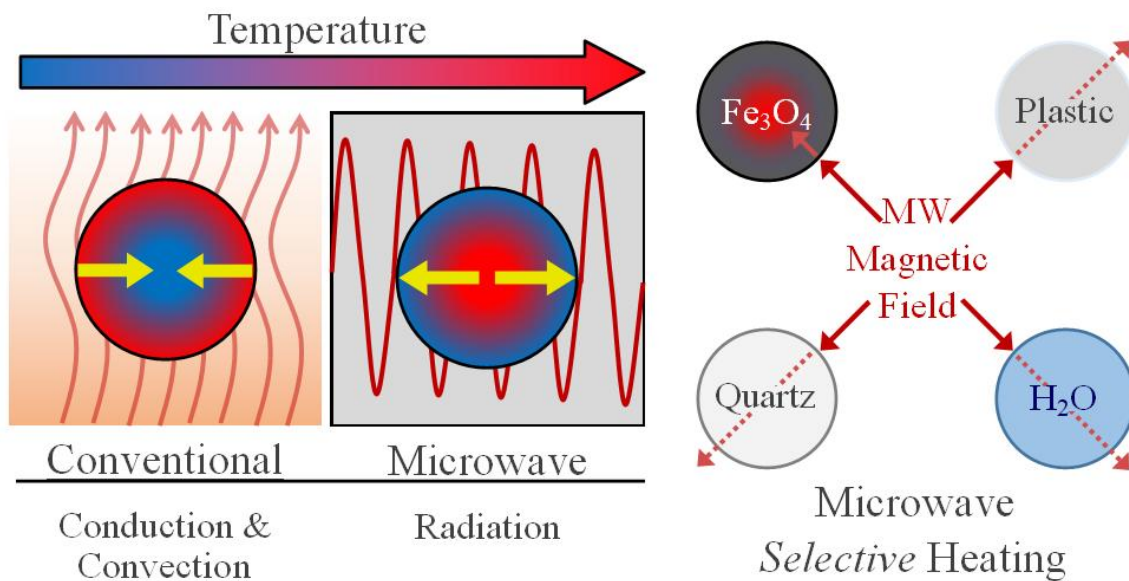


Figure 5.1 – Schematics of conventional vs microwave heating mechanisms & selective nature of microwave heating

This is a limitation of microwave heating when compared to conventional heating. For larger particles and highly effective conductors the microwaves will only penetrate a small distance into the surface of the material and so this type of heating becomes impractical. Given we can use particles comparable to the skin depth i.e. powders, microwave heating can be a highly applicable method.

Figure 5.1 illustrates this idea but it is also important to keep in mind that in microwave heating the surrounding medium is often not heated directly. This will create a temperature gradient at the particle-medium boundary which is not the case for conventional heating. This temperature gradient could be significant if effective microwave absorbers are used and heated by hundreds of degrees in a few seconds, and so they will also dissipate heat more quickly to their surroundings than in a conventional system.

5.1.2 MONO-MODE HEATING

Microwave heating using resonant cavities can be done using many different modes, or even combinations using multi-mode approaches. Many people will be familiar with multi-mode cavity heating as this is the method employed by standard domestic microwave ovens to heat food [193]. These systems use hundreds of Watts and aim to heat significant masses of food quickly and evenly, but their multi-modal fields are more difficult to model and predict than mono-mode systems.

Mono-mode cavities are preferable for scientific experimentation as they have more easily understandable and predictable field distributions. This allows easier identification of regions to study which may have very high magnetic or electric field strength that can be investigated repeatedly. As the magnetic field is the primary focus in this work it is important to choose a mode in which magnetic field strength can be maximised and is consistent. The TM_{010} mode was used throughout this work to perform magnetically-driven heating. This mode has a maximum magnetic field

formed in a ring at 0.24 times the cavity radius ($0.24 \cdot a_c$) from the interior cavity wall that extends the entire height of the cavity. The mode is independent of the cavity height as there are no field variations in z-axis and it is the fundamental TM mode, having both the lowest frequency and typically being well-isolated from other modes. The magnetic field distribution of a cylindrical cavity in the TM_{010} mode is shown in Figure 5.2(a) as well as the normalised magnetic and electric field strengths across the cavity radius in Figure 5.2(b). Figure 5.2(b) also shows the point at which a sample tube can be inserted to maximise exposure to the magnetic field. In this mode the sample would also be exposed to around 30 % of the maximum electric field strength, meaning that a combined heating effect will be realised utilising the maximum magnetic field region and a significant contribution from the electric field. For a sample like magnetite which is both magnetically and electrically lossy this could prove to be a more effective microwave absorption method.

If a cavity radius is chosen around 46.75 mm the resonant frequency will be approximately 2.45 GHz, which is a commonly used frequency as it is

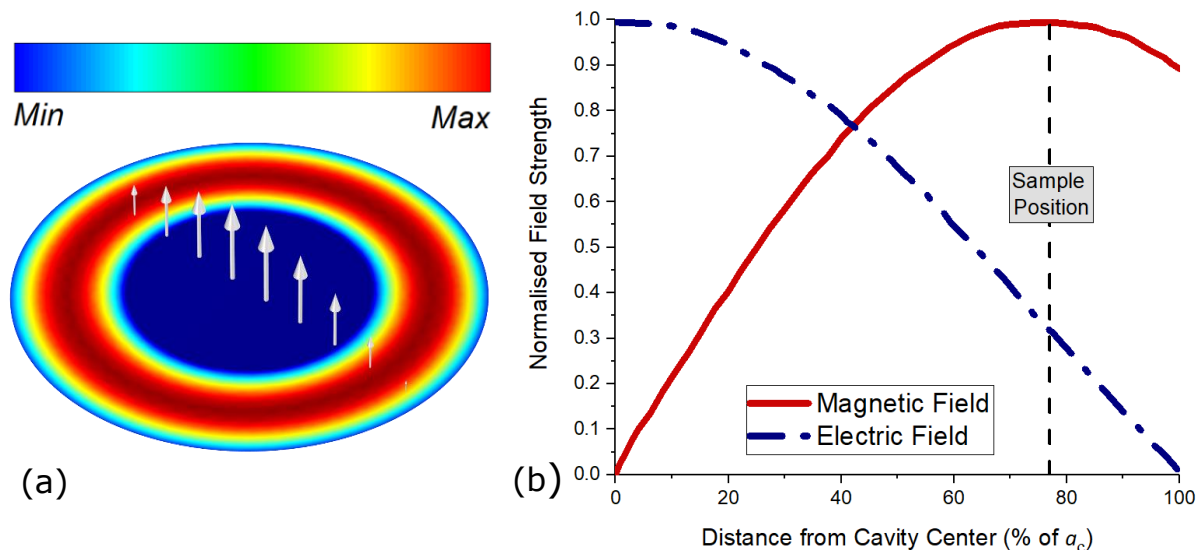


Figure 5.2 – Representations of the field distribution in the TM_{010} mode shown using (a) finite element modelling with the colour scale showing magnetic field intensity and the white arrows showing electric field intensity and (b) the normalised field strength of magnetic and electric fields through one radial slice of the cavity, as a function of distance from the cavity center, shown as a percentage of the cavity radius, a_c .

the centre of the 2.4-2.5 GHz ISM frequency band [194] and is used for most domestic microwave ovens. This is useful for comparisons across other works where specialist microwave equipment is less common and will help eliminate any effects that could be attributed to performing experiments at a significantly different frequency. Using this radius the position of the magnetic field maximum occurs approximately 11.2 mm from the cavity wall.

5.2 EQUIPMENT

5.2.1 CAVITIES

The resonant cavities used here are similar in construction to those used in Chapter 4 for MCP measurements, being constructed from 6082-T6 aluminium and forming a cylindrical cavity. These cavities have 10.0 mm holes in both the top and bottom of the centre of the cavity designed to allow samples to be inserted into the centre, each with a 20.0 mm tall choke to restrict any microwave fields spilling out of the cavity. The cavities also have a 10.0 mm diameter hole drilled vertically through the cavity near one of the cavity walls in a spot where the magnetic field is maximal, as determined by Figure 5.2. This allows samples to be placed reliably in the ideal position for magnetic field stimulation. Aligned with these holes is a thin vertical slit cut into the exterior cavity wall running most of the cavity height. This slit allows viewing of the sample when positioned in the magnetic sample hole both visually and by temperature monitoring equipment. Figure 5.3 shows side and top views of this type of cavity with the viewing slit and magnetic field cavity sample positioned next to the slit. This slit has minimal effect on the field distributions as it is aligned parallel to the surface currents on the cavity walls, minimising the obstruction to current flow.

The cavities in Chapter 4 were excited by either a small antenna or loop probe with SMA connectors, but this is not sufficient for cavity heating applications. These small coupling structures allow a very weak coupling

strength which is often desired for making sensitive measurements, but when applying much greater power levels and coupling to the magnetic field in the TM_{010} mode a more substantial loop coupling structure is required. A custom loop is constructed from a section of wire soldered to a modified N-type connector. This creates a separate coupling “barrel” which is inserted into the side of the heating cavity, opposite to the side with the viewing slit. This barrel is not affixed directly to the cavity but is held in place by two grub screws which can be tightened from outside the cavity with basic hand tools. This allows the coupling loop to be moved in and out of the cavity and rotated to manually adjust the coupling strength by adjusting the effective area of the coupling loop. This type of coupling loop structure is shown in Figure 5.3, with an enlarged view shown in Figure 5.4.

These coupling loops feature thicker wires than those used for perturbation measurements, which are able to handle higher current and therefore power levels which are required for microwave heating. These loops work through Faraday’s law of induction; TEM waves are supported in the coaxial cables allowing current to flow through the custom loop.

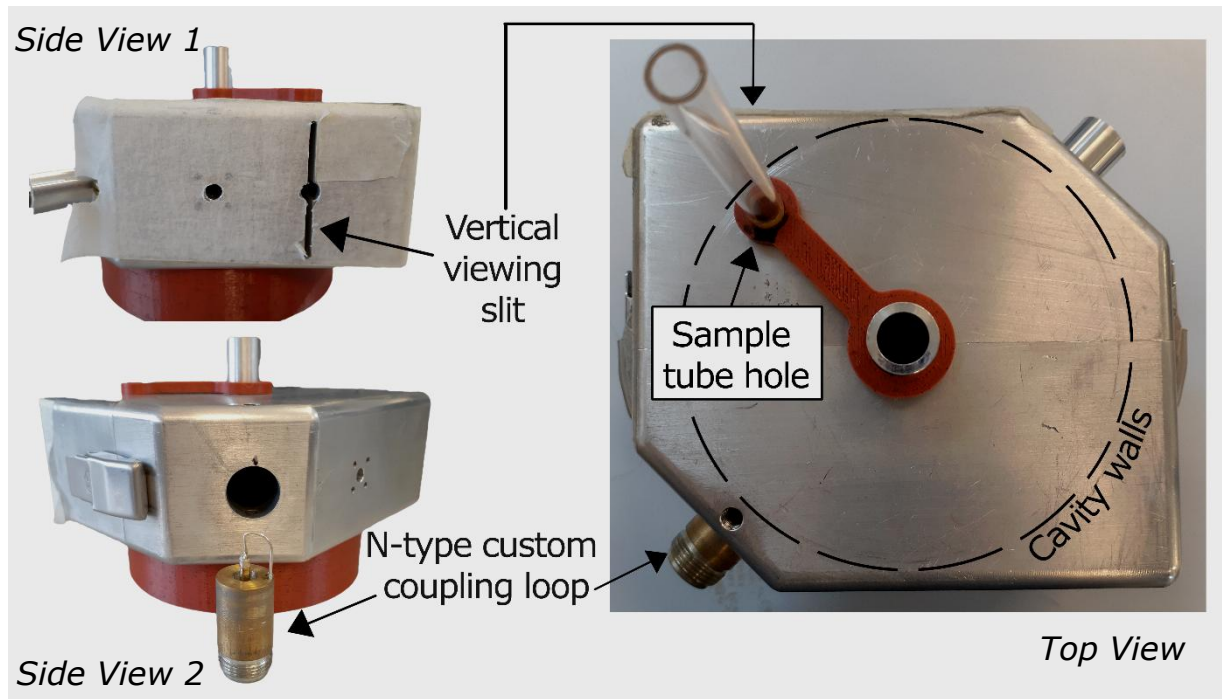


Figure 5.3 – Cavity side views and top view showing viewing slit, sample tube location and N-type coupling loop structure.

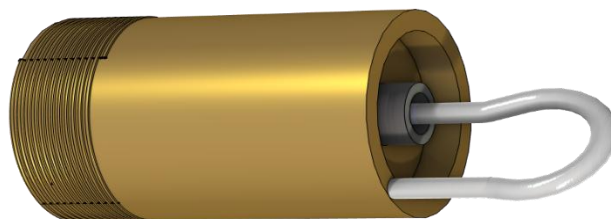


Figure 5.4 – Modified N-type connector acting as a coupling loop

This creates a localised magnetic field around the loop wire, which when positioned in the maximum magnetic field region of the cavity and aligned so that the “surface” of the loop is perpendicular to the magnetic field lines i.e. intercepting the most magnetic flux, can transfer power into the cavity, creating the resonant field distributions as in Figure 5.2(a).

This style of cavity can be constructed with slightly different radii to produce different resonant frequencies. Some equipment can only operate in certain narrowband frequency ranges, which might mean the cavity frequency does not fall within the range. To accommodate this a duplicate cavity can be machined with a slightly different radius and used in the exact same way. This will be further discussed when the microwave generating equipment is explained.

5.2.2 SAMPLE POWDERS

The same powders used in the MCP measurements of Chapter 4 are used here. These are magnetite (Fe_3O_4 or iron (II,III) oxide) and haematite (Fe_2O_3 , iron (III) oxide). Both magnetite (310069)($< 5 \mu\text{m}$, $>95 \%$) and haematite (310050)($< 5 \mu\text{m}$, $>96 \%$) were purchased from Sigma-Aldrich. For more details of these powders refer to section 4.4.1 in Chapter 4.

5.2.3 QUARTZ TUBING

Similarly, quartz tubing is used for containment and support of the powders here as was done in Chapter 4. Quartz is chosen for its low microwave loss characteristics and ability to withstand high temperatures

which are both important qualities for high temperature microwave heating. Quartz tubes with an outer diameter of 8.0 mm and inner diameter of 6.0 mm are the standard choice throughout the remainder of this work, with both open-ended and rounded closed-on-one-end tubes used. Open-ended tubes have lengths of 100.0 mm making them long enough to extend throughout the entire cavity height, even in the central part with the fitted chokes. Tubes with one closed end also have 100.0 mm variants as well as shorter tubes, measuring 50.0 mm in length. The longer of these tubes can be either extended through the entire cavity length or, like the smaller tubes, be situated so the closed end sits vertically close to the middle of the cavity.

When using open-ended tubes, it is necessary to support any sample within the tube. To achieve this, small amounts of quartz wool are used to support powders. These allow the powders to remain stationary while allowing gases to flow through the tube and have no appreciable effect on the microwave coupling or heating of samples.

5.2.4 PORTABLE MICROWAVE APPLICATOR

To provide microwave energy to the resonant cavities there are multiple possible solutions such as magnetrons or solid-state semiconductor-based generators and amplifiers [195][196][197]. The chosen solution here is the use of a solid-state microwave generator and amplifier as the base of a portable system that is aptly named the portable microwave applicator (PMA). The PMA is useful as it can be used for a range of microwave applications such as measurements or heating applications and can also be used for a variety of multidisciplinary applications. A solid-state solution is generally considered more precise than magnetron systems, being digitally controlled and capable of high frequency resolutions. Solid-state systems are able to respond rapidly to changes in the EM properties of a load through digital locked loops, but often at the cost of maximum power capabilities which magnetrons excel at. Solid-state systems

typically use low-loss coaxial cables for signal propagation, minimising losses from generation to application when compared to magnetrons and waveguides. The efficiency of power absorption in samples can be seen to be superior in solid-state systems, but given the lower efficiency at the power generation step, the overall efficiency between the systems is still largely comparable [198].

The PMA consists of a signal generator (34 MHz – 4.4 GHz, Windfreak Technologies SynthNV) [199] with integrated power meter connected to a microwave amplifier (Mini-Circuits® ZHL-100W-242+) [200] with maximum output power of 100 W between the frequencies of 2.0-2.4 GHz, which is mounted to an appropriate heat sink and fan for cooling. The amplifier output connects to a three-port circulator and then into a directional coupler which then provides the microwave output signal. The directional coupler provides feedback to the signal generator, and the return signal path flows through port three of the circulator into an attenuator to protect the amplifier from high reflected power levels. The signal generator, amplifier and fan are powered from an external power adapter which can be connected to any standard mains socket. The signal generator is controlled through a standard USB connection that can be connected to most PCs or indeed laptop computers. These components are all mounted to a portable acrylic board measuring approximately 0.50×0.30 m and weighing only a few kilograms. An external power meter (Ladybug LB480A) and attenuator are used for initial calibration of the PMA power levels. A schematic diagram of the PMA is shown in Figure 5.5.

The PMA is controlled through custom-built software based on National Instruments LabVIEW environment. This controls the power level output, frequency and duration of the microwave signal as well as recording the reflected signal power. At set intervals the output power is briefly reduced to minimal levels and a frequency sweep is performed to continually maintain the optimal frequency for power transfer to the load. During

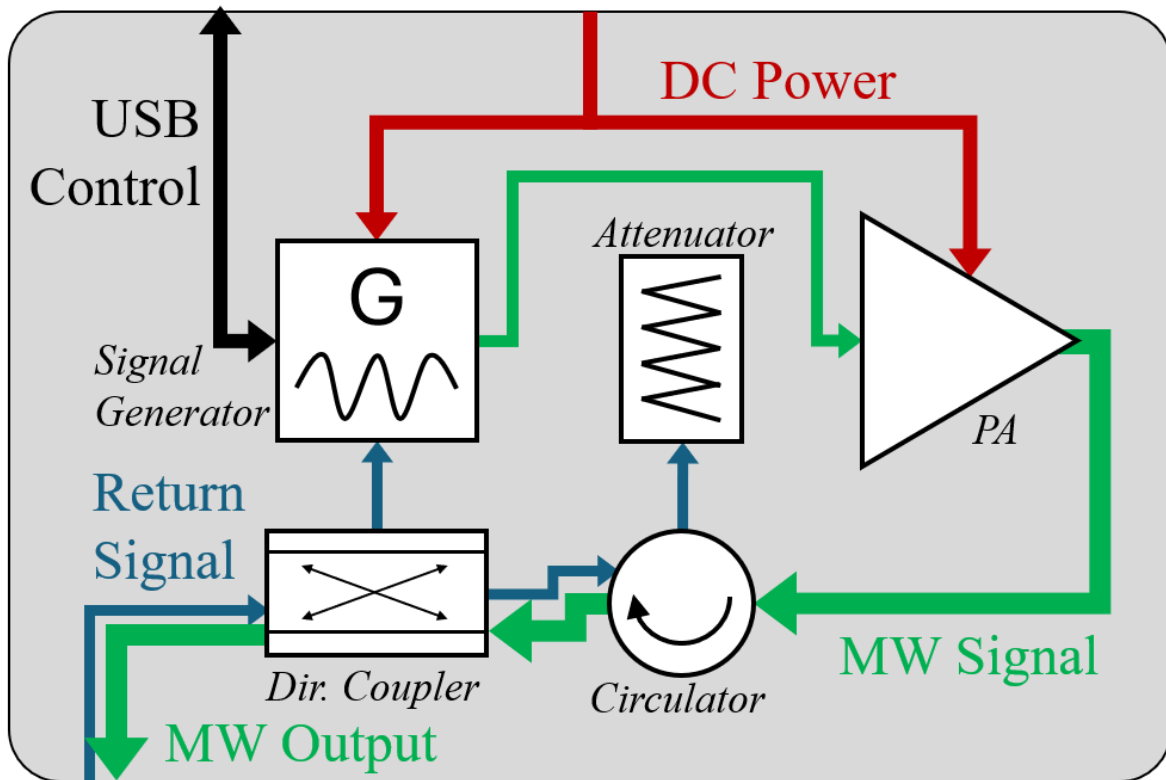


Figure 5.5 – Schematic diagram of the PMA system showing basic signal flows these frequency sweeps the S_{11} curve is recorded. When controlling the microwave output the primary controls are the target output power, duration, sweeping interval and coupling strength (which is adjusted manually before microwave application).

5.2.5 PYROMETERS

Pyrometers are effective temperature measurement tools used extensively in non-contact temperature monitoring applications throughout industry and research fields [201][202][203]. Non-contact temperature measurement is required for microwave heating analysis as any temperature monitoring solution inserted into the cavity will alter the electromagnetic fields, interfere with the heating and potentially cause damage to the microwave equipment.

Two infrared pyrometers were used to measure temperatures of samples during microwave heating, both from Micro-Epsilon. A CT-SF22 capable of measuring between -30 and 975 °C, and a CTM-3CF75H3 capable of measurements between 250 and 1800 °C [204]. For convenience the CT-

SF22 pyrometer will be referred to as the low-range pyrometer (Low) and the CTM-3CF75H3 will be referred to as the high-range pyrometer (High). Using 3D printed threaded holders, the pyrometers can be affixed to the side of the cavity to view the sample through the viewing port or on top of the sample to view the sample from above. An illustration of the two possible pyrometer orientations is shown in Figure 5.6.

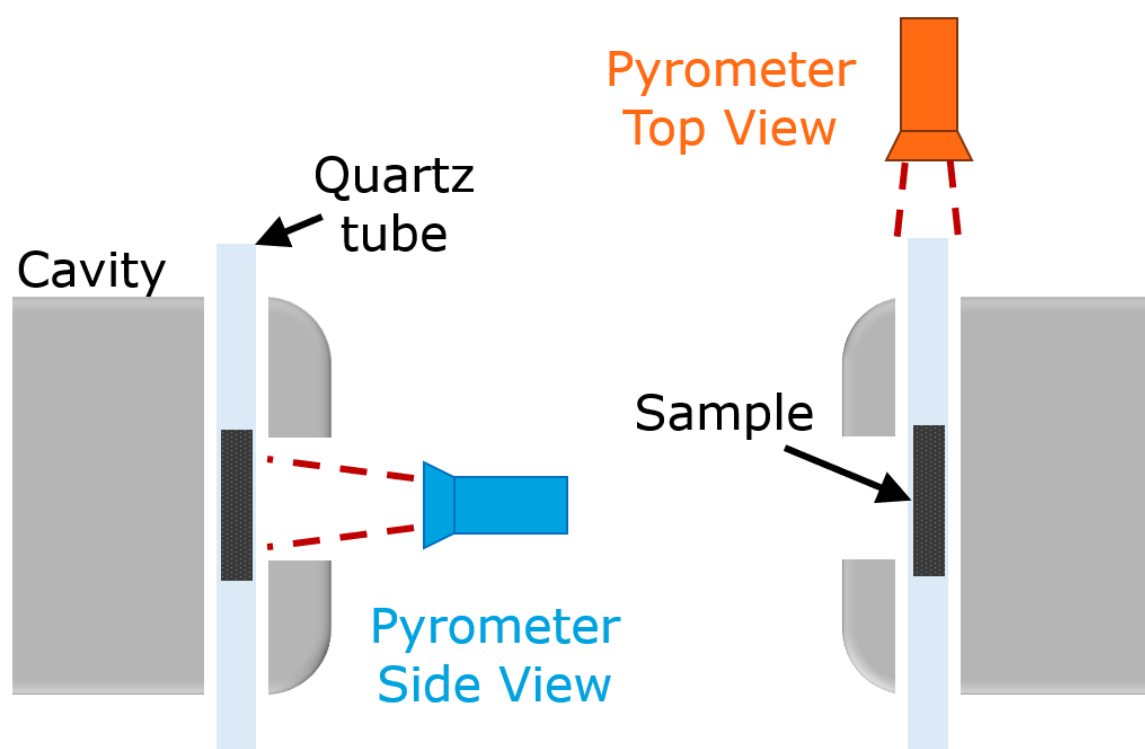


Figure 5.6 – Pyrometer orientations; they can either view the sample side-on through the viewing slit or top-down through the open end of the quartz tube

5.2.6 INFRARED CAMERA

An infrared thermal camera is also used for temperature monitoring by viewing the full height of the sample through the cavity viewing slot. Like pyrometers, IR cameras are utilised in industrial temperature monitoring applications with the added benefits of a wide optical range and video feedback to see temperatures across a whole region instead of a single point [201][205][206][207]. A Micro-Epsilon TIM 640 is used with a temperature measuring range from -20 to 900 °C [208]. The IR camera is used exclusively in the side view orientation.

5.3 METHODOLOGY

5.3.1 ELECTRICAL SETUP

Details of the procedure for setting up the electrical parts of experimentation equipment are included here for reproducibility. The required parts include the PMA, microwave cavity, appropriate coaxial cabling to connect the PMA output and resonant cavity, an external power meter (Ladybug LB480A) and attenuator, and a PC with software capable of interacting with the PMA. The software is custom-built for these types of PMAs by colleagues previously at Cardiff University and is based on the National Instruments LabVIEW software package. The key functions of the software are to run a power calibration, control the centre frequency and power level output from the signal generator and amplifier, and log the microwave data including details such as incident power, reflected power, S_{11} , and centre frequency. The software also includes an automatic frequency sweep function running at a default interval of 2.5 seconds whereby output power is scaled back to milliwatt levels and an S_{11} sweep is performed to assess the current coupling and determine a new centre frequency if required.

The first step is to connect the attenuator and power meter to the PMA output. The frequency of the power meter and PMA are set at the desired values and power output is calibrated. The external power meter can then be disconnected and the PMA connected to the microwave cavity. A manual coupling adjustment is performed using a real-time S_{11} measurement at low power levels with an empty quartz tube present in the cavity to eliminate its effect on frequency shift. The coupling barrel can be moved in and out of the cavity and rated to adjust the effective loop area and achieve a suitable coupling level. Typically, cavities used for heating in this work could achieve an initial coupling level between -25 and -30 dB for an empty cavity (between 99.7 and 99.9 % power transfer). Critical coupling ($S_{11} \rightarrow -\infty$) in practical terms can be

considered when S_{11} drops below -35 to -40 dB i.e. 99.97 to 99.99 % power transmission. Critical coupling could not be achieved here but the closest acceptable match is always used before heating every sample while the sample is at room temperature. Once suitable coupling is achieved the centre frequency is stored and a sample can be loaded. With the sample to be heated in place the coupling can be manually adjusted again if required and the loaded centre frequency stored.

Once the coupling step is complete the PMA output settings can be modified. This includes setting the desired power levels, duration of heating, frequency sweep intervals and output pulsing scheme (if applied). The output power of the PMA can be set in Watts or dBm, however the software actually uses dBm values to communicate with the PMA which can cause small rounding errors as it is a logarithmic scale; 30 dBm is 1 W, 40 dBm is 10 W and 50 dBm is 100 W. The rounding is never more than 2 or 3 Watts from the specified value.

5.3.2 SAMPLE LOADING

The powders are weighed using a benchtop electronic balance with a tolerance of ± 0.005 g. When heating powders it can either be done in an open-ended quartz tube or a rounded closed-end tube. The open tubes allow the passage of inert gas over the powders to perform experiments without external oxygen present but do require a small quartz wool support to hold the powder in place. For all experiments in this chapter except the repeated heating of magnetite closed-end tubes are used with the powders exposed to air. The powders are placed into the tube and settled using an electronic toothbrush to apply vibration and remove large cavities between powder particles.

When loading into the cavity the sample tube can be placed in two possible regions, one with high magnetic field near the cavity wall and one with high electric field at the centre of the cavity. See Figure 5.2 and Figure 5.3 for details of physical placement of samples in the cavity and

their relationship to fields in the TM_{010} mode, which is the only mode used for heating throughout. Almost all experiments use the outer sample hole dominated by the magnetic field. The central hole which is characterised by maximum electric field and minimum magnetic field is only used when the two heating methods are compared in section 5.4.4.

5.3.1 EMISSIVITY CALIBRATION

Infrared pyrometry requires knowledge of emissivity to be performed accurately. Emissivity is a quality of materials to describe their ability to emit thermal electromagnetic radiation primarily in the infrared and visible portions of the EM spectrum. Emissivity is a relative quality ranging between 0 and 1, using an ideal black-body radiator as a reference [209][210]. Materials can also be characterised by their transmissivity (how much radiation passes through) and reflectivity (how much radiation is reflected). It is easy to consider these qualities for the visible spectrum as we experience this normally. Dark painted objects will have high emissivity (and thus high absorptivity) whereas reflective objects like polished metal will have low emissivity and high reflectivity. Transmissive objects are transparent or semi-transparent such as glass, and these allow a high proportion of visible radiation to pass through without reflection or absorption. However, when performing IR temperature measurements these qualities must be considered relative to infrared radiation. Some materials which may appear highly transmissive to visible light could appear opaque to IR radiation; quartz is one such material which appears deceptively transmissive.

First, the measurement wavelength(s) must be identified. The three IR measurement tools used have three different spectral ranges. The Low pyrometer has a spectral range of 8-14 μm occupying most of the long-wave infrared (LWIR) spectrum. The High pyrometer has a spectral range of only 2.3 μm occurring in the short-wave infrared spectrum (SWIR). The IR camera has a spectral range of 7.5-13 μm , again mostly part of the

LWIR. These spectral ranges exist in the windows where the atmosphere is highly transmissive and through Wien's displacement law [211], correlate to wavelengths where particular temperatures have maximum spectral energy density [209][212]. The LWIR range is associated with temperatures from 207 to 386 K (-66 to 113 °C) and the 2.3 μm wavelength used by the higher range pyrometer correlates to a maximum energy density at 1260 K (987 °C). This is why the temperature measurement range of the camera and Low pyrometer is from just below zero to 900 °C and the High pyrometer can measure from 250 to 1800 °C.

Observations made on various magnetite heating experiments showed a disparity between observed temperatures and visible glowing within the sample as a result of very high temperatures. The magnetite could be visibly seen to have heated to hundreds of degrees based on the visible glow but measured temperature may only be 200 to 300 °C. This was observed in the case of many magnetite samples and suggested there was a significant lag (3-8 seconds) between the sample reaching its maximum temperature and the pyrometers or camera reporting the true temperature. This indicated that the exterior surface of the quartz tube was actually the point of measurement and the lag could be accounted for by thermal conduction from the sample outwards.

Data detailing the emissivity of quartz in the LWIR spectrum showed large variations in emissivity over the spectral range, often displaying significant decreases from 0.95 to 0.5-0.6 in the 8-9.5 μm wavelength region [213][214], making it difficult to select a single consistent value for the camera setting. It was also noted that emissivity can be temperature dependent, and measuring temperatures up to 900 °C this could have a significant impact on the recorded temperature values, making them inaccurate. To determine the appropriate emissivity of the quartz used here a calibration procedure was devised. This involved heating a quartz tube to 900 °C while measuring the temperature

simultaneously with a thermocouple and the IR camera with an emissivity setting of 1.0 (perfect black-body radiator). An emissivity value of one will be too high as it is a non-ideal system and therefore the reported temperature will be lower than the actual temperature recorded by the thermocouple. The ratio of the two temperatures will then give the appropriate emissivity value for the quartz, and the value the camera should be set at.

A quartz sample tube was heated using a tube furnace up to 900 °C in steps of 100 °C over the course of approximately 2.5 hours. The programmed values for furnace temperature were set up to 1000 °C as the quartz tube was not placed directly in the centre, but close to the end of the tube for easy access by the camera and thermocouple meaning lower temperatures were anticipated at the tube location. A Type-K thermocouple is used; the voltage output of a thermocouple is generated by temperature changes in the probe material and as such is directly related to the temperature change through a linear scaling coefficient called the Seebeck coefficient [215][216][217]. For a Type-K Chromel-Alumel (Chromium, Nickel, Aluminium alloy) thermocouple the quoted Seebeck coefficient is 41 µV/°C and has a fairly linear relationship between voltage and temperature [218][219].

The plot in Figure 5.7 shows on the left axis the temperatures of the furnace settings (dashed), the thermocouple (solid black) and the camera (solid red) recorded temperatures of the quartz tube. The right axis shows the ratio of the camera temperature and thermocouple temperature to provide an effective emissivity of the target quartz material (solid blue). The thermocouple temperature, T , is calculated using inverse polynomials of the form shown in (5.2) using the thermocouple voltage, V , in µV and the c coefficients shown in Table 5-1 [219][220].

$$T(^{\circ}\text{C}) = c_0 + c_1V + c_2V^2 + \dots c_iV^i \quad (5.2)$$

Table 5-1 – c coefficients for Type-K thermocouple inverse polynomials

i	Temperature: 0 to 500 °C	Temperature: 500 to 1372 °C
	Voltage: 0 to 20,644 μ V	Voltage: 20,644 to 54,886 μ V
0	0	$-1.318058 \cdot 10^2$
1	$2.508355 \cdot 10^{-2}$	$4.830222 \cdot 10^{-2}$
2	$7.860106 \cdot 10^{-8}$	$-1.646031 \cdot 10^{-6}$
3	$2.503131 \cdot 10^{-10}$	$5.464731 \cdot 10^{-11}$
4	$8.315270 \cdot 10^{-14}$	$-9.650715 \cdot 10^{-16}$
5	$-1.228034 \cdot 10^{-17}$	$8.802193 \cdot 10^{-21}$
6	$9.804036 \cdot 10^{-22}$	$-3.110810 \cdot 10^{-26}$
7	$-4.413030 \cdot 10^{-26}$	—
8	$1.057734 \cdot 10^{-30}$	—
9	$-1.052755 \cdot 10^{-35}$	—

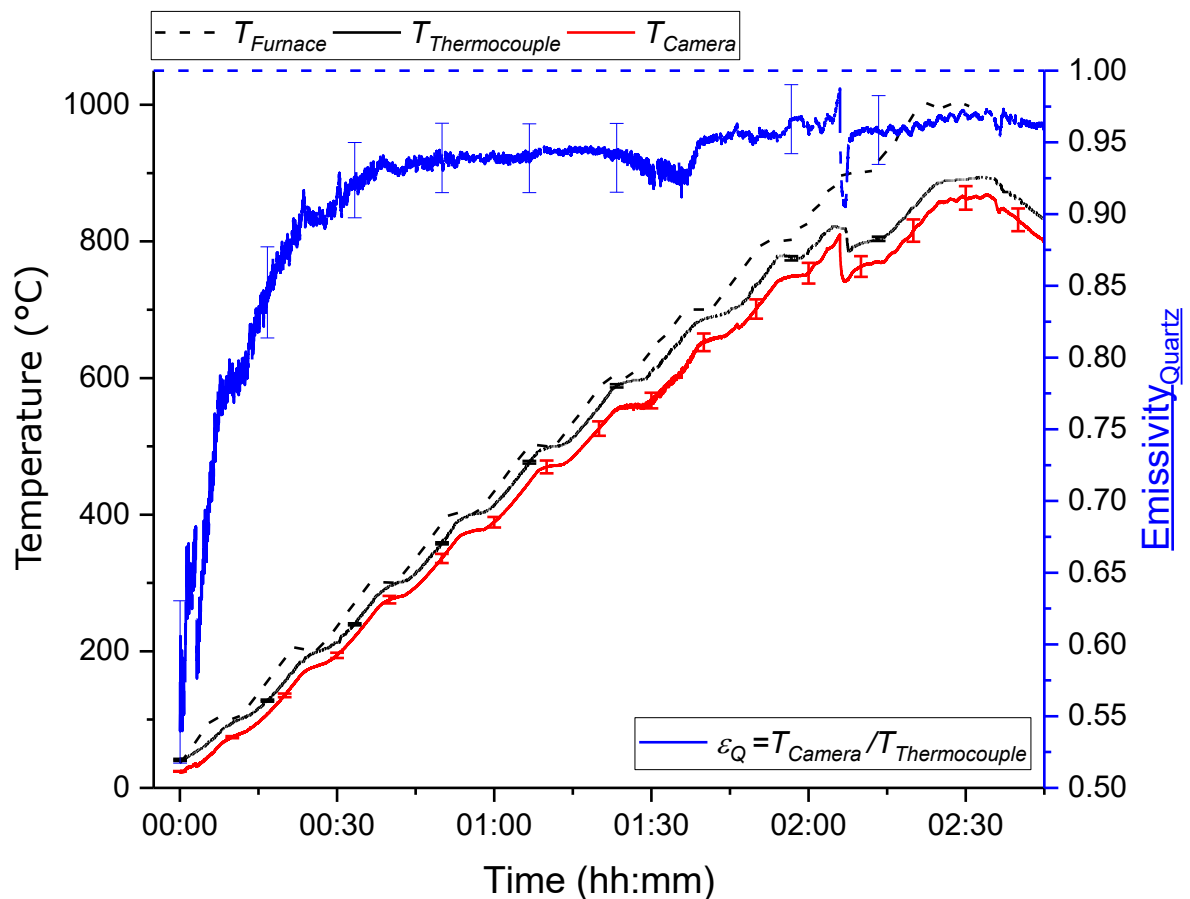


Figure 5.7 – Temperature of quartz in tube furnace showing furnace set temperature (dashed), thermocouple temperature (solid black), IR camera temperature (solid red). Right axis shows the ratio of these measured temperatures as the effective emissivity of quartz (solid blue).

Figure 5.7 shows the thermocouple and camera temperatures rise in line with the furnace temperature with a small delay due to time for the quartz to heat and the non-central position within the tube furnace. These recorded temperatures deviate more from the set temperature as the temperature close to the open end of the furnace would show an exponential decay [221] as the 1000 °C centre of the furnace creates a massive gradient with the ambient air temperature. The error associated with the thermocouple measurements and polynomial equations is at low temperatures dominated by the thermocouple inaccuracy at ± 1.5 °C across the whole operating range. The camera has an error of ± 2 °C or ± 2 %, whichever is greater. This is greatest at ± 18 °C at 900 °C.

As the emissivity of the camera is set to 1.0 here, the ratio of the camera temperature to the thermocouple temperature gives the approximate emissivity setting that should be used. This is shown on the right y-axis and the solid blue line. Although this is plotted against time, as the temperature rises approximately linearly this is very similar to the same plot with temperature on the x-axis between 20 and 900 °C. The associated errors from both temperature recording devices are shown on the emissivity plot. For the majority of the temperature range (200-900 °C) the emissivity of quartz is shown as being between 0.90 and 0.97 with a gradual linear increase throughout this range. The emissivity from 20 to 200 °C shows a significant positive gradient, increasing quickly from 0.52 to 0.90. This is not considered to be accurate. It is very unlikely quartz has such a dramatic temperature dependence up to 200 °C in this portion of the IR spectrum and it is far more likely this portion of the curve is the result of some error in temperature recording, data processing or calculation. It is suspected that this is due to the lack of cold junction compensation used with the thermocouple. This involves maintaining a part of the thermocouple wires at a fixed temperature (usually 0 °C) which then means the thermovoltage can directly measure the temperature difference to achieve the absolute temperature. The

effect of this error is much more pronounced at low temperatures and when the measured temperature is hundreds of times greater than the reference temperature (room temperature) the effect is negligible. This error may have also been reduced by using a more gradual heating rate, so the relative temperature change at low temperatures was not as drastic.

Discounting this erroneous part of the emissivity calculation, the emissivity of quartz can be considered to be consistently between 0.93 and 0.97 for the most important part of the temperature range required for measurement of high-temperature magnetite (200-900 °C). The emissivity can be treated as a constant 0.95 for the purposes of further temperature measurement, with the awareness that the temperature values recorded may not be *exactly* correct but are within reasonable tolerances and indicative of the true temperature.

5.3.2 PYROMETER SPOT SIZE

Another limitation of pyrometers is the spot size. The spot size of a pyrometer is defined by the diameter of the measurement area, typically circular with standard lenses. In pyrometer datasheets this is often quoted as a distance-to-spot ratio, D:S, with a higher ratio indicating a higher optical resolution. The lower range pyrometer (CT-SF22) has a ratio of 22:1 but this is only applicable for a distance of 1100 mm. At zero distance the spot size is at a minimum of 6.5 mm which increases to 10.9 mm at 110 mm and continues to increase beyond this distance. The higher range pyrometer (CTM-3CF75H3) has a D:S ratio of 75:1 at its focal point which is at a distance of 110 mm with a spot size of 1.5 mm. At zero distance the spot size is the same as the other pyrometer at 6.5 mm but decreases to the focal point. After 110 mm the spot size increases to 4.4 mm at 150 mm and continues to increase from there [204].

These combinations of spot sizes and focal distances are important to consider when using the pyrometers to measure the temperature of the samples in quartz tubes. The standard diameter tubes have outer diameters of 8 mm. The side mounted position for the pyrometers makes the lens a distance of 12.5 mm away from the sample tube edge. This means the Low pyrometer has a spot size greater than 6.5 mm and less than 10.9 mm, and the High pyrometer has a spot size between 4.0 and 6.5 mm. Assuming a linear relationship between spot size and target distance, in the side view configuration the Low spot size is approximately 6.8 mm and the High spot size is approximately 6.0 mm. These values indicate that both pyrometers should be suitable. This is because the cross section of sample here is at most 6 mm wide and the whole tube is 8 mm. Assuming heat is radiating equally in all directions, the IR emitted by the quartz tube should be sufficiently captured by either pyrometer in the side view setup.

Mounting the pyrometers above the sample requires a greater distance of 65 mm (30 mm to the top of the quartz tube) from the lens to the sample surface. This makes the spot size for the Low pyrometer still between 6.5 mm and 10.9 mm, although larger than the side view orientation. The High pyrometer has a spot size slightly less than 3.8 mm. Assuming again a linear relationship the Low spot size is approximately 7.0 mm and the High spot size is approximately 3.3 mm. The Low pyrometer is less suitable in this configuration as the spot size is much closer to the tube diameter and will be more likely to incorporate background IR readings and decrease the average temperature reading. This configuration with the High pyrometer is the most suitable as it is possible to have a very small spot size that provides room for positioning error and ensures the entire area under measurement is the sample itself. However, if any tubes are required to be connected to the quartz tube to either collect produced gases or provide an inert atmosphere, this method of temperature measurement becomes impractical.

Another issue present here is that the quartz tubes are round. These rounded surfaces and the reflective metal of the cavity will cause reflections of IR radiation and mean the recorded temperatures are unreliable. Although the pyrometers are secured using threaded 3D printed holders and appear to sit in exactly the same place each time they are mounted, there is also slight deviation in the angle, distance and precise targeting of the pyrometers. When the spot sizes are so close to the size of the measured object there is very little tolerance for error. If the spot size is exactly the size of the sample cross section, it and the sample tube would have to be perfectly aligned for each temperature measurement to be consistent. To achieve this, a combination of precisely machined threaded metal mounts and laser alignment equipment should be used, which were not available here.

A test was performed using 0.1 g magnetite samples under microwave irradiation in the magnetic field sample hole and the two pyrometers concurrently. The Low pyrometer is used in the side configuration and the High pyrometer is used in the top-down configuration. This minimises the spot size for each pyrometer, reducing errors due to background IR readings. In the top-down configuration the High pyrometer is measuring the top surface of the magnetite sample directly and not the quartz tube. The sample is subjected to a 40 W target power from the PMA for 120 s. An identical setup is used for another 0.1 g sample with the camera measuring from the side slit in the cavity. These samples are repeated at least 6 times and the data averaged. This is displayed in Figure 5.8.

This data shows the High pyrometer measures maximum temperatures around 820 °C, reached after 65 s of MW irradiation whereas the Low pyrometer records maximums of only 390 °C after 85 s. The camera records temperatures of 410 °C after only 50 s, capturing the rapid heating that is also visible in the bright orange glow achieved by magnetite samples in these tests.

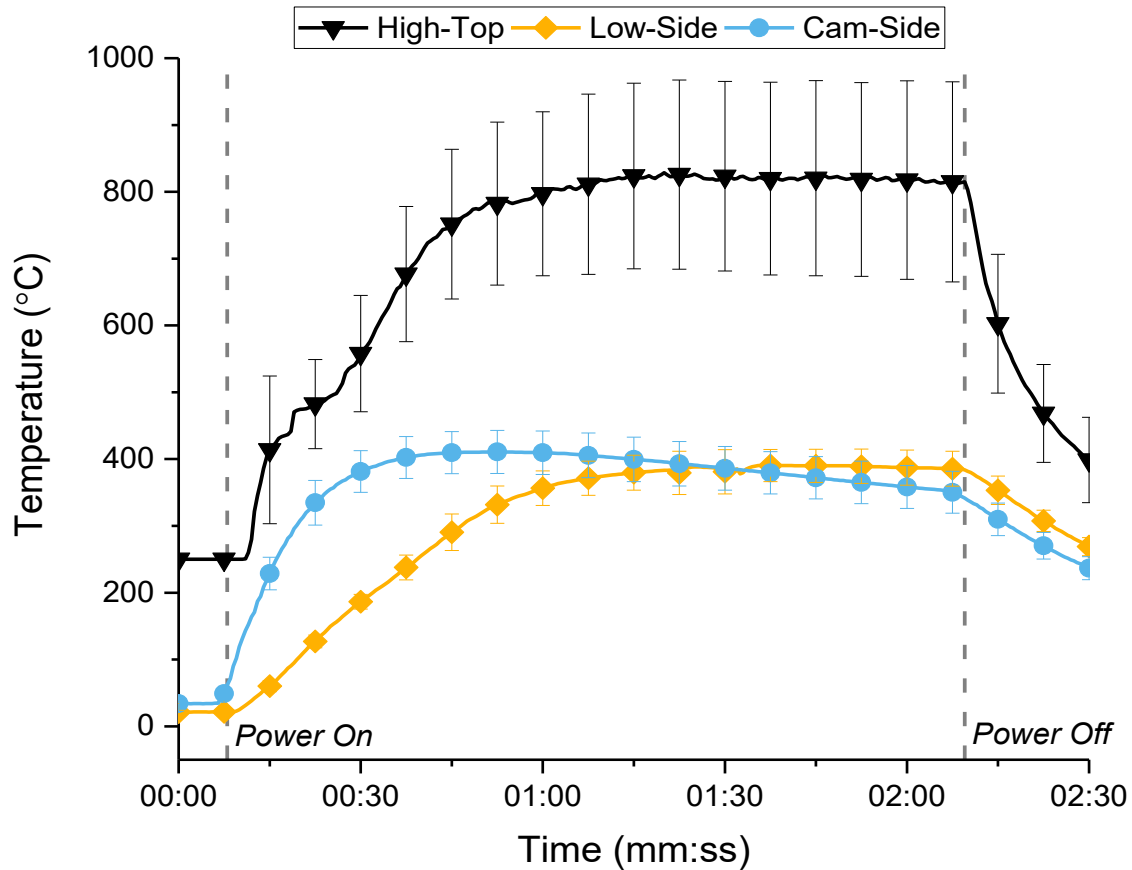


Figure 5.8 – Comparison of temperature measurement methods for a 0.1 g magnetite sample subjected to a maximum of 40 W of microwave power.

There is a much greater degree of variability in the High pyrometer values while both the Low pyrometer and camera give a greater degree of certainty in their results. Given the small spot size of the High pyrometer used in this configuration it was expected the results would be highly consistent, but this was not the case. The varied results may be due to small misalignments in the pyrometer holders, or the measurement of relative hot/cold spots in the sample. The Low pyrometer results are significantly lower in maximum temperature when compared to similar later results but are consistent with each other suggesting a systematic error such as pyrometer misalignment may have occurred here.

The IR camera and Low pyrometer were chosen to continue experimentation with given the sizeable variability in the High pyrometer measurements, and the incompatibility of top-down measurements with later planned testing.

5.4 RESULTS - HEATING MAGNETITE AND HAEMATITE

5.4.1 Simulation of Magnetite Heating

Using the data collected through permeability and permittivity measurements of magnetite powder in this chapter a simulated model can be constructed to anticipate the heating potential of the powder and assess how it may disturb the magnetic and electric fields when placed in the cavity. If a material is very lossy it can significantly dampen the fields when placed in the resonant system. If this were to happen, effective microwave heating may become difficult due to the lack of effective power transfer to the cavity. Alternatively, if a substance is too low loss it will not effectively absorb the EM energy and the primary heat dissipation method in the load will be through the cavity walls.

A simulation is constructed using finite element modelling software (COMSOL Multiphysics) to observe the field alterations caused by a magnetite sample. A 2D axis-symmetric model is constructed to represent the cross section of one half of a cylindrical cavity containing a magnetite sample through the magnetic field sample hole. The magnetite sample is constructed as a rectangle approximating the cross-sectional dimensions of magnetite samples used in heating experiments (6 mm wide, 20 mm tall). A detailed simulation of a powder material is incredibly computationally intensive so has been simplified and treated as a single solid. This means the simulation will not capture how the fields behave at particle surfaces and within the sample mass. The temperature-dependent permeability and permittivity values measured in Chapter 4 for the lowest frequency modes (closest to 2.45 GHz) are applied to the magnetite material with thermal conductivity, density and specific heat capacity used as in section 4.4.5. Given the packing of the powders measured in Table 4-7 the relative density of the magnetite rectangle is modified to 20 % of its stated bulk density to more closely resemble how powders were packed throughout this work.

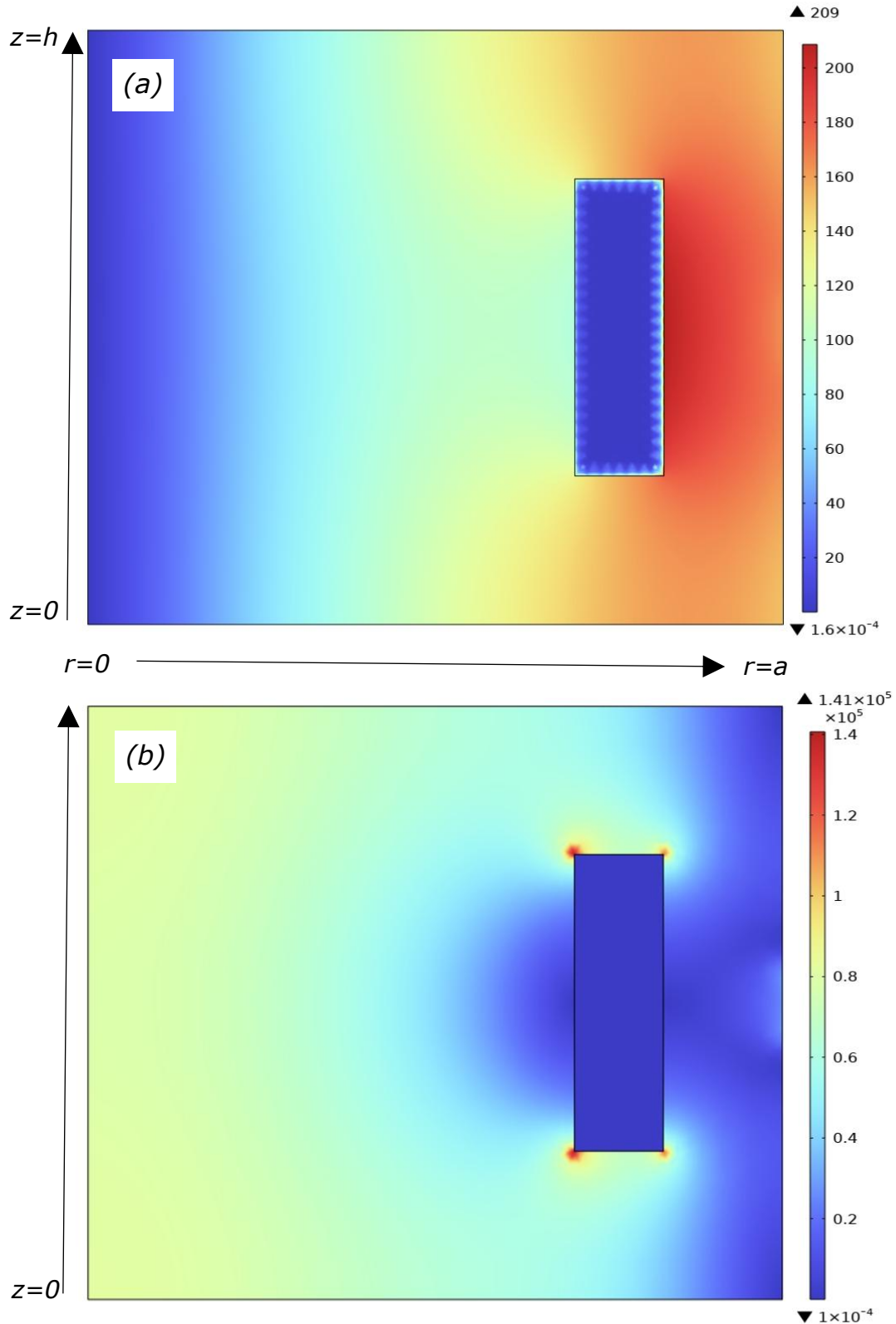


Figure 5.9 – Simulated 2D axis-symmetric magnetic (a) and electric (b) fields in one half of a TM_{010} cavity containing a rectangular magnetite sample. (a) is measured in A/m and (b) is measured in V/m. Magnetite is modelled as having temperature-dependent permeability and permittivity up to 200 °C and a relative density of 20 % of its bulk value to simulate a powder packing scenario.

A port on the cavity exterior introduces 50 W of microwave power at 2.45 GHz and the magnetite's effect on the magnetic and electric fields can be observed. Surface plots of both fields are shown in Figure 5.9(a) and (b). The magnetic field shows peak values of 209 A/m in the cavity and in the 0.25 mm skin surface of the magnetite. Given the stated particle diameter of the magnetite is 5 μm this is well below the 250 μm skin seen here. This indicates that in the actual powder each particle is likely to be subject to the highest magnetic field strengths in the cavity, and given the magnetic loss of the magnetite powder, will absorb significant energy from the magnetic field.

The electric field shown in Figure 5.9(b) shows significant field enhancement at the corners of the magnetite rectangle, up to $1.41 \cdot 10^5$ V/m. This is obviously not an exact representation of the real powder geometry, but given magnetite powder is cubic in nature it may be indicative of similar effects which could happen at the microscopic scale. These field enhancements at the corner points are approximately 2.1 times the maximum field strength at the centre of the simulated cavity. This is due to dielectric polarisation mechanisms which cause accumulation of charges, especially at points such as square vertices. If this effect were to occur for individual magnetite particles, or even clusters of particles this could mean dramatically increased field strengths between particles, which could lead to highly rapid heating rates [9].

The simulation is further modified to include heat transfer nodes to simulate the temperature that might be reached by this magnetite sample given 50 W of absorbed power. The temperature of the centre of the magnetite sample is recorded over 3 minutes of continuous 50 W MW application. The temperature of this point is shown in Figure 5.10 for three possible values of electrical conductivity of the magnetite [222]. This shows the rapid heating behaviour of the magnetite powder that can be expected.

In this simulation the low conductivity sample (1,000 S/m) is shown to heat to over 800 °C in around 30 seconds. The medium conductivity sample (5,000 S/m) also heats rapidly to 500 °C in 30 s and plateaus at 630 °C after 90 s. The high conductivity sample (10,000 S/m) heats slower than the others, reaching 400 °C after 50 s and plateauing at 480 °C after 100 s. This shows the screening effect of higher conductivity materials, which reduces the skin depth and does not allow EM fields to penetrate deep into the material, thereby reducing heating rate. These simulations show the capacity of magnetite powder to be rapidly heated by the combination of magnetic and electric fields present in this region of the TM₀₁₀ mode, and show how the magnetite might disturb present EM fields within a section of the cavity.

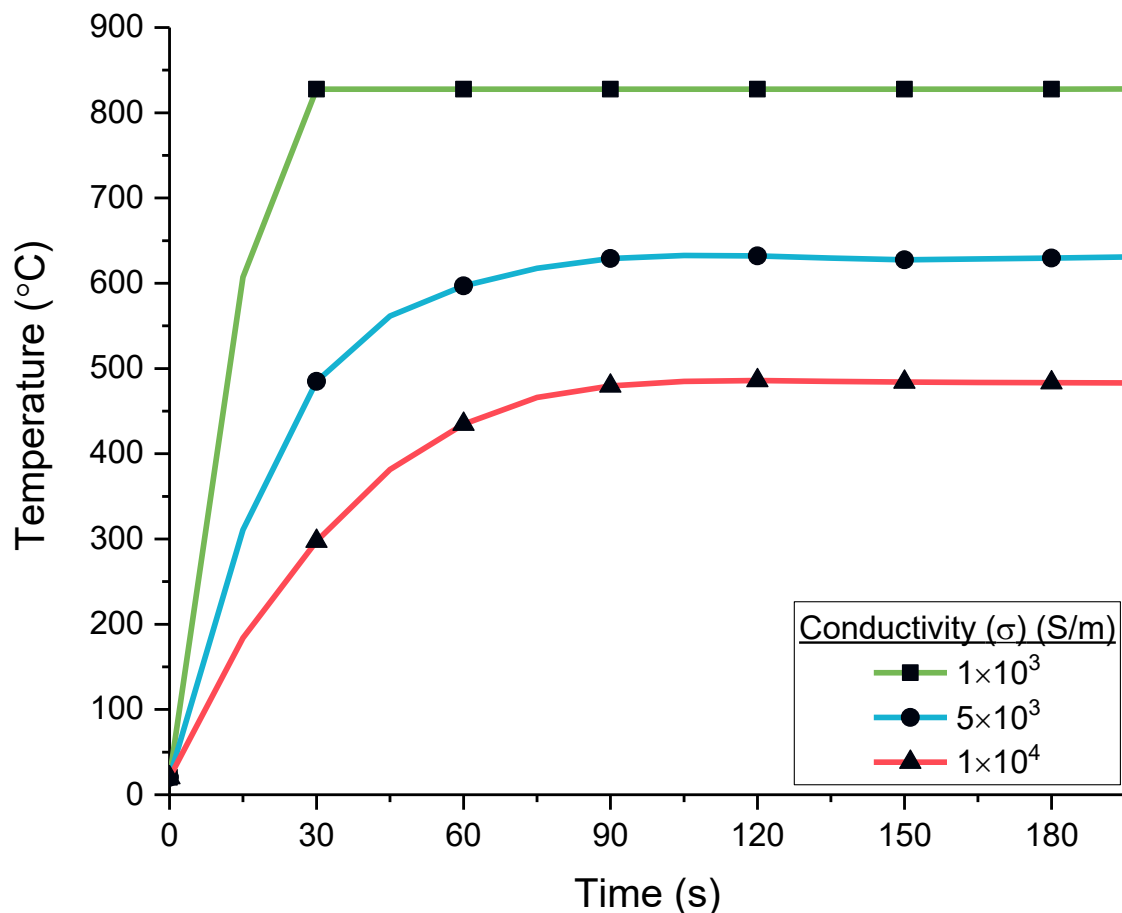


Figure 5.10 – Simulated temperature of the centre of the magnetite sample shown in Figure 5.9 subject to 50 W of absorbed power for up to 3 minutes. Three different electrical conductivities are used to highlight their impact

5.4.2 LOW POWER LEVELS

To continue the comparison of powders performed in Chapter 4, both magnetite and haematite powders are subjected to higher power levels than before to induce microwave heating and observe differences in the powders' behaviour. Initial heating experiments were performed using a 30 W target output power from the PMA heating for 60 seconds while measuring the temperature from the Side view using the Low pyrometer. Varied masses of each powder were used from 0.1 to 0.4 grams in increments of 0.1 g. Using these masses, it was possible to achieve initial coupling values of S_{11} in excess of -20 dBm (>90 % initial power transfer) consistently.

Multiple runs were performed for each powder and mass, typically four samples but always between three and five sets of usable data were collected. The temperatures for magnetite samples of each mass value are averaged and shown in Figure 5.11 alongside the averaged recorded delivered power by the PMA, which is the difference between the PMA incident power and reflected power. The delivered power is therefore the power consumed by the total load which includes the sample to be heated and the cavity itself; when heating a material with significant microwave loss this dominates the power absorption, and the delivered power can be considered indicative of power directed to the sample.

In Figure 5.11 the microwave power is activated at $t = 5$ s where the temperatures begin to increase and the power data begins. In the first ten seconds of heating the temperature of all samples increased very rapidly by hundreds of degrees. Magnetite masses of 0.1 g reached over 400 °C within five seconds and then continued to heat quickly until reaching a maximum of 615 °C by the end of microwave application at $t = 65$ s. For masses of 0.2, 0.3 and 0.4 g similar behaviour is seen with reduced temperatures reached with increasing mass. The 0.2 g samples reached an average maximum temperature of 514 °C, 0.3 g reached 420 °C and 0.4 g reached 357 °C. Generally, the smaller mass samples

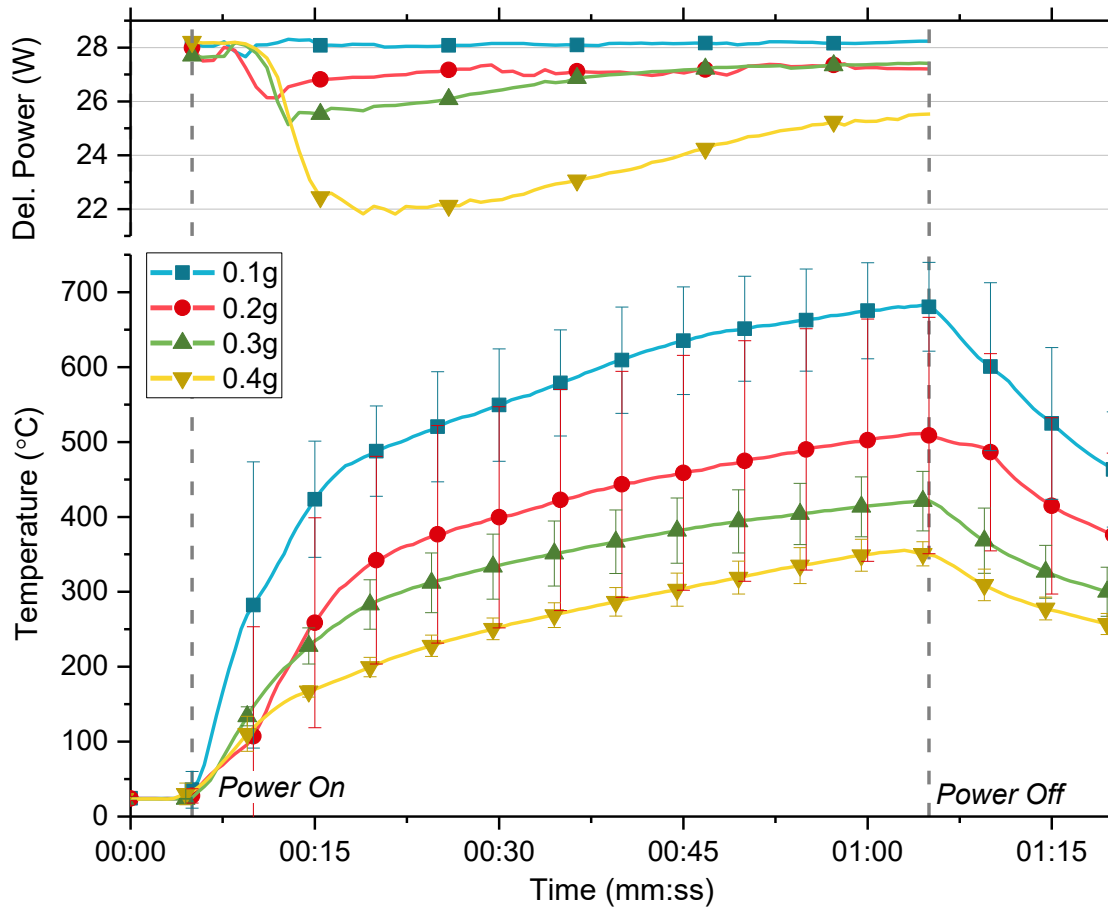


Figure 5.11 – Average temperatures and delivered power levels to varied mass samples of magnetite during microwave heating

showed much broader ranges of recorded temperatures. Some 0.1 g samples reached temperatures from 650 to 767 °C with one as low as 350 °C, whereas all the 0.4 g samples followed very similar temperature profiles to each other with maximum temperatures between 331 and 370 °C, approximately ± 20 °C of the average.

The delivered power in Figure 5.11 shows average delivered power levels between 28 and 22 W. Although 30 W was the target power for these experiments, due to the PMA software the actual target power was closer to 29 W, with incident power levels typically between 28.3 and 28.7 W for all samples. The 0.1 g samples show delivered power levels consistently close to the incident power levels at around 28 W for the entire heating duration. The 0.4 g samples show a high initial power level close to 28 W that drops rapidly to 22 W representing around 6 W of reflected power.

The periodic frequency sweeps adjust the centre frequency to maximise power transfer which gradually improves from this minimum, reaching 25.5 W of delivered power by the end of microwave power application. This can be seen to a lesser extent for the 0.2 and 0.3 g samples. These significant drops in power are likely primarily driven by the presence of greater sample volumes causing weaker coupling as they interfere more with the resonant fields, and the rapidly heating samples which will change their electromagnetic properties. This supports the collected data from Chapter 4 where magnetite was heated and it became more magnetically and dielectrically lossy. A sample which becomes more lossy here would decrease the Q , broaden the bandwidth and reduce power transfer, which is what is happening when the delivered power initially drops.

Similar data is collected for haematite samples as shown in Figure 5.12. The conditions are the same for these samples as those for the magnetite samples with incident power levels between 28 and 29 W and masses from 0.1 to 0.4 g. No rapid temperature increase is observed for haematite as the samples heat steadily throughout the duration of microwave exposure. Maximum temperatures reached by the samples varied between approximately 75 and 138 °C with a similar variance in sample groups. The heating rates were non-linear, starting at slightly higher levels then slightly decreasing towards the end of microwave application although the difference is minimal over this timeframe. Similarly to the magnetite, a negative correlation is seen between mass and recorded temperatures of the samples with the smallest mass reaching the highest temperature.

Delivered power levels during the haematite heating showed different behaviour to the magnetite samples. Initial levels are between 20 and 25 W which immediately drop by 1-2 W then rapidly rise to near the maximum level, near 28 W and remain consistent throughout the remainder of the microwave application. For the 0.4 g samples the

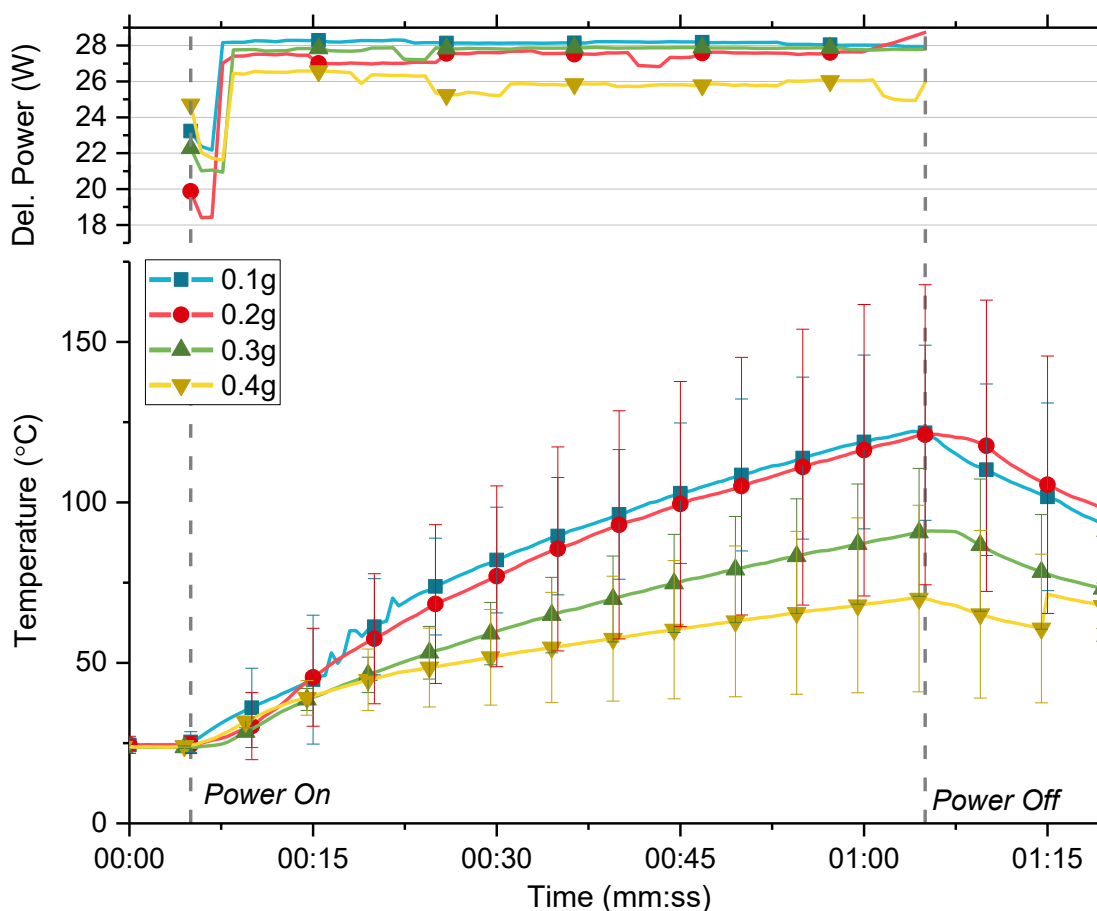


Figure 5.12 – Average temperatures and delivered power levels to varied mass samples of haematite during microwave heating

consistent power levels were closer to 26 W. The relatively steady heating rates and delivered power levels support the data collected through MCP of haematite as shown in Chapter 4 which indicates haematite's electromagnetic properties are not temperature dependent, especially below 100 °C.

While heating in the magnetic maximum region the haematite heats to significant temperatures of between 70 and 120 °C but not rapidly enough or to high enough temperatures to be considered a strong microwave susceptor material, and is therefore unlikely to be suitable as a rapidly-heating magnetic microwave catalyst. It is suspected the haematite samples' heating behaviour is a combination of the magnetic field and reduced electric field still present in this mode configuration (see Figure 5.2(b)). As the characterisation of haematite suggested both very

low magnetic and dielectric loss it is difficult to determine which of these is the primary driver in this case. Haematite's magnetic and electric loss values were measured at around 0.01 to 0.04 across all measured frequencies and temperature ranges up to 198 °C. This makes haematite a poor absorber of microwave radiation, but still clearly capable of dissipating an appreciable amount of energy as heat, unlike a low-loss microwave material like quartz.

In these tests the delivered power to the load initially drops but then remains high for the majority of the heating duration. As haematite is not a highly lossy material like magnetite it cannot effectively absorb this energy. In this case the contribution to power dissipated in the load from the cavity i.e. power lost due to currents induced in the metal walls, is a much greater proportion of the total power dissipated in the load than when magnetite is heated. The temperature of the cavity was not measured but it is likely acting as a sink for the delivered power here, given haematite is a poor microwave absorber, and it would likely display a greater relative increase in temperature when compared to the magnetite experiments.

Based on the rapid heating behaviour seen in Figure 5.11 it was believed increased power could result in more rapid heating and extended durations could allow samples to reach a visible steady maximum temperature. Returning to magnetite and increasing the target power to 50 W and heating duration to 120 s provided the data shown in Figure 5.13. This shows samples of 0.1 g and 0.4 g and the average temperatures of these groups where MW power is applied at $t = 10$ s.

This showed exceptionally rapid heating in the 0.1 g samples reaching 730 °C in 12 s, 760 °C in 48 s and decreasing back to 725 °C by the end of the MW application. The 0.4 g samples did not heat as rapidly, heating to 400 °C in the first 12 s, 600 °C after 40 s, 700 °C after 80 s and

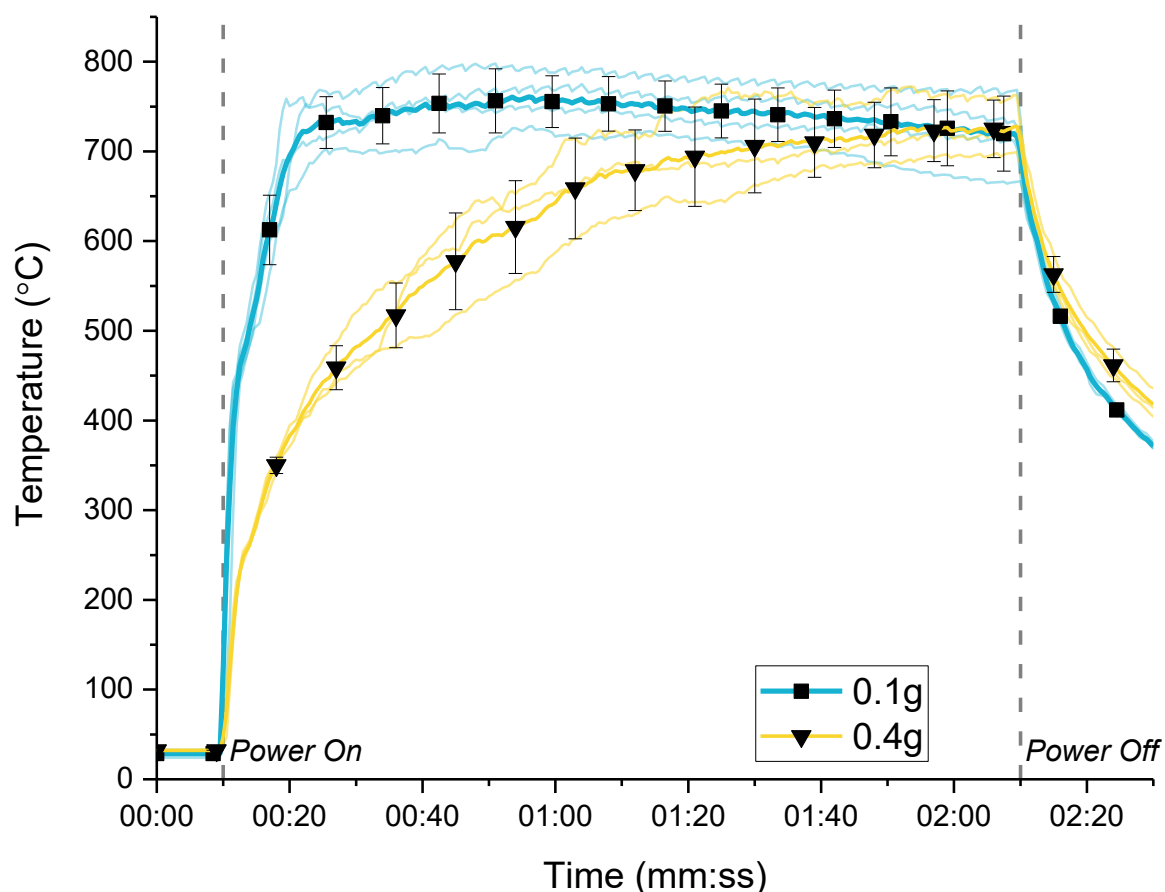


Figure 5.13 – Temperatures of 0.1 g and 0.4 g magnetite samples in response to 120 s of 50 W MW power

reaching a very similar temperature to the 0.1 g samples at the end of MW application at 725 °C. Increasing the power provides more energy to be absorbed by the magnetite leading to both higher maximum temperatures and increased heating rates.

The rate of temperature change in these samples is highest at the initiation of MW heating reaching 120 °C/s for the 0.1 g samples and 62 °C/s for the 0.4 g samples. For the smaller samples this rapidly decays to almost zero as shown by the flat temperature plot. The 0.4 g samples' heating rate showed an exponential decay from the peak to around 3 °C/s at 40 s and 1.2 °C/s by 80 s. This data shows increasing power can result in increased heating rates which could be essential depending on the applications. It also appears similar maximum temperatures can be reached even with significantly different masses, given a suitable duration of power application.

5.4.3 HEATING LAYERED POWDERS

Magnetite and haematite powders were loaded into quartz sample tubes in three layers. One was ordered first with magnetite, then haematite, then magnetite and the other in the opposite configuration; first haematite, then magnetite and finally haematite. Approximately 0.5 g of powder was used in each layer with the intention not to achieve exceptional temperatures but to demonstrate the mechanism of microwave selective heating. These significantly larger masses of powder can seriously impact the initial coupling achievable when preparing to apply microwaves but with the concurrent heating of layered powders it should be apparent the difference in microwave absorption between the two materials. As with the initial heating experiments, the stated target power was set at approximately 30 W.

A snapshot of the IR video for both of these layered samples is shown in Figure 5.14 using the TIM 640 IR camera. They are time-synchronised, both occurring at approximately 25 seconds into a 30 second heating cycle. This timestamp was chosen to highlight the difference in recorded temperatures between the powders while minimising the apparent conductive heat transfer between the hotter and cooler powders. The white boxes approximate the physical location of each of the powder layers and exclude the transition regions where the powders meet. These boxes report the maximum temperature in that region alongside it with a text label of "Mag" or "Haem" for magnetite or haematite on a scale from 26 to 180 °C.

The temperatures observed were consistently higher for magnetite-filled regions with significant differences of at least 25 °C, often more. The sample with the single magnetite layer showed much higher temperatures than the multiple magnetite layer samples. This is because the magnetite is lossy and the haematite is not, so the magnetite dominates the energy absorption. When only one magnetite sample is present it absorbs a vast majority of the energy and heats up more quickly and to higher

temperatures. When two magnetite samples are present the absorbed energy is split between them. These two magnetite layers surrounding a haematite layer also provide conductive heating from both above and below. This haematite layer will also slowly heat due to minimal microwave absorption and these effects combine to create a fairly uniform heating of the central haematite powder layer.

In the left portion of Figure 5.14 the top layer of magnetite can be seen to be significantly hotter than the bottom layer, by around 25 °C. This is likely due to the difference in masses between sample layers. Layers were measured to be around 0.5 g each (± 0.025 g) but precision was not a priority as this was a demonstration of the selective nature of the heating and the difference between magnetite and haematite samples. There will also be a contribution to the heating of top layers in both layering configurations from conductive rising heat from the lower layers. This can be seen in the right portion of Figure 5.14 as the much hotter magnetite sample heats the lower edge of the top haematite layer.

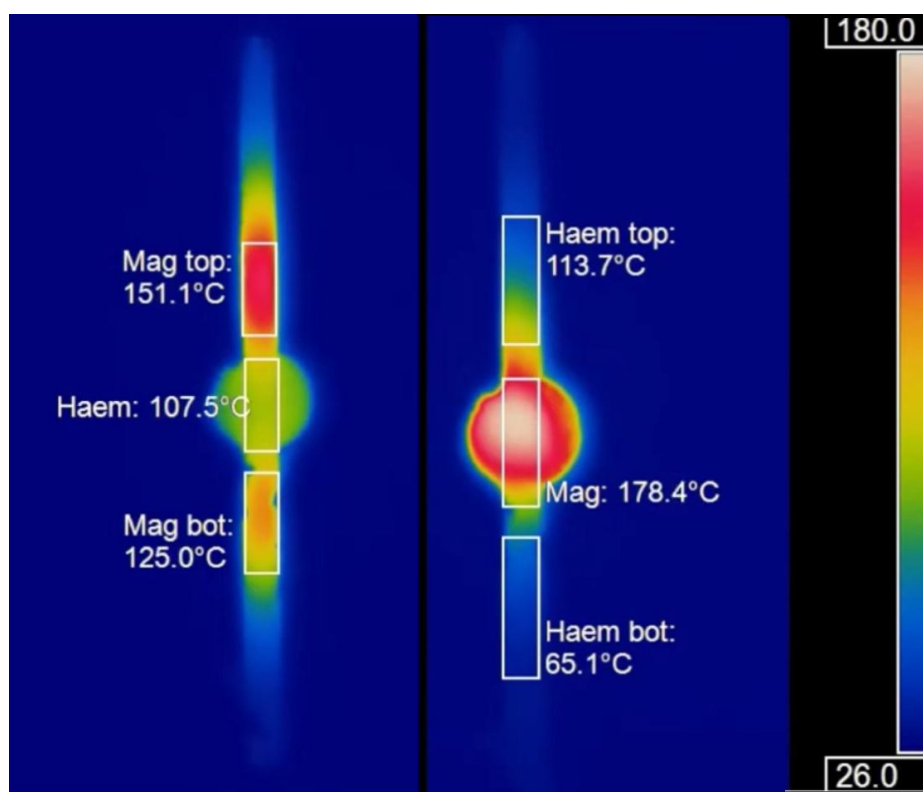


Figure 5.14 – IR images of layered iron oxides under microwave heating (max 30 W, 30 s). Left image shows magnetite, haematite, magnetite layers. Right image shows haematite, magnetite, haematite layers

This is a visual example of the selective nature of microwave magnetic heating. Using a material such as magnetite which can be rapidly stimulated by microwave magnetic fields it is possible to heat it to higher temperatures quicker than other similar materials. This selective heating demonstration was performed with a relatively large combined sample mass for this cavity set up of approximately 1.5 g with limited power input and a short duration. Increasing power and duration and reducing sample mass to increase power transfer will certainly yield higher temperatures and more rapid increases that would be applicable for performing reactions, such as the destruction of polymer materials.

5.4.4 MAGNETIC VS ELECTRIC DRIVEN HEATING

Magnetite samples were tested for their heating capabilities in both the magnetic and electric field maximums. It is much more common to use the electric field for heating in most applications including other research and industrial uses, and so existing equipment could be more easily adapted if magnetite was shown to heat effectively in electric-field driven scenarios. Masses of magnetite of 0.1 g were used with PMA target power levels of 50 W for all samples over a duration of 120 s. Shown in Figure 5.15 are two plots of magnetite samples heated through magnetic-driven heating and electric-driven heating, with the Low pyrometer data shown on the left in Figure 5.15(a) and the camera data shown on the right in Figure 5.15(b).

Magnetic-driven heating is performed as described before using the hole near the cavity wall to place the sample in the magnetic field maximum with additional non-zero electric field also present. Electric field heating is performed in the TM_{010} mode but with the samples placed through the centre of the cavity, where the electric field is maximal and magnetic field is almost zero. This can be seen in Figure 5.2(b) as being where $x = 0$, or aligned with the y -axis and in Figure 5.3 where the top view shows a central hole through the cavity. The lower range pyrometer was used in a

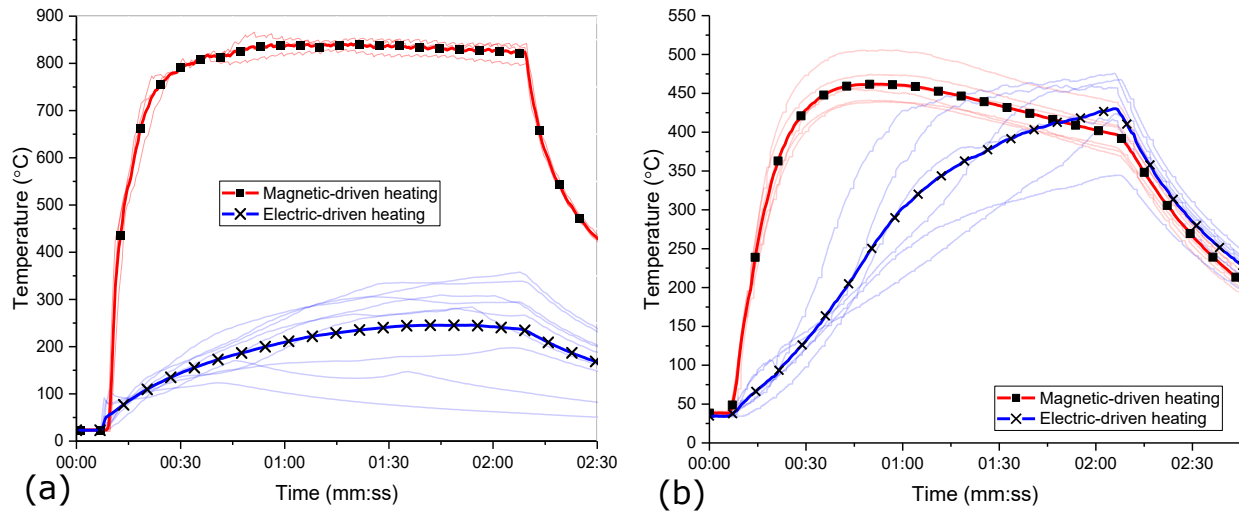


Figure 5.15 – 0.1 g magnetite samples heated with up to 50 W MW power in both the magnetic field and electric field maximums in the TM_{010} mode. (a) is measured using an IR pyrometer while (b) is measured using an IR camera

side-view orientation to capture Figure 5.15(a). Assuming a linear relation between spot size and distance to target, the spot size for the magnetic sample is approximately 6.9 mm, and the spot size for the electric sample is approximately 8.9 mm meaning the data for the electric field is definitely capturing at least some data which is not the sample tube. This is one reason for the significantly lower average temperatures reached of around 200 °C and the large variability observed in this data set. The camera does not suffer from this issue as it was manually focused to match the distance of the sample for each group.

Observed here is a massive disparity in the pyrometer values indicating consistently high-temperature rapid heating in the magnetic field to over 800 °C. Given the calculated spot size and the uniformity between samples it is believed the data captured primarily reflects the actual temperature observed at the sample tube exterior and minimal inference or background temperatures were incorporated. The electric field heating seen by the pyrometer is significantly lower, achieving typical temperatures less than 250 °C at their maximum with similarly slower heating rates. Given the spot size these temperatures are likely lower than the actual temperatures of the sample, but by how much is

impossible to determine given the exact target and spot size of the pyrometer are unknown here.

The data recorded by the IR camera shows much more similar maximum temperatures reached by both heating configurations, with magnetic samples averaging a maximum of 472 °C and electric samples averaging a maximum of 430 °C. Magnetic samples still show rapid heating behaviour and consistency between samples while electric samples again show variability between samples, with 100s of degrees between samples at similar points in the heating cycles. The samples that were driven by electric heating in Figure 5.15(b) show more gradual heating for the first 35 s up to approximately 200 °C where the heating rate is at its maximum. Above this temperature the heating rate generally decreases, exhibiting a slower climb to the maximum at the end of MW application. This data correlates with changes observed in the permittivity of magnetite with increased temperature from Chapter 4. In the TM_{010} mode the imaginary permittivity was observed to decrease slightly up to around 100-110 °C then increase from 0.25 to over 2.0 at 200 °C where it is transitioning to maghemite. This is reflected in the increasing heating rate from 100 to 300 °C. This may suggest that if the temperature range could be expanded in Figure 4.16 that a decrease would be seen after approximately 300 °C to a steady or slightly decreasing value at higher temperatures.

It is unclear why there is such a difference in temperature for both sets of the magnetically heated samples with the pyrometer data showing > 800 °C and the camera showing > 450 °C at maximum. Both the camera and pyrometer were using the same emissivity value of 0.95 with similar mass and power. The spot size of the pyrometer should be a suitable size to incorporate only the sample and omit most if not all of the background radiation, however this seems the most likely source of erroneous temperature data. Samples were consistent within their groups but not across them. This could mean that the true temperatures of these

samples were around 450, 800 or somewhere in between. Due to the inconsistency observed with pyrometer measurements previously the camera measurements are deemed to be more accurate and the camera is used exclusively hereafter.

The magnetic heating data also showed stable maximum temperatures from the pyrometer, but the camera showed a quick rise to maximum and then a slow decrease in temperature of approximately 60 °C over the following 90 s. This was observed on many magnetite samples when measured with the camera and it is thought to be caused by a combination of factors. Moisture present in the sample powder would contribute to the initial rapid heating but be quickly removed by the high temperature reached throughout the sample leading to a slow decrease to a stable temperature. The magnetite is certainly reaching temperatures great enough to transition to maghemite using the available oxygen in the air or any produced water vapour, and the different permeability and permittivity of this material (or mix of materials) could have lower losses, causing the maximum temperature to decrease.

5.4.5 REPEATED HEATING OF MAGNETITE

Magnetite has been shown to heat quickly and to temperatures exceeding 400 °C, with some dependence on sample mass and microwave power levels. To assess its suitability as a catalyst material samples of magnetite powder were heated repeatedly to see if their ability to reach required temperatures diminished or improved after multiple MW heat treatments. These tests were performed in an inert atmosphere to minimise any oxidation of the magnetite due to oxygen available in the air. Sample masses were generally increased to at least 0.4 g of magnetite per test to more closely resemble the amount practically used in a catalysis reaction. Microwave target power was also increased to ensure sufficient temperatures could be achieved, in excess of 550 °C.

A sample of magnetite weighing 0.4 g was placed in an open-ended quartz tube while supported on a small amount of quartz wool. The sample tube was purged using nitrogen gas for at least five minutes before microwaves were applied. The nitrogen flow continued at the lowest flow possible to maintain a nitrogen atmosphere over the sample. The sample was heated using a MW target power of 84 W for 120 s and then allowed to cool back to at most 40 °C before again applying MW power and heating again. The data collected after performing this for five cycles is shown in Figure 5.16.

The sample reached a maximum temperature of 636 °C during the second heating cycle at approximately 55 to 60 s after initial MW activation. The sample typically reached maximum temperature during this point with values between 621 and 636 °C with the exception of the

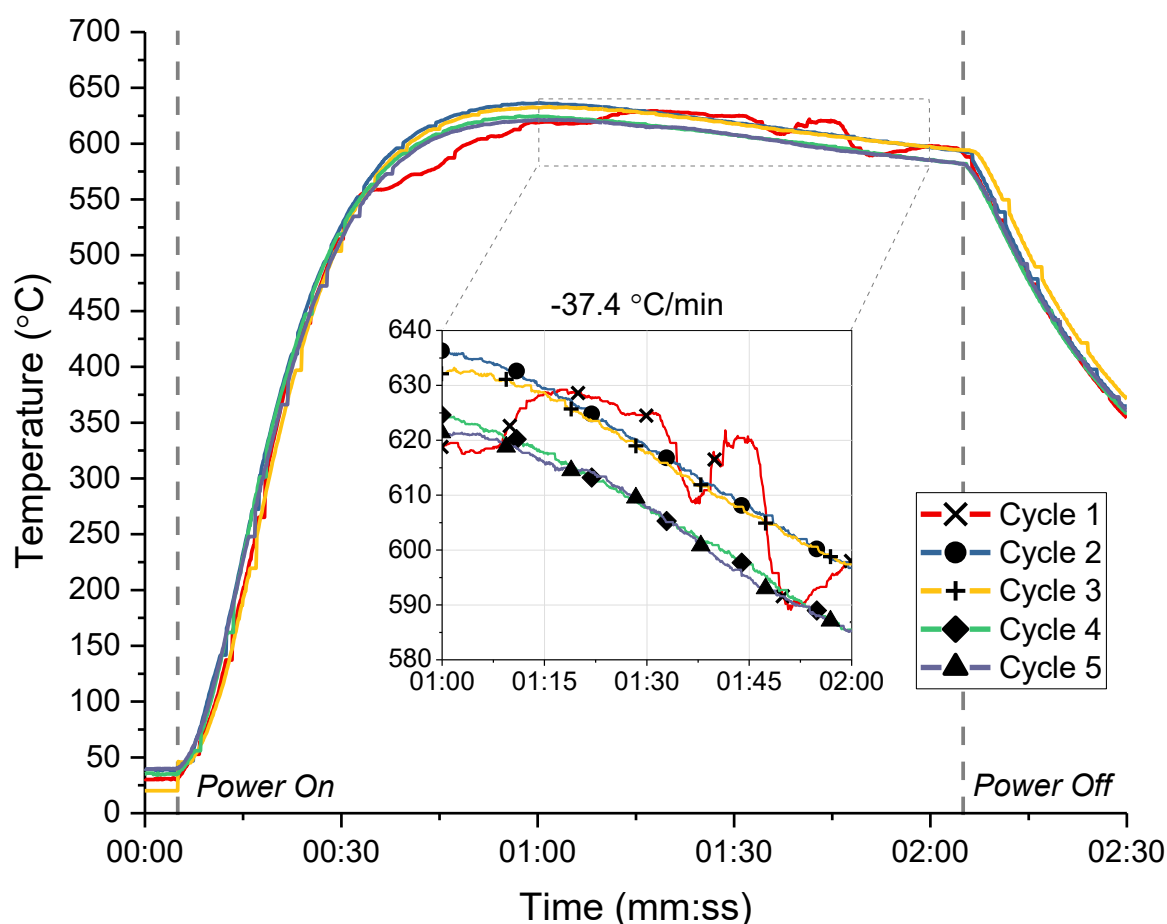


Figure 5.16 – Repeated microwave heating cycles of a 0.4 g sample of magnetite using 84 W of target power for 120 s

initial cycle which displayed slightly more irregular behaviour with temperatures fluctuating between 590 and 630 °C during the MW application. This irregular behaviour is unusual and atypical of other experiments performed. This may be fluctuations due to small amounts of moisture present in the magnetite powder. At high temperatures this may provide small amounts of available oxygen for partial oxidation of magnetite to maghemite. This could also provide hydrogen available for reduction reactions. Small alterations in the material composition could also result in small changes electromagnetic properties, meaning coupling and power delivery would subsequently change, but only by small amounts. During the initial rapid heating region, the sample typically rose by 540 °C in 30 s. The next 20 s shows continued heating at a decreasing rate until samples reach their maximum. The following period from 60 to 120 s shows relatively stable high temperatures which slowly decrease at a rate of -37.4 °C/min. After the microwave power is turned off the samples rapidly cool as before.

Successive cycles show a potential marginal decrease in heating capability of magnetite samples. From cycle 2 to cycle 5 the difference between recorded temperatures is -15 °C; the camera error in this temperature region is approximately ± 12 °C. Overall, the sample can be seen to heat consistently to temperatures over 550 °C with no apparent significant degradation in heating ability. After heating it was noted that the sample was incredibly dry but not substantially reddened as was previously seen with samples which were heated to these temperatures while under a normal atmosphere, presumably becoming oxidised. Given the repeatability of heating of magnetite here in comparison to the elevated temperature permeability and permittivity measurements made in Chapter 4, the phase change from magnetite to maghemite has not occurred to the bulk of the sample.

This experiment was reperformed using a 0.45 g sample of magnetite under the same experimental conditions with a comparable target MW

power of 82 W. This sample was heated six successive times, reaching maximum temperatures between 570 and 582 °C (with one outlier at 594 °C). The shape of all curves is similar to the ones shown in Figure 5.16 with similar spreads in temperature of around 15 °C. The negative gradient was also present but slightly lower than in Figure 5.16, at -17.4 °C/min. This negative gradient could be driven by heat loss to the environment, with the greater temperatures reached in Figure 5.16 meaning a larger temperature gradient and thus more rapid cooling effect. The sample with more mass will also have more thermal mass to maintain temperatures and have a smaller surface-area-to-volume ratio which will reduce heat loss. It could also be a result of increased temperatures making the magnetite less electromagnetically lossy, even though no transition to maghemite is occurring. The maximum temperatures of later cycles are not significantly decreased, suggesting this effect is something only happening during the heating, and not an inherent modification to the magnetite itself. This could be confirmed with more detailed material testing including XRD or post-heating MCP assessment.

This data suggests magnetite can effectively heat to temperatures over 550 °C repeatedly in an inert atmosphere. This indicates it could be a suitable reusable catalyst for various catalytic applications, including the rapid degradation of common plastic waste material such as polyethylene, polypropylene and other hydrocarbon sources.

5.5 CONCLUSIONS

Limitations of infrared pyrometry were explored including the spot size of pyrometers and material emissivity. Pyrometers were deemed to be unsuitable for temperature measurement in this scenario without further equipment that could ensure consistent precision placement of both pyrometer(s) and sample tubes. The effective emissivity of quartz tubes was determined for the IR camera with a spectral range of 7.5-13 μm up to 900 °C. This was performed using a thermocouple and tube furnace to

measure quartz tube temperature over the span of a few hours and correlate that with reported values from the camera. Effective emissivity was found to be approximately 0.95 through the majority of the temperature range.

Mono-mode microwave heating of magnetite powders using typically between 30 and 85 W of output power from custom-built solid-state microwave application equipment has been performed. Masses of magnetite and haematite between 0.1 and 0.4 g were heated with a maximum of 30 W, with magnetite reaching vastly greater temperatures than haematite. Magnetite is much more electromagnetically lossy than haematite, both magnetically and electrically, allowing it heat effectively to over 550 °C (in the smallest mass samples) after one minute of heating. The largest masses of magnetite (0.4 g) consistently reached more than twice the temperature of the smallest masses of haematite (0.1 g) at > 300 °C compared to < 150 °C. This shows indications that magnetite has high potential for use as a rapid heating microwave catalyst even at a maximum of 30 W while haematite is not useful under these conditions.

Layering of magnetite and haematite powders demonstrated the nature of microwave selectivity. Significant masses of powders placed in alternating layers and heated concurrently showed significant temperature differences with magnetite clearly becoming much hotter than the haematite exposed to the same fields. This is useful as it further demonstrates the applicability of microwaves for selective heating, and the effectiveness of magnetite in this regard as when mixed with a low-loss microwave material, extreme temperatures could still be reached, allowing useful microwave reactions or material processing to be performed by heating the magnetite as a microwave susceptor material.

Magnetite samples of 0.1 g and 0.4 g were heated with up to 50 W of MW power and both reached temperatures above 720 °C, with the smaller mass showing extremely rapid heating and the larger mass taking two

minutes to reach its maximum. Although at a slower rate, higher masses could reach very high temperatures with limited power inputs. This and previous experiments highlighted issues with reliability and consistency of heating results leading to investigation of temperature measurement equipment.

The differences between MW heating that is magnetically driven and electrically driven were investigated using magnetite and both a pyrometer and IR camera. Key differences observed include higher temperatures among magnetically driven samples, more consistent heating behaviour and rapid initial heating to a maximum temperature with a slowly decreasing temperature thereafter ($-10\text{ s }^{\circ}\text{C/min}$).

Electrically driven samples showed much more varied heating behaviours and maximum temperatures, although they still showed tendency to increase in temperature at the end of the standard two-minute MW application period used. Higher temperatures could be possible using electric field heating and extended durations, although highly rapid heating is much more achievable and reliable with magnetic field regions.

Repeated heatings of magnetite samples in inert atmospheres again showed rapid, consistent and high-temperature heating. Samples did not significantly degrade in their ability to achieve high temperatures exceeding $550\text{ }^{\circ}\text{C}$ even after multiple heating cycles to these temperatures. This is attributed to the fact the inert atmosphere prevented any oxidation or phase changes in the powder that would significantly alter the electromagnetic properties. After cooling they were largely if not completely electromagnetically unchanged, highlighting magnetite's reusability.

The exploration of microwave heating of magnetite powder agrees with the electromagnetic characterisation of magnetite up to $200\text{ }^{\circ}\text{C}$ showing it to be an electromagnetically lossy material, especially in magnetic fields. It heats exceptionally well in magnetic fields and with power levels under 100 W samples of magnetite powder often exceeded $600\text{ }^{\circ}\text{C}$ even after

issues with pyrometer measurement were addressed. It can be heated repeatedly under an inert atmosphere without degrading and losing this highly effective heating characteristic. All these qualities discussed show magnetite powder to be a highly promising material for highly selective microwave heating, in particular for rapid destruction of common polymer materials above temperatures of 550 °C. This will be explored in detail in Chapter 6.

Chapter 6

6 MICROWAVE-ASSISTED DESTRUCTION OF PLASTICS

6.1 RAPID PLASTIC DESTRUCTION

Plastic pollution continues to affect the environment with more and more plastics produced than ever before [55][56]. Even if new plastic production were to cease today there will still be incredible amounts of waste plastic that exist as both macro and micro plastics. As of 2019, estimated total generated plastic waste values exceed 350 Mt [222]. These plastics are generally hydrocarbon-based i.e. they consist primarily of hydrogen and carbon atoms and can be considered rich sources of these elements which after use, often become waste. This is important because the waste plastics can be transformed into a number of other materials including useful monomers, intermediate hydrocarbon products, hydrogen gas and solid carbon products like carbon nanotubes (CNTs) [9][10][12][35][224][225]. These materials can prove useful, and so their generation from waste material means additional value is extracted concurrently with waste removal. Of the possible products, hydrogen gas is perhaps one of the most beneficial. Hydrogen is contained in almost all plastics to varying degrees and can be used as a clean fuel source in fuel cells which generate only water as a by-product, something which is desperately needed for global energy production to combat climate change [226]. Plastic waste as a viable hydrogen generation stream would be an extremely valuable development to tackle plastic pollution and generate clean energy.

There are many types of plastics and therefore many types of plastic waste. Some plastics are used far more than others and can have varying degrees of reuse and recycling rates. By far the most common plastic waste producing sector is packaging which can be used for all sorts of applications such as food and drink, electronics, medicines, cosmetics and more [55]. Although plastic packaging is incredibly useful and versatile, its abundance has led to much recent research into the transformation or destruction of plastics into useful products. This includes diesel oil mixtures [5][11][227][228] and mixtures of hydrocarbon gases, for example syngas [229][230].

Many of these methods utilise a two-step process to create intermediate gases, waxes or oils and further transform these products into hydrogen gas. A microwave-assisted one-step process for converting plastics directly to hydrogen gas has been investigated previously with highly promising results [9][231][232]. This is performed with rapid heating to high temperatures, avoiding the production of intermediate products and is discussed in more detail in Chapter 2, section 2.3.2.2. This process was chosen to be further investigated with the use of magnetite as a highly effective microwave susceptor; in particular with magnetite heated via the primary driver of magnetic field microwave heating. This has been shown to be a method capable of sufficiently rapid heating to temperatures over 600 °C in the previous chapter.

6.2 EQUIPMENT

In general, the equipment used here is the same or very similar to that used in the previous microwave powder heating work. Details are included here for completeness and clarity of any changes and additions to used equipment.

6.2.1 CAVITIES AND QUARTZ TUBING

Two cavities are used for plastic decomposition experiments. Both are cylindrical cavities identical to the construction of those used in Chapter 5

and shown in Figure 5.3. They are used exclusively in the TM_{010} resonant mode and samples placed only in the sample hole designed to expose samples to the maximum magnetic field region as in Figure 5.2. The only reason for using two cavities is to machine them with slightly different radii to achieve different resonant frequencies in the TM_{010} mode as dictated by (3.32). This is because an additional PMA was constructed to achieve power levels over 100 W and the operational frequency range of this new equipment did not support the original cavity resonant frequency. The two cavities used are one with radius 49.0 mm ($f_{010} \sim 2.342$ GHz) used in Chapter 5 and another with radius 46.8 mm ($f_{010} \sim 2.452$ GHz). The smaller cavity is designed to have a TM_{010} frequency in the centre of the new system's operating range of 2.4-2.5 GHz. Both cavities are identical in all other dimensions including sample hole diameters, viewing slit size and coupling architecture. The same coupling loop can be removed from the original cavity and used directly in the duplicate.

Quartz tubing is also used as before. The 8 mm outer diameter open-ended tubes are the only type used for this section as they can be fitted with flexible tubing both on the top and bottom to allow nitrogen gas to flow continuously over them.

6.2.1 NEW PMA SYSTEM

Other works that have studied plastic destruction using microwaves have used power levels in the hundreds to thousands of Watts. Rapid heating of magnetite has been shown to achieve over 500 °C within 30 seconds with under 100 W in Chapter 5, however, this was done with only the magnetite sample present. When adding plastic into the microwave cavity the increased mass of material will dampen the coupling, meaning power transfer won't be as effective. This means greater input power may be required to achieve required temperatures. As the current PMA was limited to below 100 W of microwave output power a new system was

required to allow greater power levels and ensure sufficient temperatures could be reached with the increased sample mass.

A new PMA is constructed based on the Mini-Circuits ZHL-2425-250X+ Solid-State High-Power Amplifier [233] and the ISC-2425-25+ Signal Generator and Controller [234]. This system is capable of consistent power outputs of 300 W at the cost of available bandwidth, only operating in a 100 MHz window from 2.4 to 2.5 GHz as compared to the 2.0 to 2.4 GHz range of the previous PMA. This model of amplifier can also be chained together with other similar amplifiers to increase the maximum power output, but this feature has not been utilised here.

This system is built with the same philosophy as previous PMAs with the components mounted on an easily portable board. This system benefits from not requiring other external passive microwave components like a circulator or attenuator, as the amplifier has in-built protection against high reflected power, up to 200 W. This amplifier requires a heat sink as before (although smaller) a thermal paste compound and a high flow fan to keep it cool. This fan, the signal generator and the amplifier all require different DC voltage and current levels which require an AC-DC converter and a further DC-DC voltage supply to power these parts. This results in a significantly lighter board than previously used at only a few kilograms, with a similar footprint.

6.2.2 SAMPLE POWDERS

Magnetite powder is the same as detailed before in sections 4.4.1 and 5.2.2 with a quoted average particle diameter less than 5 microns.

A variety of plastics are used for experimentation here. The primary focus is on HDPE which is supplied from two sources. Both virgin plastic material and post-consumer plastic waste material were used here. Virgin polyethylene was sourced from Sigma-Aldrich (427772, powder) to represent a pure plastic product without impurities. This polyethylene is of significantly lower molecular weight than typical HDPE waste, with an

average value of 4000 g/mol as reported by gel permeation chromatography (GPC) [235].

Post-consumer high-density polyethylene (HDPE) was obtained from waste plastic supermarket milk bottles. These were processed into a powder using a standard domestic blender. Analysis of the size of particles in this sample is shown in section 6.3.3. This represents a more realistic plastic waste product that could show up in landfill or waterway waste patches. Although this type of product does not appear to contain any dyes it could still contain additional chemical additives or impurities from the manufacturing process. This could lead to the production of additional unexpected products. This sample of post-consumer HDPE was generously provided by Dr. Xiangyu Jie and colleagues while at the University of Oxford as they had performed similar experiments.

Similar post-consumer plastic waste was obtained for polypropylene (PP) from a supermarket food container, polystyrene (PS) from laboratory sample boats and polyethylene terephthalate (PET) from a supermarket food container. These were processed multiple times using a domestic blender. The smallest particles suitable for powder mixing were filtered out between each processing run. These plastic powders were not analysed for particle size approximations as with HDPE particles but were sieved through an 18-mesh filter (1 mm aperture size).

6.3 METHODOLOGY

Investigation of plastic destruction is more involved than previous work on heating of magnetite powder alone. As the plastic is expected to produce hydrocarbon gases greater precautions must be taken to ensure safety and practical collection of products. This includes use of gas collection and safety equipment, new microwave equipment and multiple analysis techniques to study the products created. These methods and equipment will be discussed here before results are presented, as well as

the general procedure taken to perform experimentation on plastic samples.

6.3.1 GAS COLLECTION SYSTEM

As the production of gases like hydrogen, methane and carbon monoxide are expected during this process, precautions must be taken to collect these in a safe way and ensure that they aren't inhaled or ignited. All experiments that may produce these gases are performed in a closed fume cupboard which ensures sufficient ventilation of any released gas. The potential volumes of expected gases are still relatively small and not enough to cause serious harm while in the fume cupboard, meaning any additional respiratory protection is not required. Open flames and any potential sources of sparks are kept out of the gas production area to reduce the risk of ignition.

Samples are purged with an inert gas to remove available oxygen, which as a highly reactive element could result in oxidation of the catalyst and additional undesirable gaseous products being formed. Nitrogen gas was used as the inert gas in this case which is fed through plastic tubing with an inner diameter of 5 mm and controlled using a flow meter. This tubing is connected to the lower end of the quartz sample tubes with the upper end connected to a short section of tubing which feeds into a gas collection bag. The gas bag is controlled by a manual valve to allow gas flow or prevent it. The positive pressure and flow of nitrogen will force produced gases to flow to the gas collection bag. The schematic of the gas-collection and experimental set up is shown in Figure 6.1.

Any solid products will remain in the sample tube with any other remaining solids from the catalyst-plastic mixture and any produced liquids or waxes from the reaction. The capability to analyse any liquid or wax-based products was not available so only gaseous and solid products are considered for further analysis.

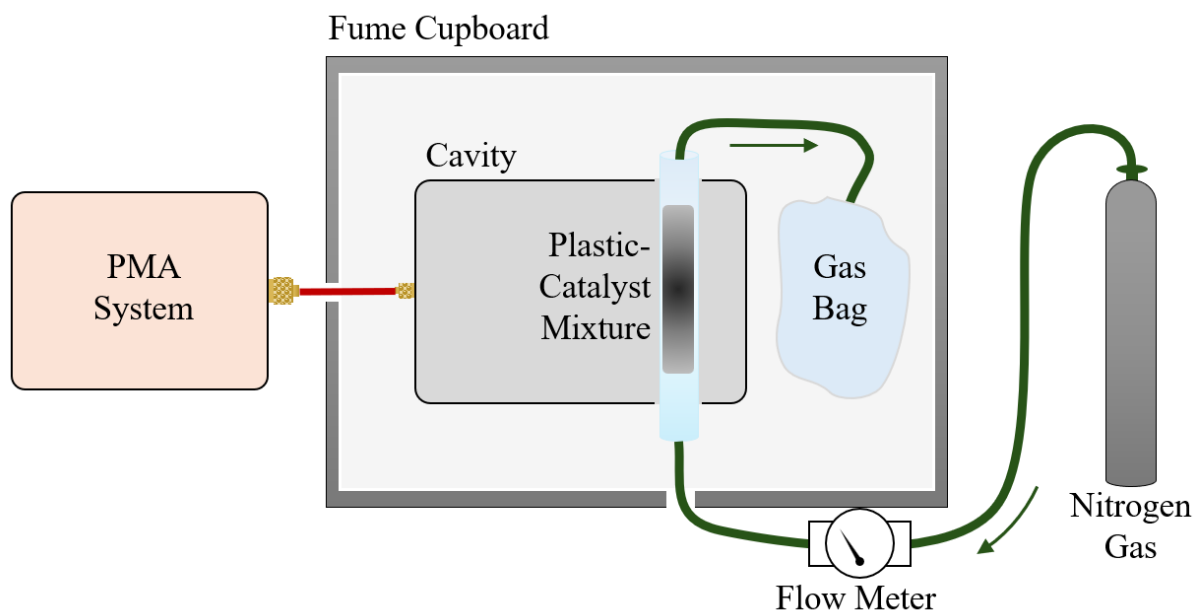


Figure 6.1 – Schematic diagram of microwave application and gas collection system

6.3.2 PROCEDURE

The PMA is connected to the cavity as with previous microwave heating experiments and the coupling loop manually adjusted to maximise initial power transfer. The power settings on this PMA are slightly different to the one used previously as they include a target power and centre frequency but also an operating frequency range. This PMA system uses a digital locked loop (DLL) which is an algorithm in the signal generator/controller which performs the same function as the frequency sweeping feature on previous PMA versions. This performs frequency sweeps at regular intervals to search for a centre frequency which is more closely matched to the load i.e. has less reflected power than the current centre frequency and therefore better power transfer. This system can perform this at maximum intervals of 1000 ms by scanning from the centre frequency to the lower frequency bound and then looping back to the upper bound if a sufficient match is not acquired.

Samples are prepared by first placing a small amount of quartz wool in the quartz sample tubes to support the solids and allow gas flow. Masses of magnetite and the plastic under test are weighed separately and can

be loaded into the tube through a manual mixing method or a layering technique. Manual mixing is achieved by placing both powders in the same container and shaking for approximately 30 to 60 s until a homogeneous appearance is achieved from the coating of magnetite powder on the plastic. An example of the sample's visual appearance post-mixing is shown in Figure 6.2. Layering is performed by first placing half the mass of magnetite directly into the sample tube, followed by the plastic, and finally the remaining magnetite to create distinct layers of each material.

With the PMA ready and samples prepared they can be placed in the cavity and connected to the gas tubing both on the top and bottom of the tubes. Before heating the samples are purged under a low flow of nitrogen typically between 40 and 60 ml/min for at least five minutes. The gas collection bag is then connected to the tubing from the top end of the sample tube and the nitrogen purge continues for one minute with the gas bag valve closed. The microwave power can then be initiated and the gas bag valve opened to capture produced gases forced through by the positive pressure from the nitrogen gas. As with other heating



Figure 6.2 – Manually mixed magnetite and post-consumer HDPE powder

experiments the IR camera can be used to measure sample temperature during the duration of microwave application.

After a designated time for example, 3, 5 or 10 minutes, the microwave power is switched off and the gas bag valve closed. The contents of the gas bag can then be analysed using gas chromatography to determine the presence and proportions of produced gases. Any solid residue can be analysed by X-ray diffraction (XRD) to study the crystallinity of the materials and compare against known XRD patterns to determine the present solids. A scanning electron microscope (SEM) can also be used to directly observe the solid materials at high magnification which will aid in identifying remaining or produced materials, as well as any changes in structure.

6.3.3 ANALYSIS METHODS AND SAMPLE CHARACTERISATION

6.3.3.1 GAS CHROMATOGRAPHY

Due to not having direct access to gas analysis equipment this was outsourced to colleagues both in Cardiff University and Queen Mary University London. When provided with gas samples and given an expected distribution of gas species they provided the results/analysis. As such, details of GC calibration are not available.

Gas mixtures analysed by colleagues in the Cardiff University School of Chemistry were performed by Dr. James Hayward and Dr. Auttaphon Chachvalvutikul using an Agilent 7890B GC system. Initial testing of produced gases could not detect carbon monoxide due to equipment errors, but this was later rectified. This will be noted with the corresponding results.

Additional gas analysis was generously performed by colleagues Dr. Huaizhong Xiang and Dr. Xiangyu Jie at Queen Mary University London using an Agilent 8890 GC system.

The gas collected from these experiments was analysed using flame ionisation detection (FID) and thermal conductivity detection (TCD) methods to determine the present species and the approximate quantity. After the removal of the nitrogen carrier this can be formulated into a list of relative concentrations to see how much of the produced gas was, for example hydrogen or methane. The FID detector detects carbon-containing compounds such as the hydrocarbon gases expected from plastic decomposition including methane, ethylene and propane. The compounds are passed over a flame which breaks down carbon-carbon and carbon-hydrogen bonds into ions, which measurably increase the conductivity of the flame. TCD works to detect changes in thermal conductivity of the analysed mixture in comparison to a reference. The gases pass over a heated filament which changes its electrical resistance depending on the thermal conductivity of the surrounding medium; high conductivity gases draw heat away from the filament rapidly and lower the filament's electrical resistance. The difference between this sample filament and the reference causes a chromatograph peak. TCD is used primarily to detect hydrogen in this work.

6.3.3.2 X-RAY DIFFRACTION

In the decomposition of plastics, it is expected that solid remnants post-test will consist of catalyst and carbon-based materials such as carbon nanotubes. XRD is a useful tool that can identify crystalline materials. This is achieved by pointing an X-ray beam at a sample under test which will cause diffraction of the beam [86][237]. This diffracted beam is received by a detector and the intensity of received radiation plotted against the diffraction angle (2θ) provides a distinct pattern. This pattern can then be compared against databases of reference XRD data for thousands of materials to find a matching pattern and identify the material present [238]. All following XRD testing was performed using a PANalytical X'Pert Pro powder X-ray diffraction system with a copper anode and 2θ step size of 0.017° [239].

XRD analysis is performed on the unused magnetite powder to achieve a baseline reference pattern and also confirm no other materials are present. This is shown for 2θ from 5° to 80° in Figure 6.3 alongside the ICDD reference data for magnetite (ICDD: 01-089-3854). This XRD pattern matches extremely well with the reference data with all peaks over 1 % rel. intensity clearly visible. The most prominent peaks are visible at $2\theta = 18.353^\circ$, 30.151° , 35.489° , 37.104° , 43.122° , 53.509° , 57.028° , 62.621° . This high degree of similarity confirms the magnetite used is pure with no apparent crystalline impurities from any other iron oxide materials or any other materials.

The polyethylene source is also tested to provide a baseline comparison when analysing post-reaction samples. Post-consumer HDPE sourced from supermarket milk bottles is tested alongside pure HDPE powder and the results are shown in Figure 6.4 with the line plots showing the XRD data and associated auto-identified peaks marked with crosses. The HDPE sourced from the milk bottles is identified by the XRD software as being either polyethylene or n-Tetracontane ($C_{40}H_{82}$), which is an alkane

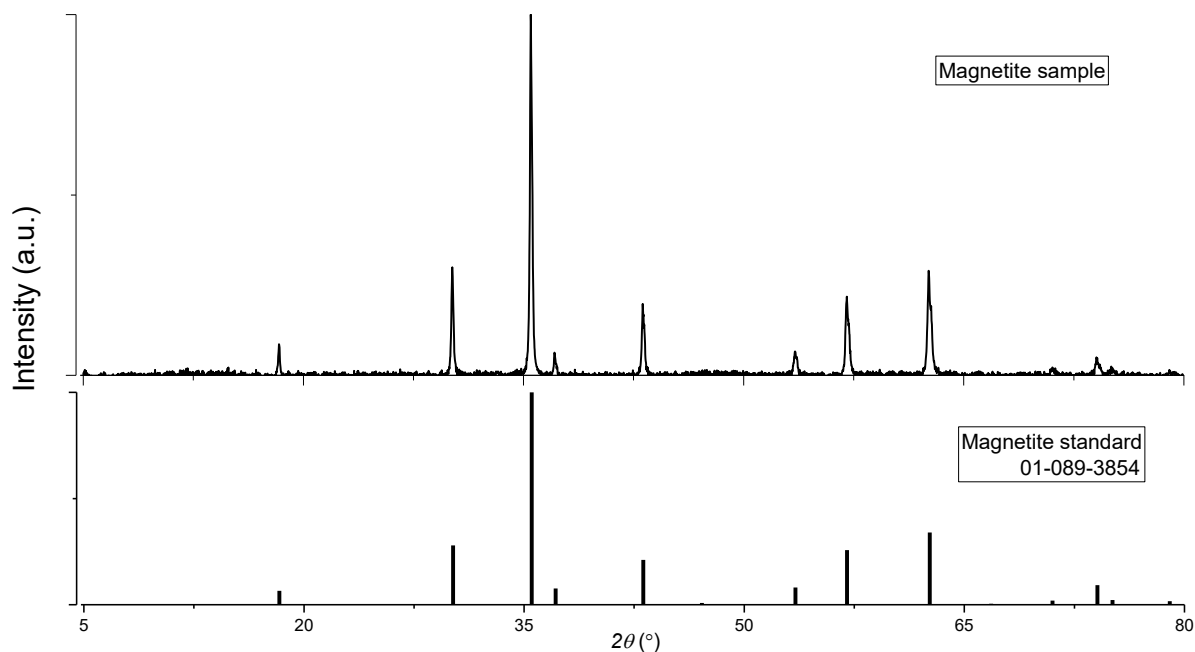


Figure 6.3 – XRD data from tested magnetite sample compared with JCPDS/ICDD reference data

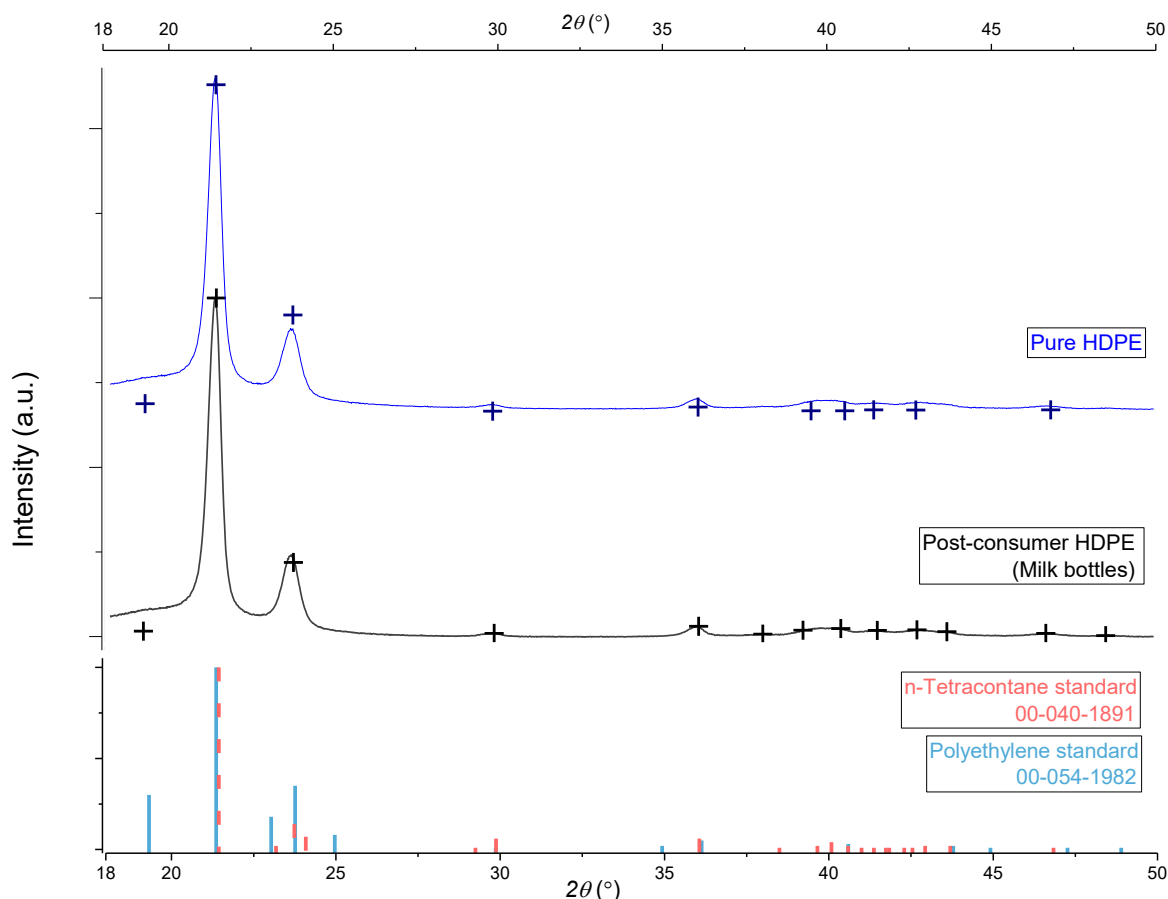


Figure 6.4 – XRD data from post-consumer HDPE source (milk bottles) and pure HDPE powder. JCPDS/ICDD reference data for PE and n-Tetracontane also shown.

hydrocarbon used in research when studying idealised reactions involving polyethylene. The reference data for both n-Tetracontane (ICDD: 00-040-1891) and polyethylene (ICDD: 00-054-1982) is displayed alongside the XRD data for the milk bottle HDPE and the pure HDPE. When visualised together, the reference data for n-tetracontane is very similar to that for polyethylene (it also being a very similar chemical composition) so it is understandable to have a misidentification in this regard. The observed data aligns well with reference data for polyethylene in particular with peaks at $2\theta = 21.345^\circ$, 23.708° , 36.054° . There are many small peaks present from 35° to 60° which are present on both polyethylene and n-tetracontane reference data which could have contributed to the mischaracterisation as n-tetracontane.

A notable absence from the tested HDPE is any sign of a peak at 19.314° , which in the PE reference data is a significant peak. A small peak was attributed to 19.163° by the XRD software however this is not prominent and could be being obscured by background noise. The broad peak visible in this region could be the result of amorphous material, and as HDPE is often classified as a semi-crystalline material this would agree with that assessment of the crystal structure. This broad peak around 19° is often visible in other instances of HDPE XRD data [240][241][242]. The data from the pure HDPE agrees strongly with the post-consumer plastic with all the significant peaks present at the same 2θ values and to the same intensity. Only in the range of 37° to 47° where peaks of very low intensity are found, are there disagreements between the samples. These peaks would not be used for identification of the presence of HDPE in a mixed sample so can generally be ignored.

6.3.3.3 SCANNING ELECTRON MICROSCOPY

A scanning electron microscope (SEM) was used for analysis of untreated and post-reaction samples of magnetite, plastic and mixtures. SEM is useful for the observation of materials of the scale of nano or micrometres. The basic principle of SEM is that a beam of electrons are fired at the sample and the scattering and generation of electrons from the sample is recorded by detectors which can then convert that information to an image [243][244]. An SEM microscope is able to achieve a much greater resolution than a standard light-dependent microscope because the wavelength of electrons is much smaller than the wavelength of visible light. Depending on the accelerating voltage of the SEM equipment, which is typically between 5 and 30 kV, the electron wavelength will be between approximately 7 and 17 pm while the wavelength of visible light is hundreds of nanometres. This is a scale factor of the order of 10^3 .

Samples were sputter coated with a layer of Au-Pd in an 80:20 ratio with a thickness of 15 nm. The coating of an electrically conductive material performs a number of functions [243][244]. This includes reducing the build-up of static electric fields, and thus limits charging artefacts visible on the image as well as increasing the number of secondary electrons available from the sample surface, thereby improving the signal-to-noise ratio and improving image quality. The coating also protects the sensitive beam source from damage by helping to secure samples to the analysis stage, ensuring no particles can be thrown around by the creation of a vacuum or when the EM fields from the beam are initiated. A TESCAN MAIA-3 Field Emission Gun SEM (FEG-SEM) was used to obtain all SEM images in this work.

Collections of SEM images of the magnetite powder and post-consumer HDPE are shown in Figure 6.5 and Figure 6.6. These images were collected at various magnifications using the secondary electron (SE) detector for the wide angle "Overview" mode and the in-beam SE detector for the high-resolution mode capable of higher magnification and resolution.

Figure 6.5 shows the magnetite powder at high magnification. This powder is quoted as having an average particle size less than five microns. To see the detail of individual particles at this level, magnifications exceeding 10k are required. In Figure 6.5 A the general structure of the powder can be seen at a scale of five microns. This shows hundreds of small particles certainly less than five microns with the biggest individual particles approximately 2-3 microns. Many of the particles are smaller than one micron and form large agglomerations where lots of small particles adhere to larger ones to form clumps. The next step in magnification is shown in Figure 6.5 C where the particles can be seen in greater detail. This begins to show the shape of the particles to consist of many cubic and quasi-spherical particles of varying sizes from 10s of nanometres to around one micron. B and D provide the

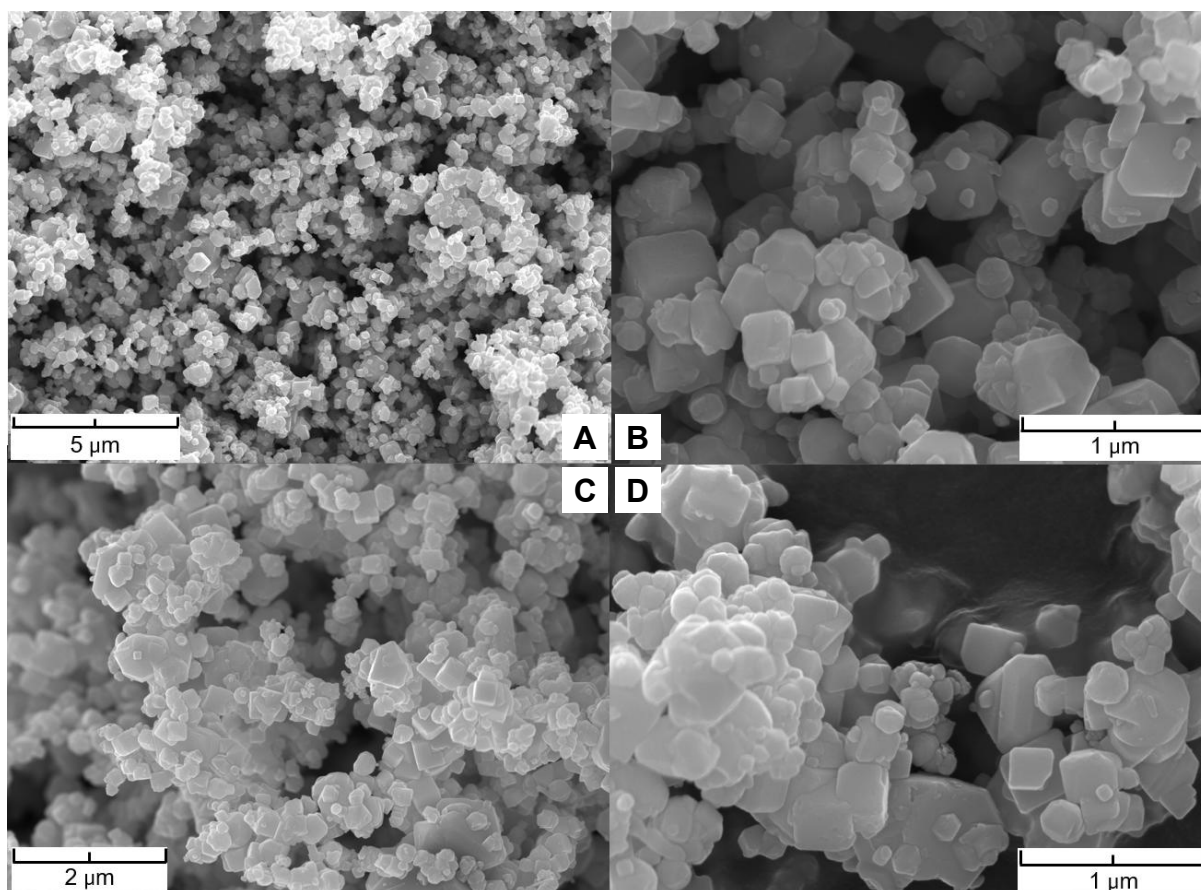


Figure 6.5 – SEM images of magnetite powder shown at magnifications of 15k-85k

greatest magnification where the cubic particles can be clearly seen. Particles with diameters less than 100 nm can be clearly seen in these images either as distinct defined particles or as part of agglomerations.

SEM images of magnetite were analysed using an image processing software called “ImageJ” [245] to determine the approximate particle sizes and distributions. Particles that were fully visible and defined were measured at their point of greatest width over four separate images. Over 200 particles were measured in each iteration and their diameters recorded. These values were then displayed in a histogram with bin widths of 0.05 µm. This plot is shown in Figure 6.7.

This plot shows the frequency of particle sizes in each range for each image analysed and a corresponding fit curve. The data was found to be best fit by a Log-Normal distribution, with few particles under 0.05 µm and above 0.5 µm but most particles observed between 0.05 and 0.35 µm

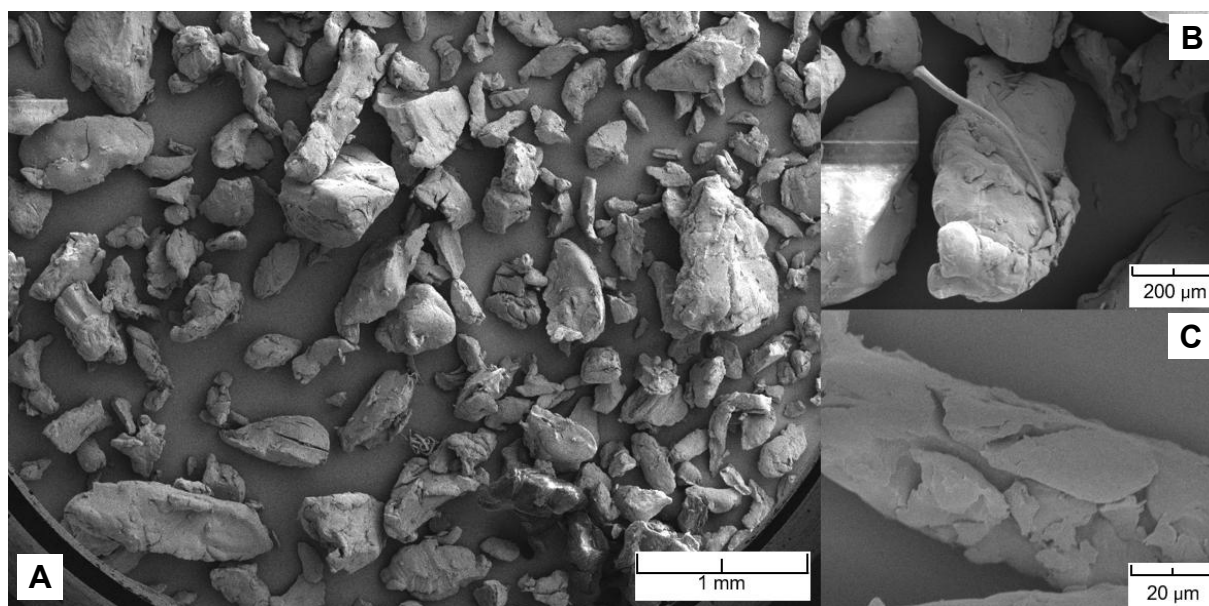


Figure 6.6 – SEM images of post-consumer HDPE powder shown at magnifications of 100 to 2.5k

in diameter. It is expected the particles follow a Normal-type distribution as they have not been sieved or otherwise filtered to remove any particular size of particle. The particles follow the Log-Normal distribution as there are particles on the order of single microns, 100s of nm, 10s of nm and likely even single nanometres. These smallest particles were the hardest to determine from the images acquired as the even at the maximum magnification used, they are still very small. This means they are more likely to be obscured by larger particles or be harder to delineate as they cluster together. An example of this is visible in the centre of Figure 6.5 D. The smallest detected particle that could be definitively delineated was approximately 10 nm while the largest was 1.1 μm. There may also be larger particles that were missed due to the narrow areas searched but their frequency would be incredibly low, which should align with this distribution. The quoted average particle size of the magnetite powder from the supplier was 1.3 μm. This data did not find any individual particles over this size and recorded a median particle size of just 195 nm with a mean of 226 nm.

Figure 6.6 shows the post-consumer HDPE on relatively low magnification below 2.5k. This is because the greatest magnifications did not provide

much detail as the particles were much larger than those of the magnetite. Some individual particles in this powder were certainly identifiable with the naked eye which is confirmed by the SEM images showing some large particles with sizes of around 0.5 to 1 mm in length. Particle shapes are irregular with varying degrees of surface roughness. As this plastic was powdered by a domestic blender these images could show the tearing and straining of the plastic under these conditions. A similar particle size analysis was performed on the HDPE powder with a Log-Normal distribution also present. The median particle size was calculated as 279.0 μm with the mean of 297.6 μm . The smallest particle measured was 40 μm and the largest 1.23 mm. These HDPE particles are approximately 1400 times larger than the magnetite particles.

Figure 6.6 B and C show more detailed SEM images of particular particles. B shows an HDPE particle measuring approximately $600 \times 400 \mu\text{m}$ with an unidentified $600 \times 13 \mu\text{m}$ strand embedded in it. This strand could potentially be an external contaminant such as a hair or clothing fibre, although its small width of 13 μm is generally smaller than most values for human hair width of around 50-60 μm . This could also be a contaminant within the plastic itself that has now been separated from the bulk of the polymer. It is most likely a strand of HDPE which has been stretched and deformed, perhaps during the initial manufacturing process or with the mechanical destruction and heat during its processing into a powder. If it is an example of a gel defect formed during the manufacturing process it would likely be much stronger than the surrounding HDPE material. This combined with its small size would make it difficult for a blender to process. C shows an even closer view of another piece of HDPE which shows a relatively smooth surface interrupted by cracks and cuts. These may have been caused by the stresses induced on the plastic during blending. These images provide a reference for these materials before any microwave catalysis was

performed. Any morphological changes in the materials or even the presence of unidentified materials can now be performed with SEM.

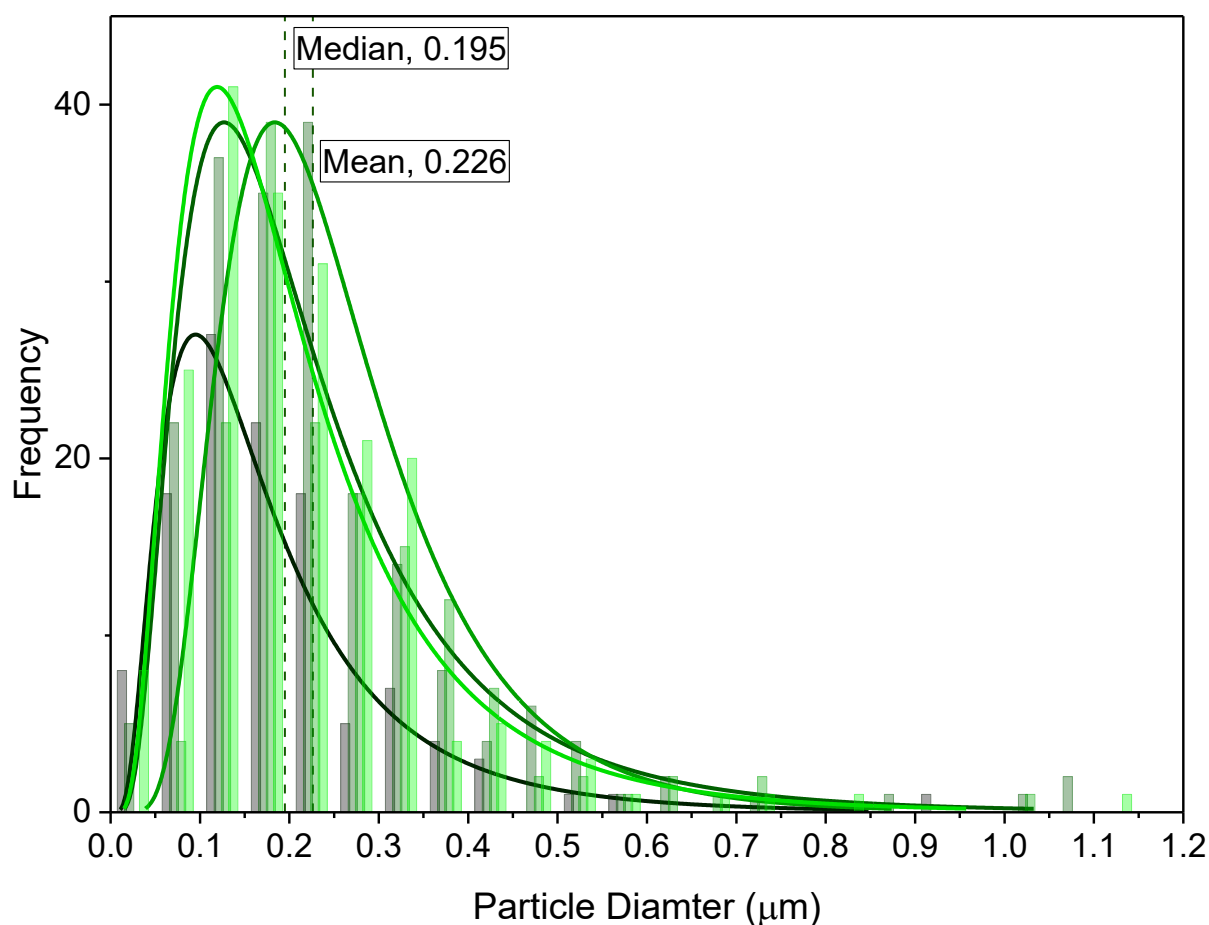


Figure 6.7 – Particle diameter distribution of magnetite powder derived from SEM images

6.4 RESULTS - PLASTIC DESTRUCTION EXPERIMENTATION

6.4.1 SAMPLE TEMPERATURES

Shown in Figure 6.8 are a selection of plots of temperatures recorded amongst catalyst:plastic mixtures during microwave application. This includes virgin PE and post-consumer PE, PP and PET. Microwave target power was 180 W for all these tests with magnetite masses of 0.30 g and plastic masses of 0.15 g. All samples were aimed for durations exceeding two minutes with two samples (one virgin PE and one post-consumer PE) stopped automatically before this time due to amplifier overheating. All

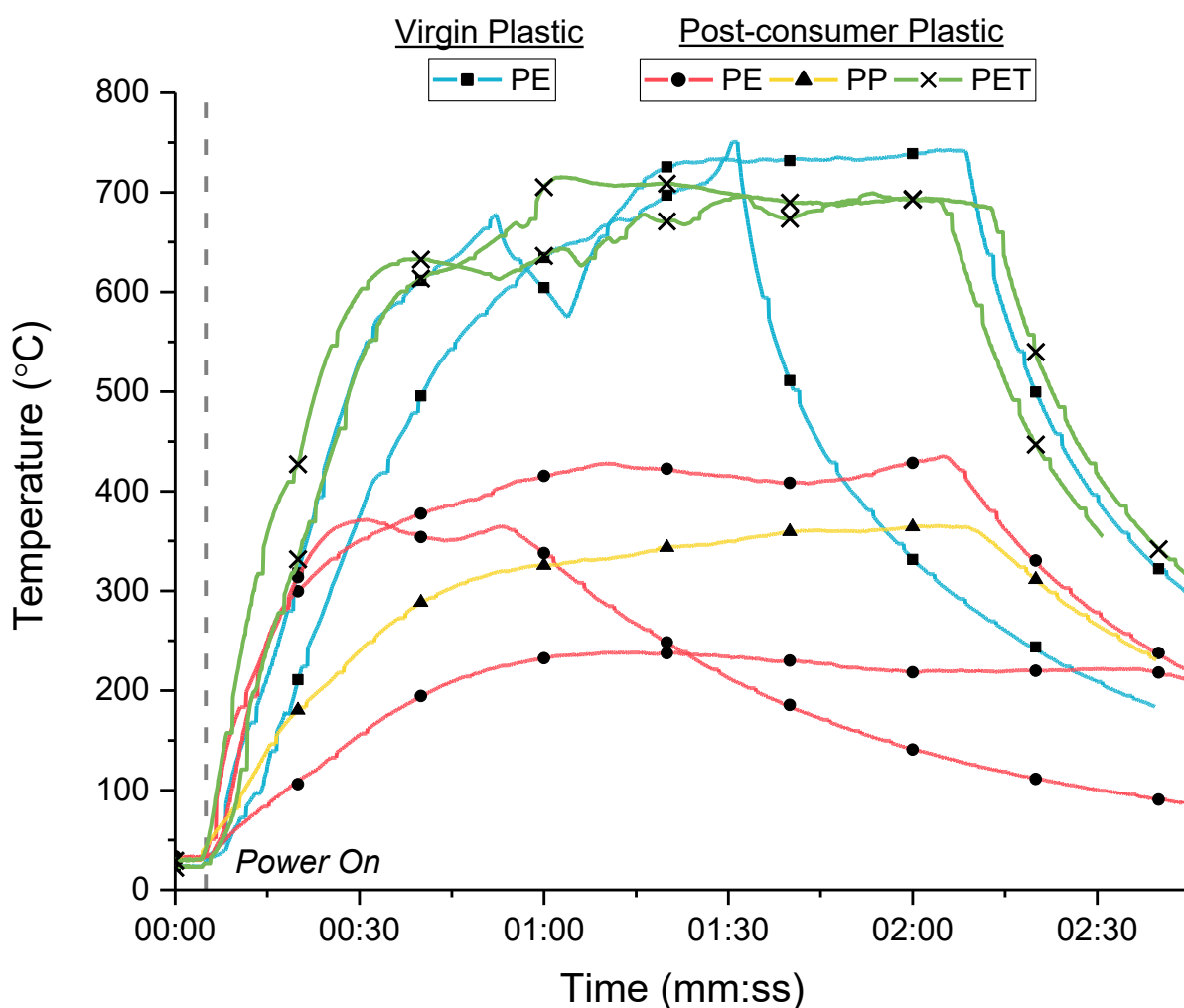


Figure 6.8 – Temperature-time plots for various mixtures of magnetite and plastics including virgin and post-consumer materials. Maximum microwave power was 180 W for all samples with 0.30g magnetite and 0.15 g plastic used in each case.

samples are time-synchronised by the MW power initiation, occurring at $t = 5$ s.

Both the virgin PE and post-consumer PET were able to achieve significantly higher temperatures than other tested plastics. These temperatures were typically in excess of 650 °C within the first minute of MW application. The curves of these samples are reminiscent of MW heating tests performed on magnetite samples alone, heating rapidly within the first 30 s to over 500 °C. During the subsequent temperature stabilising region there are far more irregular fluctuations in temperature among plastic samples when compared to magnetite alone. This is attributed to the presence of plastic material and the produced materials. Gases produced from the plastic decomposition process may here be enabling the reduction of magnetite to FeO and iron as detected in XRD traces.

It is suspected that the majority if not the entirety of the plastic in these very high temperature samples has been decomposed as the recorded temperatures far exceed the typical values for complete thermal decomposition of these plastics [246]. Given the conclusions drawn from Chapter 5 where the temperature measurements are being made on the exterior of the quartz tubes, thus causing a lag in true temperature, it is believed these mixtures achieved the required decomposition temperatures in under 30 s of microwave application. This rapid decomposition should produce few intermediate materials and tend to simple gaseous material generation e.g. hydrogen.

The post-consumer PE samples generally struggled to achieve temperatures above 400 °C even with 180 W maximum microwave power applied. Some gases were produced from these samples but it was observed that more waxy or liquid products were produced compared to other plastic types. Post-consumer PE is generally considered to have very high molecular weight. This would make it require more energy to decompose. The virgin PE used was a comparatively low molecular weight

of 4000 g/mol, making it much easier to consistently achieve temperatures required for complete decomposition.

The polypropylene also struggled to achieve high temperatures when heated, displaying similar behaviour to the post-consumer PE with reduced heating rates and maximum temperatures. This may suffer from the same issue as the PE. It is sourced from supermarket food containers that may have high molecular weights and are therefore difficult to break down. More testing and the inclusion of different PP sources should be considered.

Both the virgin PE samples exhibit an unusual behaviour where at high temperatures a short rapid temperature increase of around 25 °C is seen. For one trace this occurs at approximately $t = 50$ s which is then followed by a 75 °C drop in temperature and a following rise to plateau temperature of 740 °C. The other trace shows this short peak at approximately $t = 90$ s, which is then followed by the PMA overheating and switching off automatically. These peaks may show the formation of iron metal. This is happening at high temperatures (> 650 °C) suggesting it is when most if not all of the plastic has likely decomposed. Hydrogen-rich gases produced here could provide the reducing atmosphere to create the iron. Sudden introduction of sizeable quantities (with reference to resonant cavities) of iron metal may spike temperature as the magnetic field induces significant heating in such a high permeability material. These metal particles could also create intense local electric fields due to dielectric polarisation. These intense fields could dramatically increase heating rate between particles and lead to a spike in recorded temperatures.

6.4.2 TESTING OF HDPE WASTE

A sample containing 0.1 g each of magnetite and HDPE powder was manually mixed and loaded into a quartz tube ready for microwave application. Incident microwave power levels of 50 W were used for 3

minutes while gas products were collected, by which point no further reaction activity could be observed including visible vapours, increased gas flow due to produced gases, or uncharacteristic heating behaviour from the reactor.

The relative concentrations are shown in Figure 6.9 alongside a similar experiment from Jie et al. [9], which used an iron oxide-aluminium oxide composite catalyst at much higher microwave power levels. Below each column is the catalyst used, the primary driving field type, the incident power level and duration of application. The plastic feedstock is the same in both cases, being from the same batch produced and provided by Dr. Jie. Despite the differences in experimental set up this test was

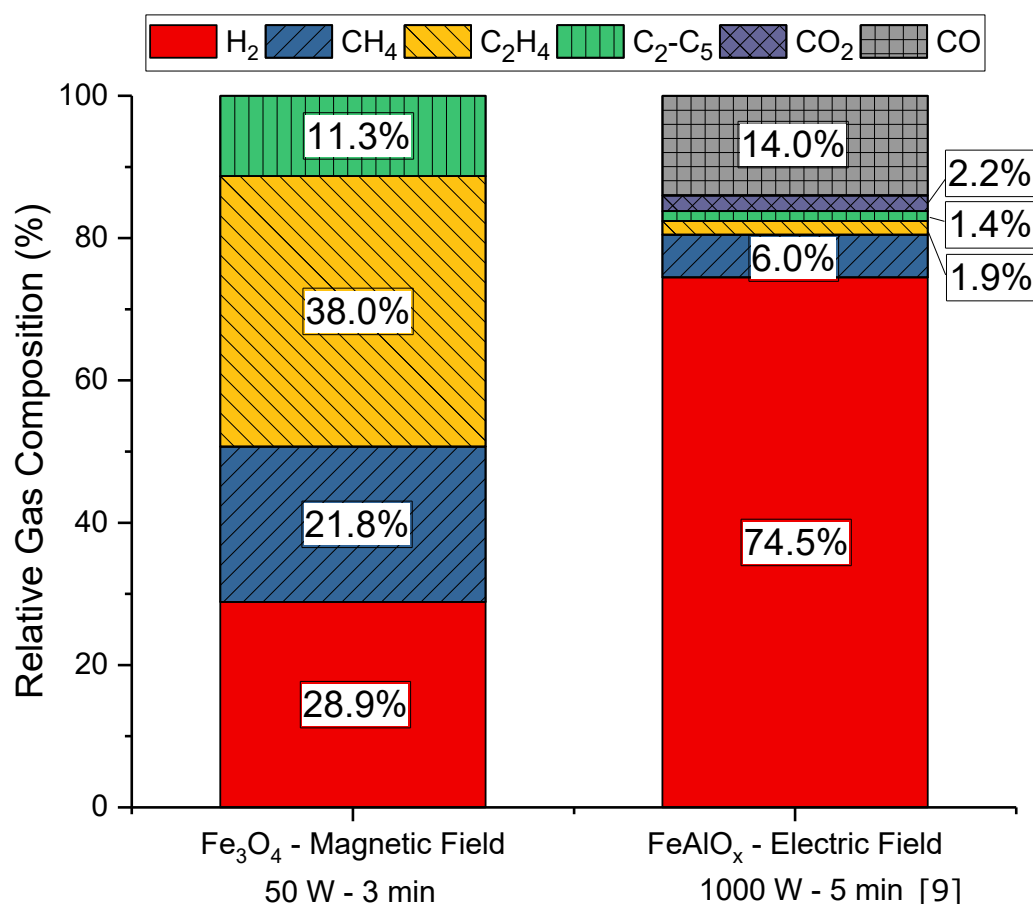


Figure 6.9 – Relative gas composition (%) of HDPE decomposed with microwave catalysis. The left bar shows the result of 0.1:0.1 grams of magnetite and post-consumer HDPE heated in the magnetic field with 50 W maximum power for 3 minutes in N₂. The right bar shows the result of 0.3:0.3 grams of FeAlO_x and post-consumer HDPE heated in the electric field with 1000 W maximum power for 5 minutes in Ar [9].

performed to simply observe what product distribution was achieved. Using the same feedstock, it was believed that a somewhat similar distribution would be observed and the experimental parameters could be explored to perhaps find a similar maximum hydrogen yield. There are however clear differences in gas composition, which is due to several factors.

Although almost 29 % of the produced sample consisted of hydrogen gas it is significantly lower than the expected proportion. There are also much greater concentrations of other hydrocarbon gases including methane (CH_4), ethylene (C_2H_4) and other longer chain hydrocarbons from C_2 - to C_5 ; in this case the three primary components detected were propene (C_3H_6), ethane (C_2H_6) and propane (C_3H_8). The greater presence of these gases and lack of significant hydrogen indicates incomplete degradation of the polyethylene. Enough energy was provided to split the polymer into shorter chains as indicated by the high concentration of ethylene, but not enough energy to split much of the hydrogen atoms from the carbon as was demonstrated by Jie with very little of these intermediate hydrocarbon materials observed. This may be due to the significantly lower power level not providing enough energy for the thermal process to occur or the lack of sufficient field strength at particle interfaces meaning the necessary rapid heating rates are not achieved [9], or a combination of both factors.

Also of note from these results is the absence of both carbon dioxide and carbon monoxide. Carbon monoxide could not be detected by the GC due to equipment errors for the analysis of this sample. Some carbon dioxide was expected and should have been detectable but was not observed. The sample was purged with nitrogen prior to microwave treatment so the amount of air and thus available oxygen would have been low to negligible, however the magnetite sample does contain a small amount of moisture which would have quickly evaporated and provided available water vapour. There may also be small amounts of oxygen present in the

plastic feedstock, which as a post-consumer product could contain contaminants or additives from the manufacturing process.

During the collection of this gas sample no temperature data was able to be recorded but the sample could still be observed through the cavity viewing slit. It was noted during microwave application that only a faint glow could be observed for a brief time. Typically, magnetite samples heated in isolation as shown in Chapter 5 achieved temperatures in excess of 500 °C and this was accompanied by an intense orange glow in the sample. The lack of significant glow and observed product distribution indicates insufficient temperatures were achieved to completely degrade the HDPE and produce high concentrations of hydrogen, instead favouring hydrocarbons such as ethylene and methane. Although it cannot be said with confidence it is suspected maximum temperatures during this testing were in the broad region of 100 to 300 °C, producing a partial decomposition through random polymer scission and limited volume of gas but not the rapid production of hydrogen that was anticipated.

Conclusions drawn from this testing are that the achieved temperature was too low and/or did not reach the maximum temperature quickly enough to achieve the desired reaction. This is perhaps to be expected with the low microwave power level of only 50 W as compared to 1000 W in the other discussed work. Subsequent testing increased input power levels, typically to between 100 and 150 W of target power.

The catalyst employed may also be having a significant effect on produced gas composition. Interestingly in Jie's paper other catalysts were also tested with magnetite among them but using the TM₀₁₀ mode for its maximum electric field [9]. As discussed in the microwave characterisation of magnetite in Chapter 4 and the electric field heating experiments performed in Chapter 5, magnetite can heat well in standard dielectric heating scenarios, however it appears to exhibit a more significant magnetic loss and rapid heating to these significant temperatures. When discussing the yield of their tested catalysts, Jie

showed magnetite to have approximately half the yield of their best catalyst, the iron-aluminium-oxide composite, which suggests it is not as effective at generating large concentrations of hydrogen through this method but was still one of the best-performing out of the 15 microwave catalysts tested in their work. It could be due to chemical structure differences inherent to the materials, although it is suspected that in the electric field magnetite did not heat as rapidly or perhaps to as high temperatures as their primary catalyst. Given magnetite's magnetic heating capabilities it is believed to be able to overcome this through magnetic field heating.

Jie also suggests that a driving mechanism for rapid plastic decomposition is the high temperature gradient and (electric) field enhancement present at catalyst-feedstock particle interfaces. It is suggested that rapid volumetric heating of particles selectively targeting the microwave susceptor materials creates localised hot spots which may not be observed by standard temperature recording devices like pyrometers or IR cameras. This high heating rate could also be being enhanced by high fields due to polarisation mechanisms, creating significant increases in local field strength ($\sim \times 3$) leading to significantly increased heating rates at the particle interfaces. This may still be happening here as there is a non-zero electric field contributing to the heating of samples along with the significant magnetic field. The electric field in this configuration is at most 30 % of the maximum field strength in the TM_{010} mode and so its contribution to increased particle surface heating rates may not be as significant.

The type of polyethylene typically used for supermarket milk bottles is of high molecular mass. It is usually quoted as being in excess of 50,000 g/mol [236] but depends on the degree of polymerisation. A high molecular mass such as this can be difficult to break apart, requiring more energy and therefore a greater microwave power input to degrade. This could have contributed to the remaining hydrocarbon chains in Figure

6.9 as the insufficient energy left many unbroken. Using a different plastic or even a different source of HDPE with a lower molecular weight should make it easier to break apart the chemical bonds and produce hydrogen gas. Increasing applied microwave power and duration of experiments should also increase energy available for polymer scission and promote plastic degradation.

6.4.3 FURTHER HDPE TESTING

An alternative source of HDPE was sourced from Sigma-Aldrich (427772, powder). This powder is a pure material that has not undergone any industrial processing to make packaging for example, and as such will not be expected to contain any additives or sources of contamination. This should significantly reduce the probability of forming unusual compounds during the plastic decomposition process at the expense of the more feasible situation of decomposing real-world plastic waste. This polyethylene is also of significantly lower molecular weight than typical HDPE waste, with an average value of 4000 g/mol. This lower molecular weight should mean the HDPE is easier to crack, requiring less energy to separate into gaseous products. This should lead to greater proportions of hydrogen and less longer chain hydrocarbon intermediate products.

Tests were performed using this powder with increased experiment duration and microwave power input. It was believed that increased power would permit the rapid attainment of higher temperatures required to quickly decompose the plastic and the extended duration would mean the feedstock and any intermediate products formed have more opportunity to reach the required temperatures for decomposition, thus resulting in greater proportions of the desired materials of hydrogen gas and carbon solids.

One test was performed using a PMA target power of 150 W with 0.3 g each of magnetite catalyst and HDPE powder for just over four minutes. Another similar test was performed using an increased power of 180 W, a

greater mass of catalyst at 0.4 g with similar HDPE quantity of 0.3 g. This test was performed for three minutes. Both these tests used the manual mixing method of mixing both powders prior to placing in the sample tube with the aim of distributing catalyst and feedstock throughout. Nitrogen gas purges were performed as usual for five minutes before the gas bag was attached, opened and microwave power activated. The temperature of these tests are shown in Figure 6.10.

Both these tests rapidly achieved their maximum temperature of 545 and 575 °C in 35 and 50 seconds respectively. This was similar to what was observed during testing of magnetite alone in which rapid high temperatures were observed, however these samples quickly lost temperature during the next minute of the experiment, dropping to between 400 and 450 °C. This behaviour is likely a result of the addition of plastic. Rapidly exceeding 500 °C will at least partially transform the

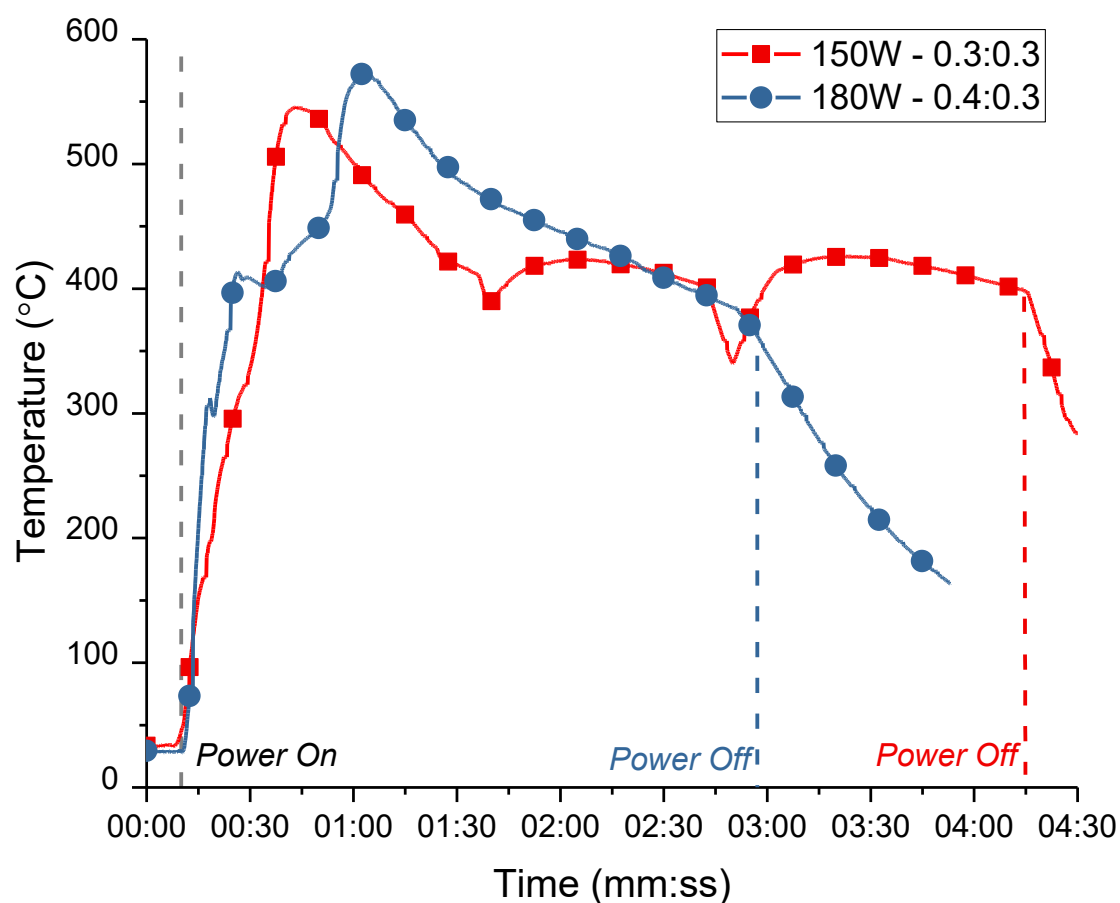


Figure 6.10 – Temperature of two Fe_3O_4 :HDPE samples at 150 W (0.3:0.3 g, 4 min) and 180 W (0.4:0.3 g, 3 min)

plastic and create gaseous, solid and liquid products. The production of these products and their subsequent reaction with the catalyst powder can significantly alter the electromagnetic qualities of the reactor contents. If the materials rapidly became more lossy it could significantly dampen the coupling effectiveness into the cavity and decrease the power transferred as compared to the initial heating behaviour. Microwave data from these experiments show the DLL system of the PMA is continuously moving centre frequency indicating it cannot find a suitable resonant peak (S_{11} dip) within the operating frequency range. When heating solely magnetite the PMA would often adjust by a MHz during the initial rapid heating phase but stabilise around a relatively stable centre frequency for the remainder of the experiment. In these experiments the resonant condition cannot be located by the DLL either due to it being shifted outside the frequency range, or due to being damped by lossy materials in the reactor, or both. The reduction in temperature seen on both traces in Figure 6.10 is believed to be as a result of the formation of compounds such as these mentioned alkanes, potential solid carbon deposits or the alteration of the iron oxide catalyst powder. During these experiments the gas bags were seen to have increased flow rate to them, filling more quickly than with the nitrogen flow alone. This is attributed to gaseous products from the HDPE decomposition.

Post-test observations included small quantities of liquid hydrocarbon condensate on the upper portion of quartz tubing which sat outside of the microwave fields. This was seen to varying degrees on many plastic tests but indicated that liquid hydrocarbons were forming (potentially due to insufficient temperatures being reached for vaporisation) or condensing from their gaseous phase after being produced from the rapid decomposition. When flowing from the region being heated inside the cavity (100s °C) to just outside the cavity (< 30 °C) there is a sharp temperature gradient which would allow some volatile compounds to condense here. As the temperature of this transition region is not closely

monitored and the liquid products were unable to be analysed it was not investigated further. The range of compounds this condensate could contain is large as anything with a boiling point between 30 and 400 °C is possible which includes heptane, octane, decane, dodecane and some even longer chain alkanes like eicosane ($C_{20}H_{42}$) or triacontane ($C_{30}H_{62}$) which may appear as solid waxes at room temperature. An example of a post-test reaction vessel with hydrocarbon condensate on the inner face of the upper section of quartz tube is shown in Figure 6.11.

The microwave data suggests that these experiments had good initial coupling (less than -20 dB S_{11}) which then decreased to a more poorly coupled state after the maximum temperatures were reached until reaching a minimum of close to -3 dB (or 50 % power transfer). This indicates that the contents of the cavity are becoming slowly more lossy



Figure 6.11 – Post-reaction tube showing waxy/liquid deposits on tube surface

and reducing the coupling quality. This process is happening gradually and not all at once suggesting it may be the result of a more prolonged reaction taking place. However, it is important to remember these experiments are taking place *primarily* in the region of intense magnetic field but also in the presence of a significant non-zero electric field component. We have no reason to suspect any hydrocarbon-based products would be magnetically lossy, but some may display small dielectric loss. These compounds are generally considered relatively low loss but even if they display a small increase in dielectric loss, the present electric field component would mean a reduction in coupling strength would be observed. It has also been noted that at elevated temperatures some plastics can become significantly electrically lossy materials [40][247]. This could be happening as the catalyst rapidly heats and then the bulk of the plastic heats with a delay, and as it heats up the combined electromagnetic properties of the sample mixture become much more lossy, reduce coupling strength and effective energy transfer into the cavity.

Very small amounts of solid carbon deposit could also contribute to this effect. During the 150 W test two significant short dips in temperature were observed at $t = 1:35$ and $2:42$. These may be the result of the production of some particularly lossy material which was then either removed by the gas flow, converted into another product, or quickly compensated for by the DLL system in the PMA. It is unclear what the cause of these dips was, but the recovery and subsequent retention of temperature is attributed to the DLL system acquiring a more well coupled frequency.

Post reaction the remaining solids in the tube were seen to be greatly reduced in volume, with the plastic having been at least partially destroyed. This left the sample with many cavities between the remaining catalyst and any products. The composition of the remaining material was generally similar to the initial magnetite powder, consisting mostly of fine

black particles with any apparent moisture removed. During some tests metallic particles could be seen in the remaining solids, either as small pieces of approximately 0.5-1 mm in diameter or occasionally larger clumps measuring 3-5 mm in diameter. It is assumed these particles would be iron metal. This could have happened due to the high temperature and presence of hydrogen gas, which can act as a reducing agent in metal oxides [249][251][252][253].

6.4.3.1 GAS ANALYSIS

Gas analysis is performed on samples collected from these tests using virgin HDPE and shown in Figure 6.12. The most striking component of this data is complete lack of hydrogen. We expect hydrogen to be one of the most prevalent products from the destruction of HDPE in this way but in this case none was detected. This could be due to systematic

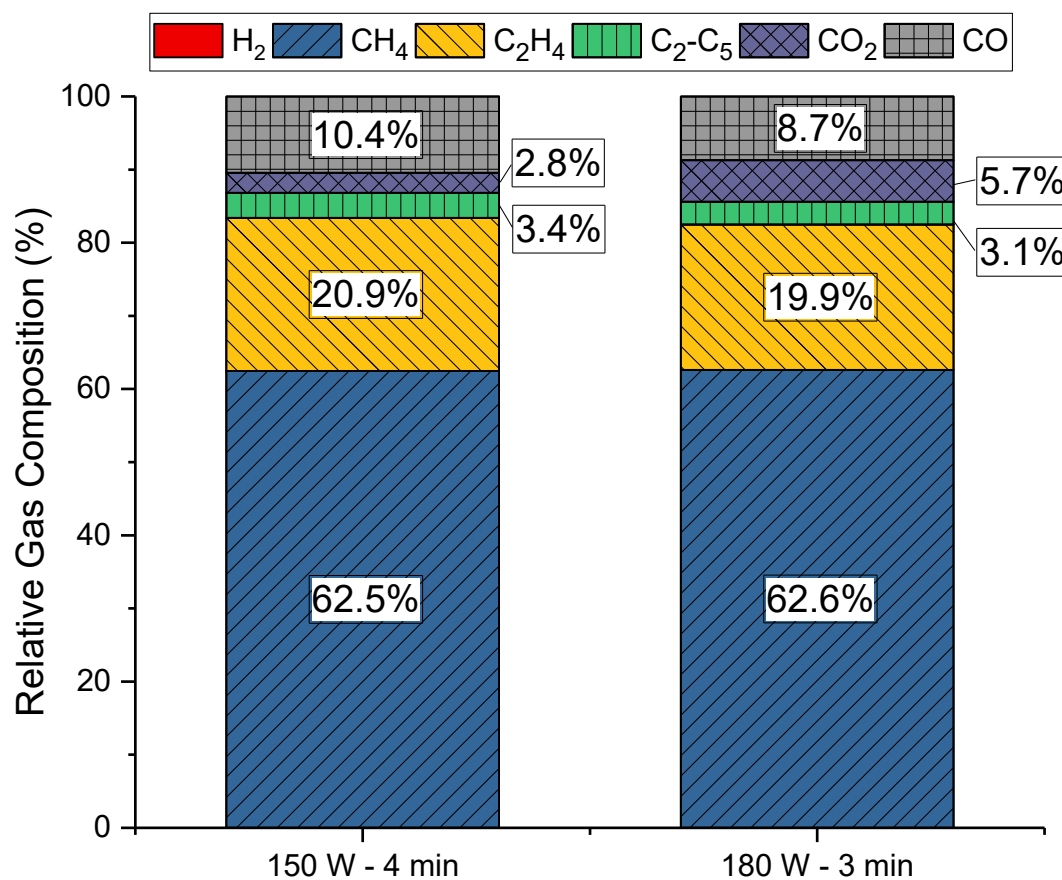


Figure 6.12 – Relative gas composition (%) of samples collected from Fe₃O₄:HDPE samples

limitations of GC detection methods. Although these systems are highly sensitive the detection of hydrogen in TCD is known to be difficult in low concentrations. These samples did not fill the 500 mL gas bags as only small quantities of gas were produced. Along with the flow of nitrogen, it is estimated that the volume of gas in each bag was below 100 mL with approximately half or more of that volume consisting of nitrogen. If the concentration of hydrogen was very low, it may not have been detectable by the GC.

Another possibility for the lack of hydrogen is from the experiment itself. It is possible that these GC readings are accurate and there is simply no hydrogen present in each sample. This could mean no hydrogen was produced and instead the production of methane and ethylene was preferred during the reaction. Carbon-Hydrogen bonds are stronger than Carbon-Carbon bonds (412 kJ/mol vs 348 kJ/mol) [86] which means C-C bonds would be more likely to break first during the reaction, which in HDPE would result in splitting the polymer chain into shorter sections such as ethylene and methane, which is what was observed. Any free hydrogen which was produced could also have reacted with other present materials in the hot atmosphere to form other hydrocarbon products that were detected [249] or provide a reducing atmosphere for the present iron oxide [249][251][252][253]. As small metallic particles were observed it is highly suspected some of the magnetite reduced into iron metal, and that the present hydrogen facilitated this reaction.

Existing work has noted lower reaction temperatures measured (300-400 °C) using significant power levels (300-900 W) and that increased power resulted in increased prevalence of light hydrocarbons preferred over hydrogen production [9][119][120]. It could be that temperatures here were too high for prominent hydrogen production and other gaseous species were primarily produced (CH_4 - and C_2H_4). It has been noted in the previous chapter about the limitations of IR temperature sensing. If the recorded temperatures are in the region of 550 °C at peak levels, there

could be localised regions exceeding this that we are simply not capturing. The primary depolymerisation reaction producing gases, waxes and solid char material could also be followed by secondary reactions occurring from these rapidly produced materials, such as waxes degrading to liquids in the reaction vessel [254].

Other than the absence of hydrogen, the gases that were detected in both cases seem to align with the expected products and relative distributions. The highest concentration is that of methane, followed by ethylene then carbon monoxide and carbon dioxide with the remainder consisting of longer chain hydrocarbon gases like propane. The low concentration of longer chain hydrocarbons is promising compared to the previous attempt at 50 W as shown in Figure 6.9, which although did show hydrogen gas, also showed greater concentrations of C₂-C₅ gases, suggesting insufficient energy. Comparisons between the 150 W – 4 min sample and the 180 W – 3 min sample show little difference in the composition of the gas mixture with very similar proportions of methane, ethylene and C₂-C₅ gases. The most significant difference between the two samples is the greater proportion of carbon monoxide in the lower-power higher-duration sample which shows 10.4 % carbon monoxide and 2.8 % carbon dioxide in contrast to the other sample showing 8.7 % carbon monoxide and 5.7 % carbon dioxide. This may indicate differences in preferred product generation based on temperature (and subsequently microwave power) or duration. Greater carbon dioxide proportion is achieved in the sample which reached a higher temperature and stayed at a high temperature for a greater proportion of the gas collection duration. This could have freed more oxygen from the magnetite via hydrogen reduction meaning carbon dioxide generation is preferred over CO.

Additional testing was undertaken with a virgin PE source and the remaining waste post-consumer PE powder. Shown in Figure 6.13 is a breakdown of the relative composition of gases obtained from three samples of plastic and magnetite mixture heated using microwaves. In

these analyses there is much greater delineation possible between some of the alkanes and alkenes generated owing to the GC method and injection duration used that allows greater material separation. These gas samples were analysed by colleagues in the Cardiff Catalysis Institute.

The two left bars show virgin PE material which was mixed in a catalyst:plastic ratio of 2:1 with magnetite with approximately 0.3 g of magnetite and 0.15 g of PE. These were heated in the TM₀₁₀ magnetic field maximum with 180 W maximum of microwave power for 120 s each with the typical nitrogen purge applied. The rightmost bar shows the result of gas analysis performed on a sample of post-consumer PE using the same conditions and masses as those for the virgin PE listed above. For all three tests the hydrogen content was minimal and is displayed alongside the corresponding bar indicated by the solid red rectangle.

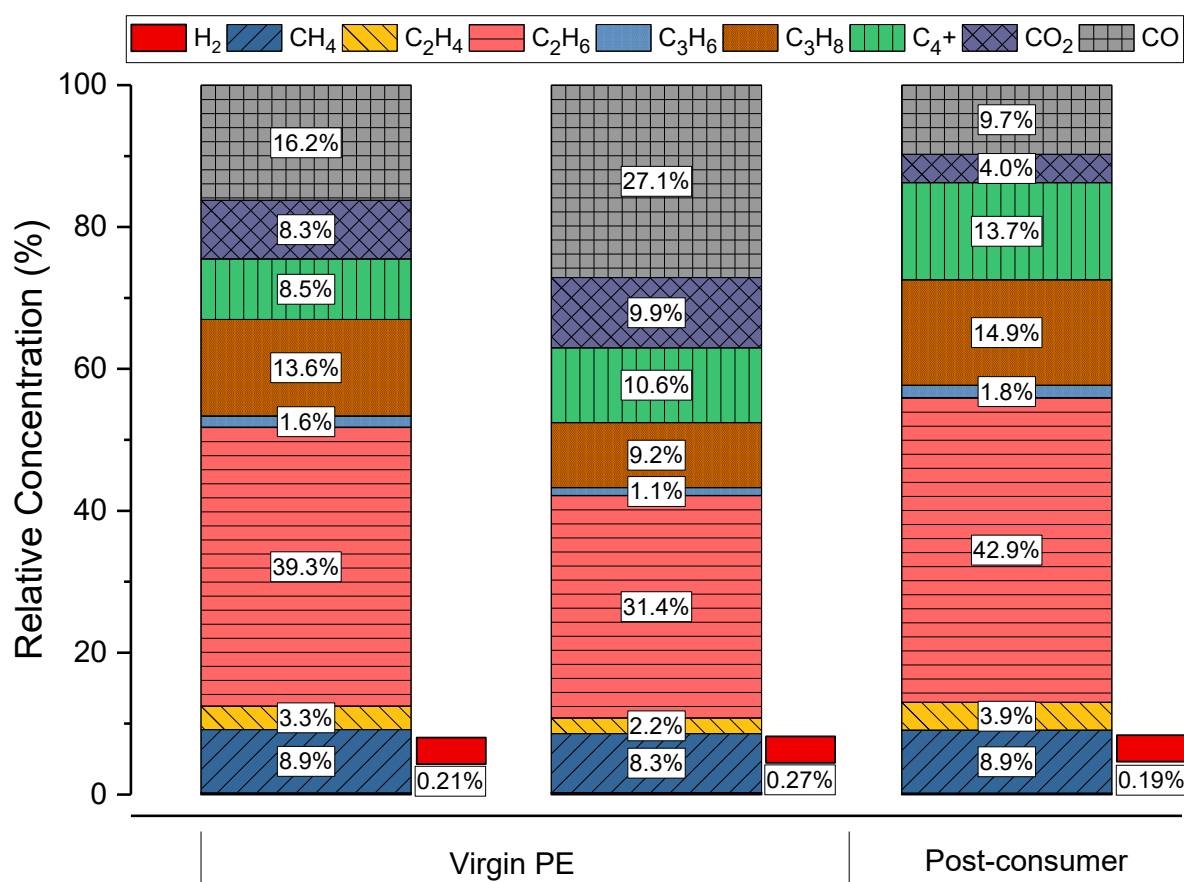


Figure 6.13 – Relative gas composition (%) of samples of virgin PE and post-consumer PE with Fe₃O₄ catalyst. 2:1 catalyst:plastic ratio with 0.15 g plastic and 180 W maximum microwave power.

The virgin PE samples contained very little hydrogen, ethylene, and propene at approximately 0.25 %, 2.7 % and 1.3 % respectively. The greatest concentrations of individual gaseous products that were identified were ethane (39.3 % and 31.4 %), carbon monoxide (16.2 % and 27.1 %) and propane (13.6 % and 9.2 %). There were also significant concentrations of methane (8.9 % and 8.3 %) and carbon dioxide (8.3 % and 9.9 %). The remainder in each case was made up of smaller amounts of longer chain hydrocarbon gases (C₄+) (8.5 % and 10.6 %).

These samples were broadly similar to each other in the identified gases and the relative quantities of each, but different to previous tests with PE. In Figure 6.9 the PE sample produced primarily ethylene, methane and hydrogen with the remaining 11.3 % consisting of C₂-C₅ hydrocarbons. That test was performed with low power, post-consumer PE and for a longer duration. We would expect a greater power and temperature reached quickly would be able to break more of the chemical bonds and produce more short-chain hydrocarbons like methane and release more hydrogen from the plastic. What we see in Figure 6.13 is almost the opposite of that in Figure 6.9 with only 12.41 % and 10.77 % of the gas composition being made up of hydrogen, methane and ethylene in each test. The greatest proportion in each test was instead ethane and significant contributions from carbon monoxide and carbon dioxide were present.

The significant proportion of carbon monoxide and carbon dioxide indicates available oxygen for reaction with available carbon. As the samples were purged with nitrogen prior to heating and experienced continued flow throughout it is believed this oxygen was acquired from within the reaction tube. The virgin PE does not contain any impurities, only carbon and hydrogen atoms so the most likely source of oxygen is from the catalyst, Fe₃O₄. Incredibly low hydrogen contents in both tests indicate either minimal hydrogen was produced or that it was largely used

up in subsequent reactions. It is believed that rapidly generated hydrogen gas in the high temperature environment was able to react with the magnetite and reduce it, forming iron and other iron oxide(s) such as FeO. Free hydrogen gas may have been able to produce water vapour from this reaction which was not detectable by the GC and likely condensed in the tubing or gas bag.

This may also explain the relatively small concentrations of other simple molecules like methane and ethylene. If the carbon and hydrogen bonds were split in these molecules the carbon would be free to react with available oxygen from the magnetite and could explain the prevalence of both carbon monoxide and carbon dioxide in the samples.

The high concentrations of alkanes ethane and propane compared to similar alkenes ethylene and propene indicate their generation was preferred. We would anticipate alkenes would be preferred here as when the polymer chains are broken they would naturally form alkenes (C_nH_{2n}) rather than alkanes (C_nH_{2n+2}). Again, this may be the result of secondary reactions. If sufficient hydrogen gas was generated from the plastic it could react with the produced alkenes to hydrogenate them. In the high temperature environment with a metal or metal oxide catalyst available this is a plausible scenario, and would account for the high proportion of propane and ethane and the low proportions of hydrogen, ethylene and propene.

The gas produced from the post-consumer PE is shown in the right bar in Figure 6.13. This shows a largely similar composition to the analysis of the virgin PE samples. This consists of small amounts of hydrogen, ethylene and propene and a major component of ethane. Key differences when compared to the virgin PE samples are more propane, ethane and C_4+ hydrocarbons, as well as less carbon monoxide and carbon dioxide.

Increased relative concentrations of longer chain hydrocarbons suggest insufficient energy was available for bond cleavage. This sample recorded

much lower temperatures than those in the virgin PE experiments. Lower concentrations of both carbon monoxide and dioxide also suggest lower availability of oxygen (and/or carbon) for reaction. This could indicate less aggressive reduction of the magnetite.

There are still significantly more alkanes than alkenes in this sample with even more ethane than either of the other samples and a significant propane proportion. This could show the hydrogenation reaction is still occurring here, using up produced hydrogen still at around 400 °C in the bulk of the materials mixture compared to the approximately 700 °C achieved with virgin PE samples [249].

Both virgin (low molecular weight) and post-consumer PE samples generated significant proportions of short-chain alkanes, especially ethane. Hydrogen was present in all samples but was a very small proportion, consistently under 0.3 %. It is believed some of the hydrogen was used in additional reactions such as the hydrogenation of alkenes and the reduction of iron oxide to iron metal. These results indicate a more closely controlled approach to microwave heating of PE would be desirable, perhaps with temperature-control functionality built into the microwave applicator equipment and associated software. Higher inert gas flow rates would also likely be beneficial to investigate. Reduction of gas-catalyst contact time could help minimise side reactions like redox, which would also facilitate re-use of catalyst for subsequent testing.

6.4.3.2 XRD ANALYSIS

XRD analysis was performed on the remaining solid residue after microwave exposure. This data is shown in Figure 6.14 for four samples of magnetite mixed with HDPE. The top two traces (green and red, A and B) used 150 W maximum MW power for a duration of 300 s and a mixing ratio of catalysts-to-plastic of 1:1. The top trace (A) used slightly less plastic (and catalyst) at 0.25 g rather than 0.30 g used for the other 150 W test (B). The bottom two traces (blue and black, C and D) used a

maximum MW power of 180 W with mixing ratios of 1.3:1 and 2:1 respectively. Trace C used 0.30 g of plastic and just under 0.40 g of catalyst for 200 s while trace D used half as much plastic at 0.15 g and 0.30 g of catalyst for a 120 s duration. Markers are present for XRD peak patterns of magnetite (Fe_3O_4), wüstite (FeO) (ICDD: 01-077-2355), polyethylene and iron metal (Fe) (ICDD: 01-087-0721) for comparison with the measured data.

Traces A and B show similar results as might be expected with very similar experimental conditions. Trace A shows the presence of undepolymerised PE with a clear peak near the characteristic 21.3° and a smaller peak visible near 23.7° . In trace B both these peaks are slightly smaller, with the latter barely visible. There is still clearly PE detectable in these samples meaning the plastic has not been fully decomposed. The

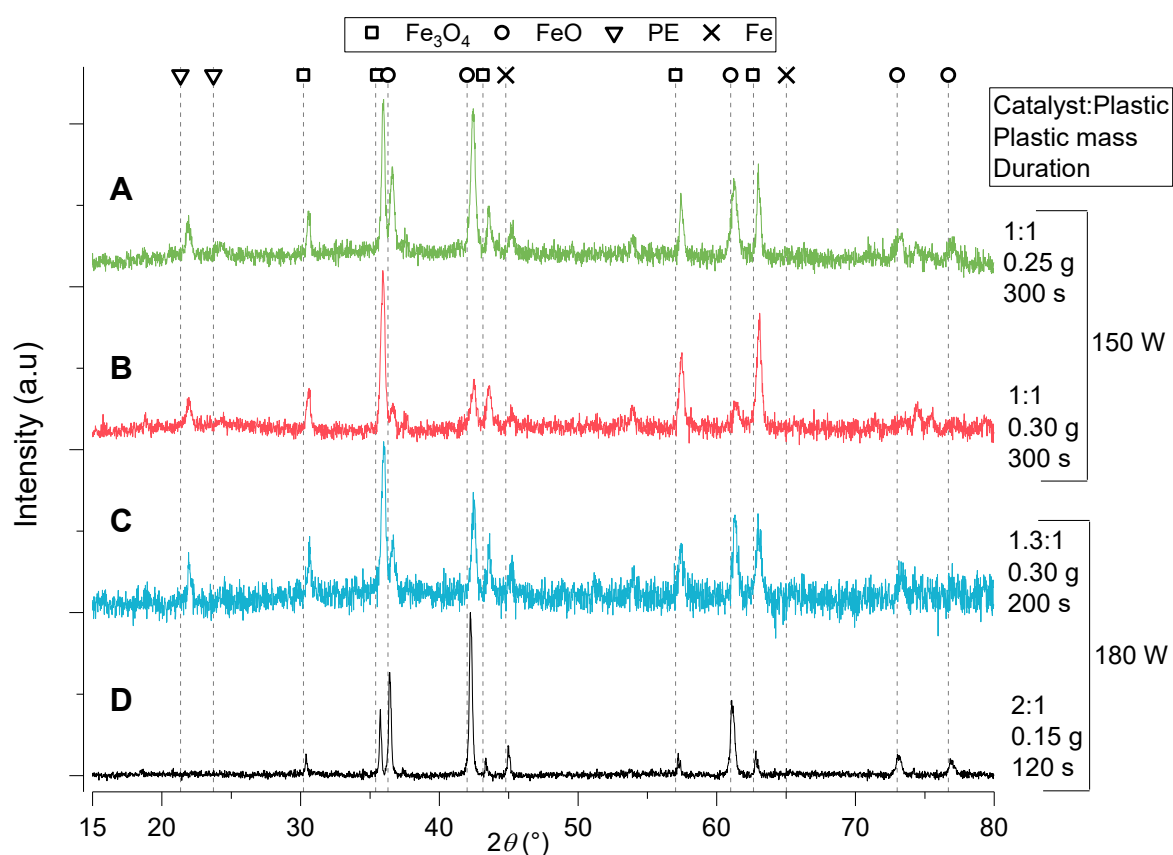


Figure 6.14 – XRD traces from four samples of remaining post-test solids using Fe_3O_4 and HDPE feedstock. Markers indicate characteristic peaks of various materials. Right of the traces shows test-specific information on powder ratios, mass, duration and MW power

next most prominent peaks are visible around 30.5° , 35.9° and 43.5° which indicate the presence of magnetite in the sample. This is what we would expect as the catalyst should remain and be the most pronounced material on the XRD trace. There are also peaks at 36.6° and 42.4° which are indicative of FeO, the 42.4° peak being the strongest, which is what is observed here. The relative strength of the FeO peaks are greater in trace A compared to trace B.

The next visible peak lies at approximately 45.1° . This is indicative of iron metal with this being the most prominent peak in its pattern. These peaks are visible but small compared to the peaks for Fe_3O_4 and FeO indicating although there is iron present there is relatively little of it compared to the oxides. It should be noted however in all four samples shown in Figure 6.14 a metallic chunk of mass 0.16 g was removed from the sample before running XRD scans as it could not be sufficiently broken down to pack the samples into the required sample holder space. This chunk is believed to be iron metal. The presence of Fe and FeO in the XRD traces suggests the magnetite was involved in a reduction reaction. The reducing atmosphere was likely created from hydrogen gas evolved from the plastic, which in the high temperature environment reduced magnetite into both FeO and Fe.

The remaining visible peaks occur at 57.4° and 63.0° indicating Fe_3O_4 , and 61.3° , 73.3° and 77.1° indicating FeO. Peaks visible on trace B around 74.5° are suspected to be a lower intensity peak characteristic of magnetite. The second most intense iron peak would be expected at approximately 65.0° but no peak is visible. A small peak is visible on both traces at 53.6° which is believed to be another low-intensity magnetite peak. Also missing from these traces is the presence of any detectable crystalline carbon products such as CNTs or graphite which would produce a broad peak around 26.0° [9][255][256]. There is also a lack of any indication of iron carbide (Fe_3C) which would produce a number of peaks between 37.0° and 50.0° [9][257][258]. There are no unattributed peaks

that can be distinguished through the signal noise in this region and thus it is not believed any solid crystalline carbon products were formed. Amorphous carbon materials cannot be ruled out through XRD alone.

Traces C and D show the samples which were exposed to a higher maximum microwave power of 180 W. C is very similar to A as it shows the presence of Fe_3O_4 , FeO , PE and Fe, with significant intensity from the magnetite remaining in the sample. This is despite the slightly altered experimental parameters between the tests with C having an increased Catalyst:Plastic ratio, greater masses of both powders, greater maximum MW power and a slightly shorter duration. Trace D is the most interesting as it shows both iron oxides and elemental iron but no PE. The intensity from the FeO peaks is much greater than other traces and the intensity of magnetite peaks are greatly reduced. The primary iron peak near 45° is also fairly small and its secondary peak is not visible. No significant metallic chunk was removed from this sample post-test. This data suggests the plastic may have been fully decomposed and that a significant portion of the magnetite has been reduced to FeO and a small amount of iron metal. This significant reduction also suggests a significant amount of hydrogen gas was produced to facilitate the conversion to FeO . Trace D still does not show any indication of crystalline carbon materials or any iron carbide suggesting none was produced. Again, this does not exclude the possibility of amorphous carbon products being present.

6.4.3.3 SEM ANALYSIS

By performing SEM analysis on a sample of post-reaction solids, we can see any remaining catalyst powders, plastic feedstock or products formed from the process. Shown in Figure 6.15 are two SEM images of a post-reaction sample corresponding to the first column of gas results in Figure 6.12 (150 W – 4 min) and the second trace, B, in the XRD plot in Figure 6.14. This image shows a wide-angle view of approximately 320 μm across (A) and an image of greater detail at only 18.3 μm across (B).

What can be seen from Figure 6.15 A is what appears to be polymer fibres of widths around 10-20 μm and 100s of μm in length mixed with iron oxide powder. There are very few remaining larger chunks of plastic, with one of the few large particles visible in A near the top left corner between the 18.99 μm and 10.30 μm measurement points. This particle has dimensions of 65.0 $\times$ 70.0 μm which would make it consistent with one of the smaller pieces of HDPE when compared with Figure 6.6 but much larger than any of the magnetite particles, which themselves can be seen adhering to it. It is also possible this could be a product of the reaction such as the iron or FeO seen in the XRD trace.

The fibres that can be seen in Figure 6.15 are consistent with the one seen in Figure 6.6 of the strand in the HDPE sample before any microwave reactions were performed. It is very likely then that these fibres are polyethylene, reinforced by the fact it is still detectable in the XRD analysis of the sample. There appears to be more of these fibres post-reaction than in the unreacted HDPE. This could be due to the majority of PE pieces being very large in comparison which could obscure the fibres during SEM and with most of these large particles destroyed what remains is only the PE fibres. It is also possible that there are more fibres post-reaction than before, perhaps being produced by the high-

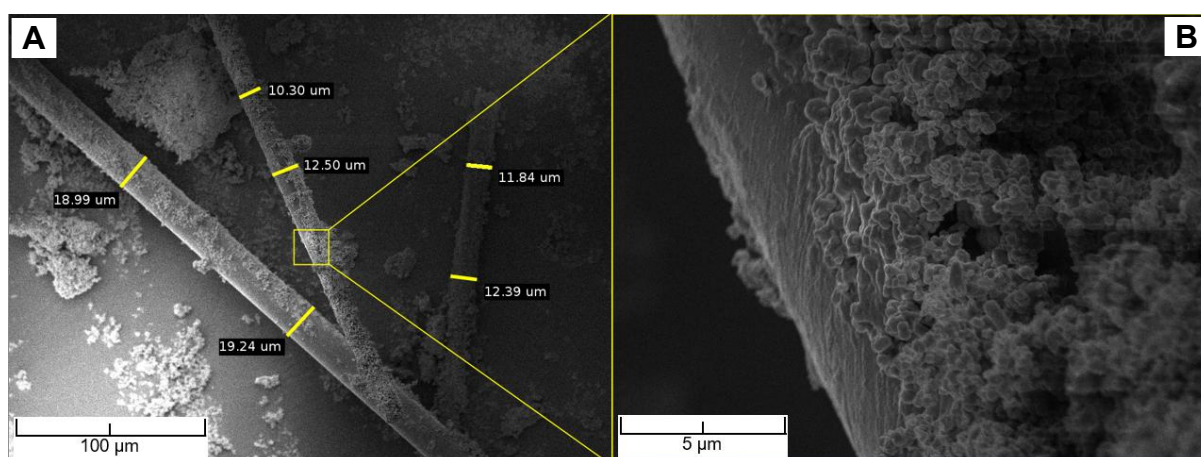


Figure 6.15 – SEM images of post-reaction solids from MW-assisted decomposition of post-consumer HDPE plastic waste. Shown in A is a 320 μm wide field of view showing remaining iron oxide and polymer material and shown in B is an enlarged section at the centre of image A, measuring 18.3 μm across which shows iron oxide powder adhering to one of the polymer strands

temperature reactions forming more of these gel defects. This scenario seems unlikely, with the more likely conclusion being that these fibres are much stronger than the bulk of the HDPE material and are able to resist the high temperatures achieved during microwave application. In TGA studies of HDPE, rapid heating rates resulted in higher temperatures for complete destruction [259]. In this particular experiment the sample's recorded heating rate exceeded 800 °C/min, rising to a maximum of around 540 °C for only a few seconds. It then cooled to below 400 °C over the subsequent 65 seconds. This may mean it began rapidly depolymerising but then stopped before the process was complete, leaving only the most resistant polymer strands.

Figure 6.15 B shows an enlarged 18 µm square region of A, highlighted by the yellow square. This shows the edge of one of the discussed fibres with iron oxide powder residue bonded to it. The powder in this image appears consistent with the magnetite seen in Figure 6.5 A, which is taken at a similar magnification intensity. It consists of many particles much smaller than 1 µm in diameter which agglomerate together to form a larger mass. This powder could be argued to appear less cuboidal in structure with more rounded particles and less apparent straight edges. Visually, it may be difficult to distinguish between Fe₃O₄ and FeO in this context. As any present FeO will have been produced from the present magnetite it would likely have a similar particle size distribution. It also has a cubic crystal structure, and in SEM images can appear very similar to how the magnetite powder was shown in Figure 6.5. Given the intensities seen in the relevant XRD trace in Figure 6.14 it is most likely remaining magnetite powder.

During SEM analysis of all samples of post-reaction post-consumer HDPE and magnetite no carbonaceous material was observed. This is in agreement with the XRD traces in which no peaks indicating carbon materials like CNTs were detected. From these tests it is concluded that the majority of HDPE exposed to microwaves was decomposed, becoming

primarily gas and sometimes liquid products i.e. volatile compounds. No solid products from the plastic decomposition were detected using these analysis methods but the magnetite catalyst was in multiple cases reduced to both FeO and some elemental iron. The presence of maghemite ($\gamma\text{-Fe}_2\text{O}_3$) cannot be confirmed or excluded as it has a very similar appearance and XRD pattern to that of magnetite. It is suspected that the reduction of magnetite was facilitated by the presence of hydrogen-rich gases.

6.4.4 TESTING OTHER PLASTICS

6.4.4.1 POLYETHYLENE TEREPHTHALATE (PET)

Polyethylene terephthalate (PET) is a very common plastic in the packaging of food and drinks. It is commonly used for thermoformed plastic drinks bottles and clamshell type packaging often used for fresh fruit. PET was chosen for additional testing here due to its abundance in typical domestic plastic streams. Among plastics it is actually one of the most well recycled types, being turned into further plastic bottles or often polymer-based fabrics. Even with this successful pathway for PET recycling there is inevitably sources of PET which are not recycled and become unusable waste. This may be after one use, or after being used as recycled material, rPET, one or more times, or from polymer fabrics which are notoriously difficult to recycle.

PET has a different chemical composition to HDPE containing repeating units of carbon, hydrogen and oxygen atoms, including an aromatic benzene ring and hydroxyl groups. This increased complexity compared to PE suggest the expected products from its decomposition will also be more complex, tending away from simpler short-chain hydrocarbons and hydrogen and towards more complex molecules such as benzoic acid, vinyl terephthalate and terephthalic acid [260].

Samples of post-consumer PET were sourced from thermoplastic drinks bottles. Sections of these bottles were cut, cleaned and processed using a

standard domestic blender. Processed plastic was collected and sieved to remove any large particles, achieving a powder consistent in size with the post-consumer HDPE previously tested. This plastic was prepared for microwave exposure similarly to previous experiments with masses of 0.15 g and magnetite masses of 0.30 g. Microwave power levels of 180 W were used throughout PET testing and test durations were typically 120 s. As before, nitrogen purges of the powder samples were performed prior to testing and continued gas flow was ensured during each test with gases collected where possible.

XRD results of two PET tests are shown in Figure 6.16 alongside a trace from a HDPE sample (the same as trace D in Figure 6.14). The XRD trace shows the markers present in Figure 6.14 with the addition of a characteristic peak for the semi-crystalline PET at $2\theta = 25.70^\circ$. The

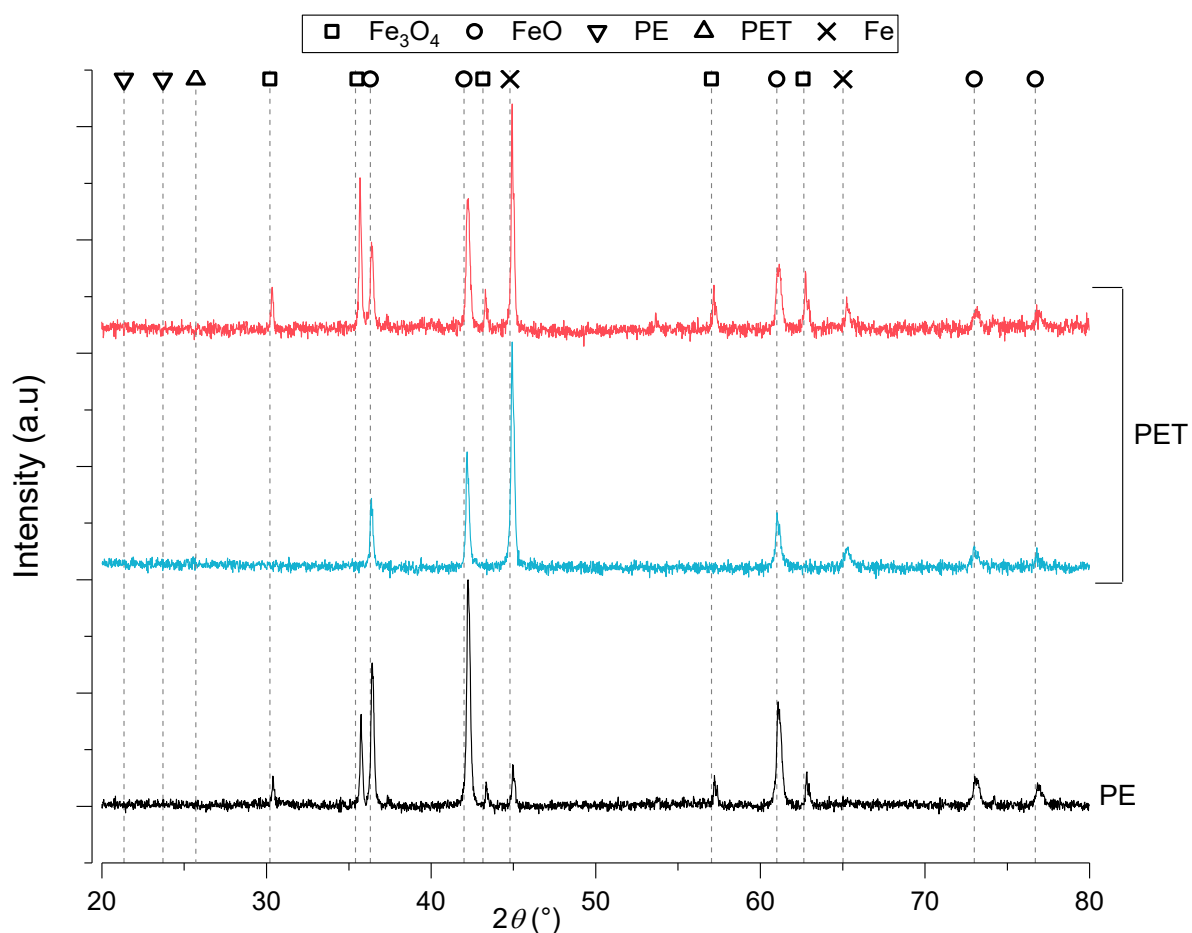


Figure 6.16 – XRD traces from two samples of PET and Fe_3O_4 and one of HDPE and Fe_3O_4 . All samples used 180 W maximum microwave power, a 2:1 catalyst:plastic ratio, 0.15 g mass of plastic for a duration of 2 minutes

topmost trace shows a similar presence of materials to that of the PE trace with no detectable remaining plastic, prominent magnetite signals as well as produced FeO and iron metal. This sample showed much greater intensity at the iron markers.

This indicates a broadly similar solid residue between the two plastic types with incomplete destruction of the plastic, some remaining magnetite catalyst and some of the catalyst which has been reduced to a different iron oxide and iron metal. This trace using a PET feedstock indicates a much greater intensity of iron suggesting a more complete reduction has occurred, which in turn suggests a more conducive atmosphere for the reduction reaction. This could indicate a higher concentration of hydrogen or hydrogen-rich gaseous products from the PET as compared to the PE.

The middle XRD trace also shows high iron and FeO intensities but indicates no remaining PET and interestingly, no remaining magnetite. This was not observed on other XRD traces recorded. This may indicate a much more complete reduction and transformation of the magnetite catalyst into both iron and FeO. It could also be the case that the intensity of FeO and iron in this sample is simply much greater than any remaining magnetite, and its characteristic peaks are relatively much smaller and therefore drowned out in the background noise. Greater relative concentrations of iron atoms in this sample could also be a reason for lack of magnetite detection as it could cause more substantial iron fluorescence, which would increase background noise and decrease the signal-to-noise ratio [261]. When the background is subtracted any magnetite peaks could have also been removed. In both of these samples there is no indication of any other crystalline materials than those mentioned. This means no crystalline carbonaceous materials such as CNTs or iron carbide.

6.4.4.2 POLYPROPYLENE (PP) AND POLYSTYRENE (PS)

Polypropylene (PP) is another commonly used plastic where like PE it is used extensively in the packaging sector with applications including various food and drinks packaging solutions, automotive parts and textiles. Also like PE, PP contains only carbon and hydrogen atoms but with a structure that is slightly more complex than PE, with every other carbon atom replaced by a methyl group (CH_3). This is still a hydrogen-rich source material and common waste material. As of 2015 PP made up a similar proportion of all primary plastic production at about 20 % with 55 million metric tons of primary waste generation [55][56]. It is a versatile material which is used across many application sectors, the biggest of which is again the packaging sector.

Polystyrene (PS) also contains only carbon and hydrogen atoms. It contains much greater proportions of carbon than other discussed plastics with repeating styrene monomers consisting of eight carbon and eight hydrogen atoms (C_8H_8). PS has been noted in other works as preferentially forming liquid products during pyrolysis processes [262][263][264], often producing a styrene-rich oil mixture which can be used for repolymerisation and production of recycled PS. This tendency to liquid products is not particularly compatible with the process and analysis tools available in this work but experimental attempts were made regardless. PS is not as commonly produced as PE and PP but is still made in quantities of a similar order of magnitude (10s of millions of metric tons) and like other plastics is frequently discarded after one use.

It is important to attempt to tackle all plastic types which contribute to plastic waste and environmental harm. The largest sector of primary plastic generation is by far the packaging sector with over 145 Mt in 2015 which has surely increased by today. As well as being the largest generating sector, packaging materials also have the shortest useful lifespans with lifetime product distributions often less than one year. Many

packaging materials can be produced, used and discarded very quickly and combined with low recycling rates this constitutes a serious issue.

Post-consumer PP was sourced from a supermarket yogurt pot and PS was sourced from common laboratory weighing boats. These plastics were cleaned, dried and processed using a household blender in an attempt to form powdered material for microwave catalytic destruction. They were exposed to microwave power in the same way as described for other plastic material, using 180 W maximum microwave power for 2-3 minutes and a 2:1 catalyst:plastic ratio with 0.15 g of plastic material. Nitrogen purges were also performed to remove available oxygen.

Testing involving both these plastic types encountered experimental difficulties which meant very little gaseous or solid samples could be collected for further analysis. These included issues with plastic processing and reaching insufficient temperatures for one-step pyrolysis to occur, meaning more significant proportions of liquid products were formed when compared to experiments using PE.

When processing the PP it tended to form long ribbon-like pieces rather than break into smaller randomly shaped particles. These long strips ranged from around 1 mm to perhaps 30 mm. When these strands were formed it was very difficult for the blender blades to further capture and break them down. This made it difficult to produce enough powder for testing. After multiple attempts to further blend and collect the PP material only around 0.1 g of sieved material could be gathered. Some of the smallest discernible strands were also used in the attempts to decompose the plastic, which were also difficult to effectively pack into the quartz sample tubes.

Processing of PS also presented challenges. The plastic readily broke into flakes measuring approximately 5 mm to 20 mm in diameter but this material also produced very little powdered plastic (<1 mm sized particles). After initially breaking into these mm-size pieces they would

adhere to the sides of the blender vessel or be pushed around by the moving air when the blender was on. After multiple rounds of processing enough powder was obtained for a single test at 0.15 g.

Tests with PP were unsatisfactory, typically struggling to exceed 300 °C as recorded by the thermal camera. Very low volumes of gas were produced with plastic tending to melt or produce liquid and wax products within the sample tubes. This made it difficult to analyse any of the products as there was insufficient gas, the solid remains were mixed or coated by liquids and waxes, which themselves were unable to be analysed.

Testing with PS produced similar results with little gas and any products formed primarily liquid. One of these tests resulted in a broken quartz tube after only approximately 45 seconds of heating. It is believed this tube contained a small amount of metal coating (iron) from a previous test that could not be removed by standard cleaning or scraping methods. A section of this metal near the centre of the cavity then may have produced significant stress during the heating process. Further testing was not pursued due to the potential incompatibility of PS with this process and lack of time to adequately investigate it.

6.4.4.3 GAS ANALYSIS

Gas analysis was performed on samples collected from both a PP and PET sample. Both these samples were types of post-consumer plastic described in section 6.2.2 and the previous sub-sections 6.4.4.1 and 6.4.4.2. Gases collected from the PP sample were believed to be minimal but even the small amounts collected could still be analysed by the GC technique. The PET samples showed more visible reactions with visibly detectable quantities of produced gas and glowing and/or sparking observable within the quartz tube.

Analysis of the relative gas composition of a sample of PP and PET is shown in Figure 6.17 with PP on the left and PET on the right. Similarly to other analysed gas samples of PE, 0.15 g of plastic and 0.3 g of

magnetite is used in each case with 180 W maximum microwave power applied for 120 s.

The polypropylene sample contains similar gas proportions to the PE samples shown in Figure 6.13 with significant quantities of methane, ethane, propane, carbon dioxide, carbon monoxide and C₄+. Small proportions of propene, ethylene and hydrogen are also present. A major difference between PP and PE is the much larger proportion of propane indicated in the PP sample.

Polypropylene has a similar chemical structure to PE so a similar gaseous distribution is reasonable to expect here. Greater relative concentrations of propane could be explained by lack of energy to fully decompose the plastic. The PP sample struggled to achieve temperatures above 300-350 °C and as a result waxy products were observed. This may explain the

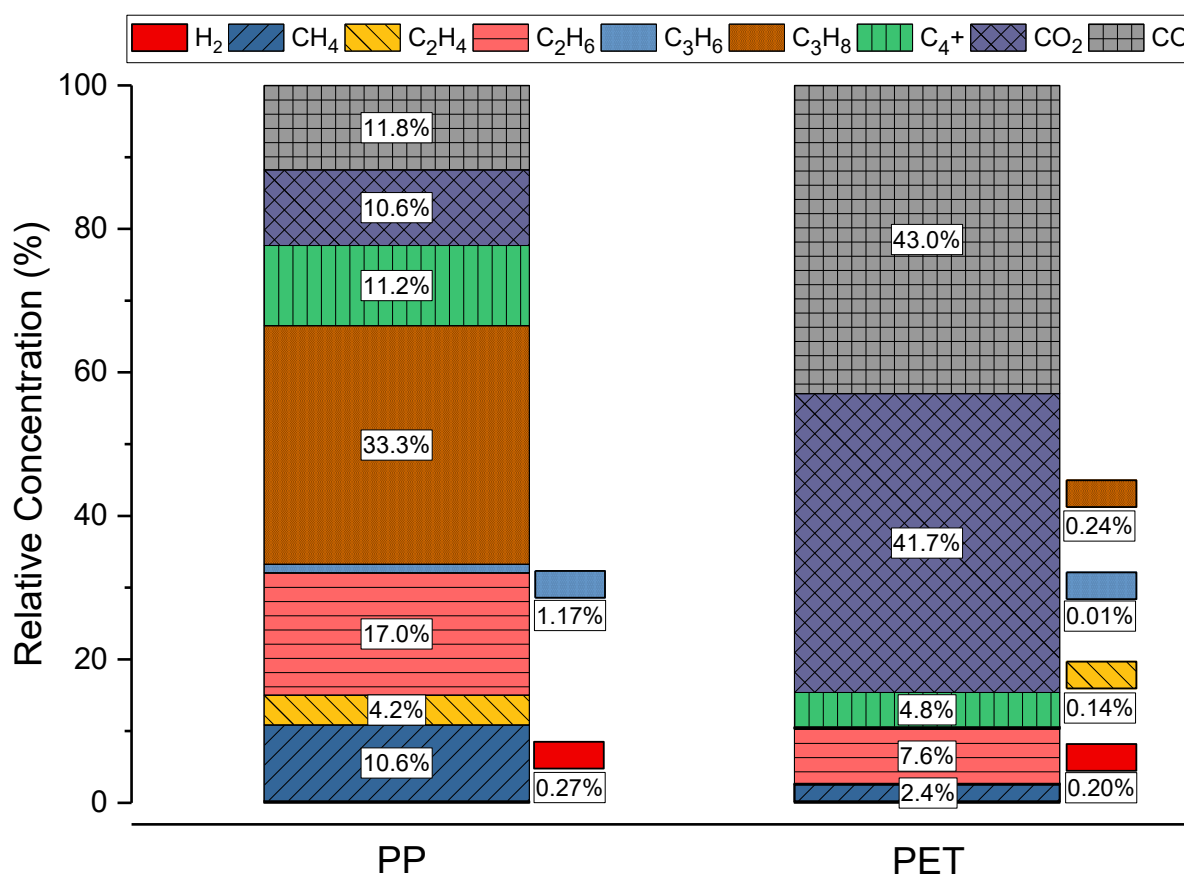


Figure 6.17 – Relative gas composition (%) of PP and PET samples heated by Fe₃O₄ microwave catalyst. 2:1 catalyst:plastic ratio with 0.15 g plastic and 180 W maximum microwave power.

lack of significant proportions of longer chain hydrocarbons which would condense and form these liquid/solid products with limited reaction temperature.

It is believed decomposition began but insufficient temperature was achieved quickly enough for rapid degradation that avoids intermediate products and may have produced more desirable gaseous mixtures.

The PET gas sample produced a significantly different mixture to other analysed plastics. This is due to its more complex chemical structure and tendency to degrade into more complex molecules such as acetaldehyde (CH_3CHO) and benzoic acid.

Observed in the sample analysis are large relative quantities of carbon monoxide and carbon dioxide (> 84 % together) with smaller amounts of ethane and methane. The C_4+ content is listed as 4.8 % but it should be noted that this consists of a number of unknown compounds that may not be simple hydrocarbons. Also present are minimal quantities of hydrogen, ethylene and propane, with trace amounts of propene.

The generation of primarily carbon monoxide and carbon dioxide from PET degradation is in agreement with the literature [265][266]. It was not expected this degradation would produce a desirable gaseous mixture but was performed to observe the effect of rapid microwave-induced degradation. PET is commonly stated as rapidly thermally degrading from temperatures of 375 to 450 °C [246][267], leaving around 20 % of initial mass. Temperatures achieved with PET samples typically exceeded the upper bound of this temperature degradation quickly (< 20 s) and reached upwards of 650 °C.

It was suspected this rapid degradation may result in reasonable quantities of hydrogen or another useful hydrocarbon gas, that could make the degradation of PET an attractive prospect for useful gas generation. Although PET powder did readily degrade under microwave catalysis and produce measurable gaseous products, the high percentages

of toxic gases carbon monoxide and carbon dioxide suggest it is not a practical polymer for further gaseous extraction testing using this method.

6.5 CONCLUSIONS

Initial testing of microwave decomposition of post-consumer HDPE yielded hydrogen, methane and ethylene, with additional smaller proportions of C_2 - C_5 hydrocarbon gases. Carbon monoxide was not able to be detected in this test due to equipment limitations. Carbon dioxide should have been detectable, but none was observed. This test was performed at low power (50 W) with catalyst and feedstock masses of 0.1 g. This demonstrated the potential for hydrogen generation from waste HDPE using microwave magnetic field heating and a magnetite catalyst and highlighted the necessity for further testing to explore the potential parameter space.

It was believed a greater relative concentration of hydrogen could be produced with increased temperatures and more rapid realisation of maximum temperatures. Increased mass of catalyst and feedstock plastic was used along with increased microwave power input and testing duration. This produced recorded temperatures above the requirement for complete PE decomposition. Combined with the observed temperature lag from measurement of the external surface of the quartz tube, this was achieved in under 30 s but these maximum temperatures were not maintained for longer than 40 s. The subsequent drop in temperature after maximum temperatures were reached is attributed to the formation of products from the partial plastic decomposition.

The composition of gases analysed from this subsequent testing revealed large concentrations of methane, ethylene and carbon monoxide. There was no hydrogen detected as part of these analyses. This gas data initially suggested that insufficient energy was provided to produce significant quantities of hydrogen. It is perhaps more likely some

hydrogen was produced given the temperature of the reactions and relative decomposition of the PE and that it was used in additional reactions. This could involve the formation of methane from hydrogenation of carbon monoxide or carbon dioxide or the reduction of the iron oxide catalyst powder into iron and other oxide forms. A potential method to combat the expenditure of any produced hydrogen is to increase inert gas flow rates. This would force produced gases to flow more quickly to the collection vessel and allow less time in the high temperature environment to facilitate other reactions.

Additional testing was performed with reduced plastic feedstock masses while maintaining masses of approximately 0.3 g of magnetite. With similar microwave settings as previous experiments a more varied gas distribution was achieved. These tests produced much greater relative concentrations of alkanes ethane and propane, and carbon monoxide. Although hydrogen could be detected in all these tests it was only in very low concentrations, again suggesting it was not preferentially produced or had been used up in subsequent reactions. Given the significant quantities of alkanes and the relatively low concentrations of alkenes it is believed hydrogenation of the produced alkene gases proceeded, using up some of the produced hydrogen gas.

These tests were performed with the intention of producing large quantities of hydrogen gas from plastic waste. In this regard they were unsuccessful, but did produce significant quantities of other useful gases like methane which could still provide value beyond the waste plastic's expected lifetime. Although the targeted hydrogen generation was not realised in these tests it is believed with more testing and closer control of reactant temperatures it could be achieved. The PE was able to be degraded rapidly through microwave magnetic heating using power levels under 180 W in all tests. The power absorbed by the samples is less than this value due to reflection and other losses e.g. in the heating of the cavity walls.

It may be the case that in fact too much power was used and scaling back the power input would be beneficial for further research. The test performed at the lowest microwave power input yielded the greatest relative concentration of hydrogen gas. During testing it was believed that undesirable gas compositions were due to lack of energy to quickly and completely break hydrogen bonds. Upon reflection, the high temperatures achieved in the presence of magnetite could have provided suitable conditions for redox and hydrogenation reactions to occur and exceeded the requirements for rapid production of hydrogen from plastics.

Analysis of solid materials showed that significant quantities of magnetite were reduced to both iron metal and another iron oxide (FeO, wüstite) in a number of reactions. Some reactions also confirmed that the PE had not been completely decomposed, with a small characteristic peak still visible. In no XRD tests could crystalline carbonaceous materials be detected. This includes carbon nanotubes, graphite or iron carbide compounds. Given the lack of hydrogen present in analysed gas samples it is possible no solid carbon products were produced, but with the suspected reduction of magnetite to iron and FeO it is believed some produced hydrogen was used to reduce to these forms. In this scenario some solid carbon residue is expected but not observed in the XRD trace. This could mean amorphous carbon products were the only ones formed. Observed on the quartz tube inner walls was often smooth dark residue. This may be the only solid carbon type produced and could be a material like carbon black. Reactive amorphous carbon may have also facilitated additional reactions such as the formation of methane from reaction with hydrogen gas (methanation), or formation of carbon dioxide or carbon monoxide through reaction with high temperature water vapour (secondary water gas-shift reaction, water-gas shift reaction). This may explain large quantities of methane and carbon monoxide observed in some reactions.

Comparisons of magnetite and PE pre and post reaction were observed using SEM. The general structure of particles was seen to be cubic for

magnetite, with average individual particle diameters of approximately 0.20 μm and significant agglomerations of particles forming larger clusters. Post-consumer PE was seen to be much larger at 285.0 μm average particle diameter, approximately 1400x larger. Post-reaction observations showed few remaining large polymer chunks and remaining magnetite (or perhaps maghemite) appearing structurally unchanged. No other products could be conclusively identified.

Of particular interest was a collection of small strand-like structures measuring approximately 10-20 μm in width and a few hundred micrometres in length. The identification of these fibres is uncertain. They could be examples of remaining polymer material. Similar strands were observed in the pre-reaction SEM imaging of HDPE powder which could be examples of toughened PE formed from cross-linking or manufacturing gel defects. The temperatures reached for the sample containing these fibres was briefly over 540 $^{\circ}\text{C}$, with consistent temperature over 400 $^{\circ}\text{C}$ for four minutes. This should have ensured all PE material was destroyed, but if these fibres represent a more thermally resistant PE formation it is possible they could still be present.

Another possibility is that these formations are formed from solid carbon material i.e. carbon nanotubes. This seems less likely as CNTs could not be detected by XRD on any samples. These fibres are also uncharacteristically large for typical CNTs, even multi-walled varieties. They could be a presentation of amorphous carbon deposits, perhaps combining with polymer strands, but this is not suspected.

Three other plastic types were tested in PP, PS and PET. The gases produced from PP and PET tests could be analysed. These showed a broadly similar product distribution for PP as for the latter PE tests with the largest concentrations of propane, ethane, methane, CO and CO₂. As PP is chemically similar to PE, consisting of only carbon and hydrogen atoms and having a similar thermal decomposition temperature, the similar distribution is reasonable. With a similar lack of hydrogen similar

conclusions are drawn for the decomposition of PP as for PE, in which free hydrogen was used in additional reactions hydrogenating alkenes and reducing the iron oxide catalyst.

Decomposition of PET produced mainly carbon monoxide and carbon dioxide, in agreement with literature. Greater availability of oxygen and carbon in the more chemically complex structure of PET tends toward production of these products. These are generally considered undesirable products as notorious greenhouse gases but rapid production of these gases from waste PET that otherwise may not be recycled could still be beneficial. Both carbon monoxide and carbon dioxide are used in a variety of industrial applications, such as syngas production, metal reduction and the food and drink industry.

The reactions involving PET also highly preferred production of iron metal. This is unlikely to be due to hydrogen production but rather the high concentrations of carbon monoxide. With CO being used as reducing agent this could have enabled the significant reduction of magnetite to iron. It is possible CO and H₂ produced in other reactions (such as the PE ones) could have also helped to reduced magnetite to wüstite and iron.

Experimental testing has shown low power microwave magnetic field heating with magnetite to be capable of rapidly degrading a number of common plastics. This produced a mixture of gaseous products, which were primarily alkanes; methane, propane and ethane. Some alkenes were also produced with most significant being ethylene. Minimal amounts of hydrogen were observed. For PE testing it is hypothesised that some of the produced hydrogen was used in the reduction of the iron oxide catalyst and hydrogenation of alkanes to produce greater alkane quantities. Significant quantities of CO and CO₂ were also often observed, with large amounts produced from PET decomposition.

Chapter 7

7 CONCLUSIONS AND FUTURE WORK

7.1 MICROWAVE CAVITY PERTURBATION

Microwave cavity perturbation is a useful technique capable of providing high-precision electromagnetic material descriptions. It is used in a variety of works which help develop scientific understanding and inform research decisions based on a material's complex permeability and/or permittivity. Detail provided in Chapter 3 and 4 provides information necessary to tackle perturbation measurements with recognition of limitations encountered such as the physical constraints of designed cavities and interactions with high temperatures.

The in situ measurements of permeability and permittivity made at elevated temperature effectively produced comprehensive descriptions of both magnetite and haematite powders. The real part of complex permeability and permittivity was calculated across the whole temperature range with a corrective method applied accounting for thermal expansion of the cavity. The corrective method was not employed for measurements of Q and subsequently the imaginary part of the complex permeability and permittivity as it was deemed too complex and time-consuming. This would certainly be an interesting investigation that could be performed in further work.

This method demonstrated the capability of the chosen magnetite powder to absorb energy from microwave magnetic fields. When approaching 200 °C the magnetite was observed to noticeably change both permittivity and permeability into what was presumed to be maghemite. The maghemite showed similar levels of magnetic loss with increased dielectric loss values when cooled to room temperature. From this,

maghemite has been identified as another potentially useful microwave magnetic catalyst material. This method could be used as a preliminary test for a great number of materials for their complex permeability, allowing suitable justified choices to be made for further testing as microwave-magnetic catalysts.

7.2 MONO-MODE MICROWAVE HEATING

Performing mono-mode microwave cavity heating on magnetite powders typically less than 0.5 g in mass achieved exceptional temperatures of over 500 °C using less than 100 W of microwave power, and often less than 50 W. Magnetite was shown to readily heat to these temperatures when using the TM_{010} resonant mode's area of maximum magnetic field intensity. Maximum temperatures were achieved quickly, often in under 30 seconds from microwave initiation. This reinforced conclusions made from the cavity perturbation data solidifying magnetite as an effective magnetic microwave absorber, and potential rapid magnetic heating powder that could be suitable as a catalyst.

Temperature measurement of microwave-heated samples was discovered to more complicated than initially thought. IR pyrometry techniques were explored including material emissivity, spectral radiance, focal distance and measurement spot size. It was concluded that IR measurements were useful when applied with awareness of the limitations such as ensuring minimal spot size and the transmissivity, or lack thereof, of utilised quartz vessels. A calibration procedure was performed for the temperature-dependent emissivity of quartz tubes.

The construction and use of PMAs was convenient for use with a small-scale system with cavities a few centimetres in diameter. These systems can be managed with basic controls of power input and frequency as well as automatic frequency adjustment to maximise power transfer. Performing cross disciplinary work in areas of chemistry and materials science highlighted the desirability of higher-level control over the

system. Chemical reactions are often performed at specific temperatures which are strictly controlled but during microwave heating performed here temperature control was not a direct aim. When materials heat their electromagnetic properties change and this directly impacts the microwave cavity coupling, which in turn affects power transfer and therefore material temperature. This feedback loop can present difficulties when using microwaves for chemical reactions as the temperature can be difficult to precisely control.

7.3 MICROWAVE PLASTIC DECOMPOSITION

The heating potential of magnetite was employed in the application of rapid decomposition of common plastic materials. The primary focus was on high-density polyethylene which is an extensively used plastic around the world, containing only hydrogen and carbon in its pure atomic structure. Waste plastics can be considered a high concentration source of hydrogen, which when separated from the carbon atoms can be used as a clean fuel source with excellent energy density. Increased renewable and clean energy generation is an incredibly important goal necessary for society to thrive in the future. Destruction of plastic waste and simultaneous extraction of valuable materials was therefore deemed a worthwhile pursuit and formed the core aim of this research.

Rapid deconstruction of virgin PE and post-consumer PE, PP, PS and PET was performed. Collection of products was performed with a basic system which allowed gas flow to a single output collection bag. Upon reflection, this system would have benefitted from increased complexity. Using additional components like a condenser or cold trap to separate volatile compounds would have enabled a complete analysis of separate gaseous, liquid and solid products. Purchase of specially designed quartz tubing for gas injection and extraction would have also aided in this. Other solutions should have also been considered for gas collection, for example, using the displacement of water in an upturned graduated cylinder to measure the volume of produced gases.

When analysed by GC the gaseous mixtures collected did not align with expectations, showing much less hydrogen and more ethylene and methane, generally. This suggests the decomposition reactions either lacked energy or did not occur quick enough, giving produced gases a chance to react with each other and form intermediate products, i.e. longer hydrocarbon chains. The hydrogen may have also been used in additional reactions such as the reduction of the iron oxide catalyst to iron and wüstite, which were frequently observed on XRD traces. It may have also been used up in the hydrogenation of alkenes to produce relatively large quantities of alkane gases like propane. More testing and analysis of plastic decomposition using magnetic microwave field is certainly warranted.

Analysis of solid products from these reactions were analysed using two techniques, XRD and SEM. These were useful in determining the present materials including remaining magnetite, FeO, iron metal and plastic. By seeing what had been produced or what was no longer present the effectiveness of each reaction could be explored. For example, when high proportions of iron were detected by XRD it was hypothesised that the magnetite had been exposed to an atmosphere with high concentrations of hydrogen, promoting reduction. To expand the analysis of solids other techniques could have been utilised such as X-ray photoelectron spectroscopy (XPS) or the additional feature of the SEM microscope, energy dispersive X-ray spectroscopy (EDX). More analysis tools, especially on the post-reaction solids, could provide a more comprehensive picture of what was happening in each reaction and the differences between them.

7.4 FUTURE WORK

This section details work that was planned to be undertaken as part of this thesis but could not be done due to lack of time or resources, as well as ideas for other related projects conceived while performing this research. Some of these ideas are small projects that may be completed

quickly with the right equipment, and some may require greater effort to realise, potentially forming a whole research project from one concept alone.

7.4.1 MICROWAVE CAVITY PERTURBATION

Here cavity perturbation was performed up to a maximum temperature just below 200 °C. This was a limitation of the available high-temperature RF cables. With cables rated to a higher temperature the measurements could be performed over a greater range. For magnetite specifically, this could allow in situ measurements of the complete transition to maghemite which would be valuable information. If this was performed considerations would also have to be made of the cavities and their coupling structures. Higher temperatures could lead to the current constructions becoming damaged or unusable. For example, any solder creating electrical connections could melt making coupling impossible.

Other cavities could be designed either with different shapes or simply different dimensions to access different frequencies. This would allow the study of materials over a greater frequency range, with a higher density of data points throughout allowing the investigation of a material's frequency dependence. Magnetite showed some frequency dependent characteristics over a broad frequency range, which could be interesting to further explore and more conclusively show.

An in-depth study of cavity Q and temperature would be a significant undertaking that could incorporate simulation, design and experimentation. This study would focus largely on microwave theory and resonant structures. There has been shown to be a complex non-linear relationship between Q and temperature for some modes that if more fully understood could lead to innovations in high temperature material measurement techniques. This could aim for increased controllability or derivation of an applicable temperature correction method, like that which was used for the cavity frequency in this thesis.

7.4.2 MONO-MODE MICROWAVE HEATING

An obvious path for further exploration of microwave heating is increased power. When using the latter PMA based on the Mini-Circuits architecture the maximum power of the system was not reached. This was due to the attainment of desired temperatures with the magnetite powder at masses below 0.5 g, where more power was not deemed necessary. This extra power capability could be explored simply by increasing sample masses to see what the limitations of the system are, both in temperature and coupling loop design and materials. Further to this, additional coupling loops could be constructed to test their effectiveness with a known material. This could include changing wire material thickness, and the effective area of the loop.

Temperature control was identified as a limitation of the performed experiments. This could be addressed with the creation of a temperature feedback monitoring and control system. The pyrometers and IR camera used have excellent additional functionality that could be used to feed temperature information back to the controlling software and allow to adjust the incident power levels to control temperature of the sample. A successful system would broaden the applicability of the PMA and microwave heating application in general to other chemical reactions, material synthesis or processing which requires temperature control.

Microwave heating could also be explored through other resonant modes, perhaps utilising another mode which has intense magnetic field at its centre like TM_{110} or TE_{011} . This could be done at different frequencies using cavities with different dimensions to explore any frequency-related phenomena. Multimode systems are often employed for easy application of microwaves to a related field as microwave ovens are relatively inexpensive and easy to operate. The effects of multimode heating on magnetite may be interesting as it displayed both a significant magnetic and electric loss from perturbation measurements. A combined heating effect from both fields could result in more effective heating behaviour.

7.4.3 MICROWAVE PLASTIC DECOMPOSITION

There are many parameters of the performed plastic decomposition experiments that could be further investigated, and areas that were not discussed which would benefit from assessment. A deeper analysis of how different plastic types respond to the microwave catalysis procedure would be useful to perform. Along with further testing of HDPE and PP, other plastics should be experimented on such as polyvinyl chloride (PVC), LDPE, polymethyl methacrylate (PMMA), acrylonitrile butadiene styrene (ABS), polylactic acid (PLA), polyamide (PA) (Nylon) and polyester (derived from PET). These less common plastics can be used in areas like construction, 3D printing and textile manufacture. Polymer textiles in particular are often discarded far too readily with growing “fast fashion” trends and their recycling rates are incredibly low. Development of a method to extract value from plastics like these would be incredibly beneficial.

The mixing ratio of catalyst and plastic material should be analysed. By varying this ratio it may answer questions about the minimum catalyst required to decompose a mass of plastic, how the ratio affects the product distribution and if there is an optimal ratio for the generation of the greatest concentrations of desired products, like hydrogen gas. Mixing ratios were generally between 1:1 and 2:1 of catalyst-to-plastic but this should certainly be explored with minimal catalyst too. There may also be significantly different ideal ratios with different plastic types.

Although it was expected that small quantities of CNTs would be produced from the test performed in this work none were detected. CNTs and other crystalline carbonaceous materials are very valuable with great utility in various applications. Various process conditions like microwave power, residence time, inert gas flow rate and sample position and structure should be explored in order to create crystalline carbon materials. To aid this and the increased separation of solid, liquid and gaseous products specialist quartz tubing should be used which facilitates this. This would

certainly be necessary when testing with more complex polymers like PVC, ABS or PMMA. Capability to separate and analyse liquid products would be beneficial.

Other catalysts could also be tested. While this work focused on magnetite as a relatively inexpensive and abundant material which can heat well in response to a microwave magnetic field, there are a number of other potential catalyst materials that could be utilised. This could include other ferrous materials like maghemite or iron-based nano powders but also other magnetically-stimulated materials like alloys of cobalt, nickel, zinc or manganese. A complete study of an array of potential magnetic catalysts could be performed using MCP measurements and other magnetic analysis measures like susceptibility.

An interesting further project based upon this work is the development of plastic decomposition towards a more realistic industrial process. Currently this work uses small masses of sample for each test, often below half a gram of combined catalyst and plastic mixture. As an industrial process this is obviously not feasible. The scaling up of this process may be challenging as microwave cavities operating around 2.45 GHz are relatively small, and their ability to hold a significant quantity of lossy material is limited as too much will reduce the coupling quality severely. This may be overcome through the use of multiple cavities operating in parallel. The Mini-Circuits-based PMA does have built-in functionality for combining the outputs of multiple amplifiers together, but this could also be expanded to run multiple amplifiers in parallel from one control system. This obstacle could be considerable to the meaningful application of this process.

7.5 FINAL THOUGHTS

I sincerely hope the work contained in this thesis has expanded the knowledge of the scientific community, developing knowledge of microwave cavity perturbation, mono-mode heating and plastic decomposition. It has been incredibly interesting to perform the work shown here and I hope it can stimulate other engineers, researchers and scientists to explore microwaves and their cross-disciplinary applicability. I greatly appreciate the opportunity afforded to me to contribute to the collective understanding of society and the support provided by UKRI Engineering and Physical Sciences Research Council and Cardiff University.

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APPENDIX 1

Presented here are integral relations associated with Bessel functions used in the derivations and simplifications of cylindrical cavity field equations, frequency and Q-factor [128].

$$\int_0^x Z_m^2(kx)x \, dx = \frac{x^2}{2} \left[Z_m'^2(kx) + \left(1 - \frac{n^2}{k^2 x^2} \right) Z_n^2(kx) \right] \quad \text{A}$$

$$\int_0^x Z_n(kx)Z_n(lx)x \, dx = \frac{x}{k^2 - l^2} [kZ_n(lx)Z_{n+1}(kx) + lZ_n(kx)Z_{n+1}(lx)] \quad \text{B}$$

$$\int_0^{u_{mn}} \left[J_n'^2(x) + \frac{n^2}{x^2} J_n^2(x) \right] x \, dx = \frac{u_{mn}^2}{2} J_n'^2(u_{mn}) \quad \text{C}$$

$$\int_0^{u'_{mn}} \left[J_n'^2(x) + \frac{n^2}{x^2} J_n^2(x) \right] x \, dx = \frac{u'_{mn}{}^2}{2} \left(1 - \frac{n^2}{u'_{mn}{}^2} \right) J_n^2(u'_{mn}) \quad \text{D}$$