

# Bio-Oil from Microwave Assisted Pyrolysis of Sewage Biosolid #

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## 1 Introduction

In the five-year period 2008-2013, Australian biosolids production, derived from sewage sludge, increased from approximately 300,000 dry tonnes [1] to 360,000 dry tonnes [2]. During this time, the proportion of biosolids disposed of with beneficial use increased from 59% to 69%; however, most of this increase was due to the diversion of biosolids from landfill to land application; however, issues of land availability and objections of odour and emission of gases such as ammonia, nitrous oxide and methane limits large scale disposal on land [3]. Of the 102,000 tonnes of dry biosolids that were not beneficially used in 2013, 62% was produced by the state of Victoria, with the majority being placed into stockpiles. In Victoria, three million cubic metres of biosolids, which is equal to 10 years of current national production, are stockpiled [4]. Stockpiling is adopted to alleviate the risk of pathogenic and heavy metal contamination from the biosolids. Few conventional methods of biosolids utilisation can overcome these concerns.

Pyrolysis of organic materials, including biosolids, yields: syngas, bio-oil, and biochar [5-7]. Syngas is a combustible fuel; bio-oil has several potential applications, depending on the chemical composition of the oil; and biochar has recently been used as a soil ameliorant in agricultural systems. Microwave energy offers a better alternative to conventional heating for pyrolysis of biosolids because of its speed and controllability. This paper explores the microwave pyrolysis of biosolids, with a focus on the bio-oil produced from the process.

## 2 Method

This study was undertaken as a set of systematic experiments. Because microwave processing is entirely dependent on the dielectric properties of the

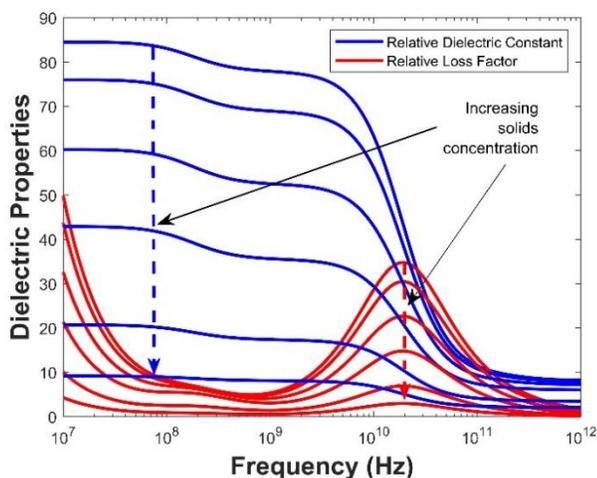
heated material, the first phase of the study was to measure and model the dielectric properties of the biosolids. This was followed by small scale experiments in a single mode chamber to properly understand the energy balance of the process and to quantify the products of the process. Finally, scale-up is an important consideration in any microwave processing system, so a larger scale experiment involving samples of at least 2 kg was undertaken.

Biosolids, acquired from the Euroa municipal waste water (sewage) treatment plant (36° 46' S, 145° 33' E), with approximately 40 % moisture content, were collected from the sewage treatment plant and used as a feedstock material in this study.

The dielectric properties of the biosolids were measured using an Agilent network analyser (PNA 8357B) equipped with a dielectric probe (Agilent 85070E Dielectric Probe kit). Dielectric loss and dielectric constant were measured between 1 to 10 GHz with an interval of 100 MHz, at room temperature (23°C ± 2°C) for biosolids with different moisture content (Fig. 1). The experimental arrangement and results for the measurement and modelling of the dielectric properties of these biosolids is thoroughly described in Brodie, Destefani, Schneider, Airey and Jacob [8]. The dielectric properties of dry biosolids at 2.45 GHz are: 1.6 + j0.08, which implies that they are almost transparent to microwave energy. Therefore, a susceptor material, which absorbs microwave energy and transfers the resulting heat to the bulk feedstock, must be mixed with the biosolids to achieve pyrolysis temperatures.

A preliminary experiment, where 80 g samples of biosolids were subjected to microwave pyrolysis in a 1.17 litre, single mode microwave chamber, was used to determine the yield of pyrolysis products and energy balance when processed at different temperatures [9]. The chamber was fed from a

variable power, 1.2 kW microwave source, operating at 2.45 GHz. The pyrolysis chamber was sealed at the top with a flanged lid that had connections to allow nitrogen gas inflow and pyrolysis gas removal.



**Figure 1:** Dielectric properties of biosolids as a function of frequency and moisture content in the range from 0.09 to 0.9 solids fraction in the biosolids.

A wave guide directional coupler was used to monitor microwave power flow into the single mode chamber. The power ratio for the coupler was 1:107.8. During the experiment, a shielded thermocouple was used to measure temperature in the centre of the sample. The pyrolysis gases were removed using a vacuum pump, and the oil fraction was condensed using a cold-water trap. The experimental arrangement for this experiment is thoroughly described in Antunes, Schumann, Brodie, Jacob and Schneider [9]. Activated carbon was used as the susceptor in these experiments.

The biosolids, biochar and bio-oil were subjected to chemical analyses to determine nitrogen, carbon, hydrogen, sulphur, oxygen and ash content for use in energy recovery calculations. The chemical composition of the syngas was determined by mass balance calculations, assuming conservation of these elements during the pyrolysis process. The following equation was used to calculate the calorific higher heating value (HHV) of the solid materials (i.e. biosolids and biochar) [10]:

$$HHV, \frac{kJ}{gDrySludge} = 0.3515[C\%] + 1.617[H\%] + 0.1232[S\%] - 0.1198[O\% + N\%] - 0.0153[A\%] \quad (1)$$

The calorific values of the bio-oil and syngas were determined from the Boie equation [11]:

$$HHV, \frac{kJ}{g} = 0.3516 [C\%] + 1.16225 [H\%] - 0.11090 [O\%] + 0.06280 [N\%] + 0.10465 [S\%] \quad (2)$$

Larger samples of Biosolids were treated in a 6 kW, 1 m<sup>3</sup>, multi-magnetron, multi-mode microwave chamber, operating at 2.45 GHz [12]. The mass of these samples was approximately 2500 g. The samples were broken up and thoroughly mixed with 10 %, by mass, of biochar that was produced from earlier experiments. The biochar acted as the microwave susceptor for these experiments. The samples were placed into a 4-litre fused quartz crucible with a close-fitting lid to restrict exposure to the air. The 6 kW experimental microwave chamber has been thoroughly described elsewhere [12].

A thermal camera (FLIR T640) was used to record the temperature of the system and the samples after treatment. Bio-oil condensed on the walls and in the drain at the centre of the 6 kW chamber’s floor. Samples of this oil were collected and analyzed in a Varian 3800 Gas Chromatograph with a 30-m long, 0.25-mm diameter fused silica column connected to a Varian 1200L quadrupole Mass Spectrometer operated in 40-500 total ion chromatogram scan mode and a Varian FID.

### 3 Results and Discussion

It has been shown elsewhere [13] that the rate of temperature increase due to microwave heating can be described by:

$$T(t) = A(e^{4\gamma\alpha^2 t} - 1) \quad (3)$$

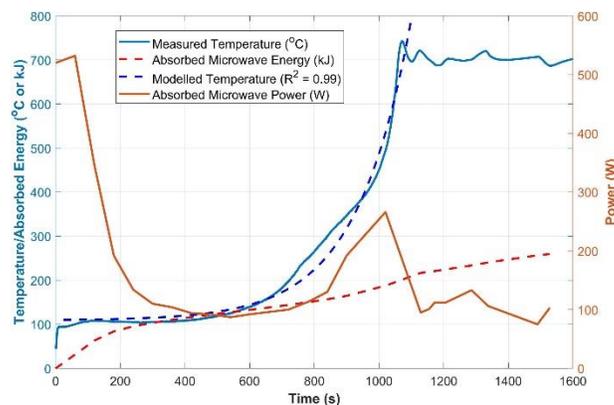
Where:  $A$  is an amplitude term (°C) that represents more complex spatial temperature distributions, described in Brodie [13];  $\gamma$  is the thermal diffusivity of the material (m<sup>2</sup> s<sup>-1</sup>);  $\alpha$  is the microwave attention (m<sup>-1</sup>); and  $t$  is time (s).

This model is consistent with the temperature rise observed in the samples (Fig. 2). Once the set point was achieved, the applied microwave energy was adjusted to maintain a relatively constant temperature in the sample for a further 10 minutes.

The amount of non-condensable syngas was calculated as the difference between dry biosolids and the combination of the biochar and bio-oil recovered during the experiment. The resulting breakdown of pyrolysis products (Table 1) was: biochar (59.9 %); syngas (37.7 %); and bio-oil (2.4 %). Percentages are expressed in relation to the mass of dry biosolids.

In the 6 kW chamber, the microwave pyrolysis process took less than 20 minutes. The processing time in the 6 kW chamber is considerably faster than conventional slow pyrolysis, which generally takes several hours to complete [3]. The outer temperature of the quartz crucible was consistently between 300 °C and 350 °C (Fig. 4) immediately after each experiment; however, the samples were consistently between 650 °C and 700 °C. The microwave chamber reached an external temperature of between 35 °C and 40 °C. It should be noted that no insulation

was used or required during these experiments; however, welding gloves were used to handle hot crucible after microwave pyrolysis.



**Figure 2:** Temperature, a temperature model based on equation (3), power, and energy analysis of biosolids pyrolysis in single-mode microwave chamber

**Table 1:** Chemical characteristics and energy values for pyrolysis products

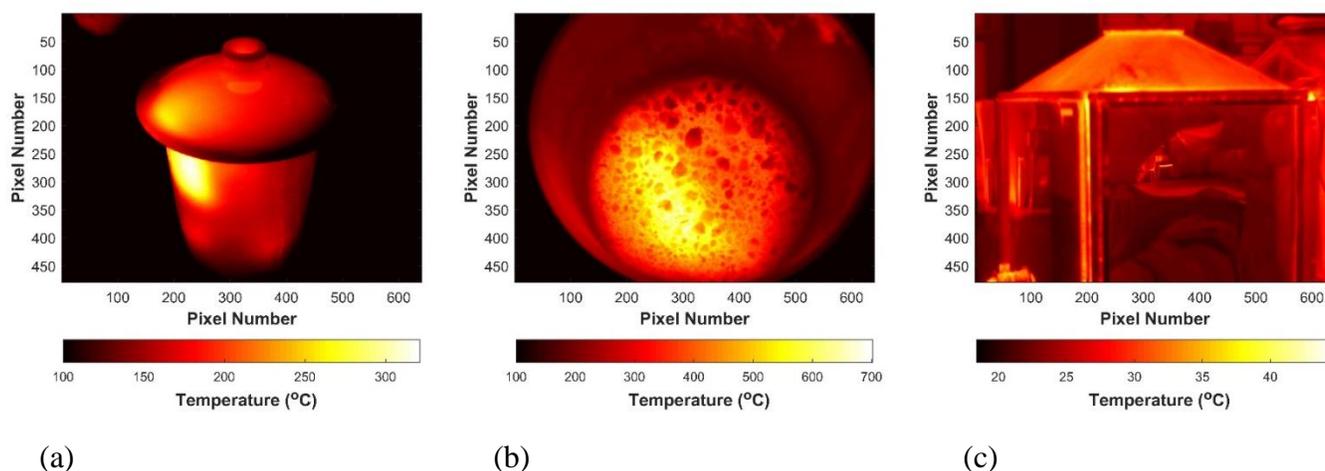
Product	N (%)	C (%)	H (%)	S (%)	O (%)	Ash (%)	Yield (g g <sup>-1</sup> )	HHV (kJ g <sup>-1</sup> )	Energy Recovery (kJ g <sup>-1</sup> )
Bio-oil	4.82	73.54	9.84	0.64	11.15	0.00	0.02	36.43	0.86
Biochar	0.70	11.80	0.00	0.50	4.37	82.60	0.60	2.34	1.40
Syngas	6.67	46.38	10.83	1.845	34.29	0.00	0.38	25.68	9.68
Initial Biosolids	3.05	26.30	4.30	1.03	15.81	49.50	1.00	13.32	-

The bio-oil, recovered from the 6 kW chamber, consisted of approximately 40 % phenols and carboxylic acids; however, a total of 45 chemical compounds, from various mass spectra, have been identified in the bio-oil. One sample’s spectrum is shown in Fig. 4. A full list of the chemical peaks, found during the study, is presented in Table 2.

There are several peaks which could not be identified. It is also interesting to note the presence of Silicone grease in some of the oil samples. This was a contaminant from the microwave chamber itself. The number of chemicals identified in the bio-oils produced during this experiment is fewer than the number identified by Dominguez, Menéndez, Inganzo and Pis [14] in their study of microwave pyrolysis of sewage sludge; however, the 30-m long Gas Chromatograph column, used in this study, was only half the length of their column. It is anticipated

that more longer chain chemicals may be present in the oil.

Preliminary analysis revealed that roughly 40% of the bio-oil was composed of phenols and carboxyl acids. Phenol has been in production since the mid-19th century. One of the early uses for phenol was as an antiseptic. Towards the end of the 19th century, phenol was used in the synthesis of dyes, aspirin, and one of the first high explosives, picric acid. As early as 1872, it was found that phenol could be condensed with aldehydes to make resinous compounds. Phenol-methanal (formaldehyde) resins are the basis of the oldest plastics, and are still used to make low cost thermosetting plastics such as Melamine and Bakelite. These resins are also used extensively as bonding agents in manufactured wood products, such as plywood and MDF.



**Figure 3:** Thermal images of (a) the quartz crucible, (b) the sample, and (c) the microwave chamber, immediately after treatment

**Table 2:** Full chemical list from GC-MS analysis of bio-oil from pyrolysis experiments

Chemical Name	Retention Time (Minutes)	Chemical Name	Retention Time (Minutes)
2,2-Dimethoxybutane	2.63	Unknown	21.98
Phenol	6.35	Dodecanoic acid	23.144
Phenol	7.325	Tritetracontane	24.183
Phenol, 4-methyl-	7.79	Unknown	24.23
Phenol, 4-methyl-	8.18	Cyclodecasiloxane, eicosamethyl-	25.74
Undecane, 5,7-dimethyl-	8.69	Bis[di(trimethylsiloxy)phenylsiloxy]	
2-methylphenol	9.515	trimethylsiloxyphenylsiloxy	26.29
3-methylphenol	9.863	Tetradecanoic acid	27.328
4-methylphenol	10.165	Cyclononasiloxane,	
Phenol, 2,6-dimethyl-	10.306	octadecamethyl-	27.36
Phenol, 4-ethyl-	10.38	Bis[di(trimethylsiloxy)phenylsiloxy]	
2,5-Pyrrolidinedione derivative	11.14	trimethylsiloxyphenylsiloxy	28.11
1,4:3,6-Dianhydro- $\pi$ d-glucopyranose	11.46	Tetracosamethyl-	
2,3-dimethylphenol	12.19	cyclododecasiloxane	28.32
Benzenepropanenitrile	12.25	Silicone grease	28.34
2,4-dimethylphenol	12.25	Nonadecanenitrile	28.474
2,6-dimethylphenol	12.303	Pentadecanoic acid	28.555
3-ethylphenol	12.639	Cyclodecasiloxane, eicosamethyl	28.85
Acetoguaiacone	17.09	14-methylpentadecanoic acid	28.929
Silane, trimethylphenoxy-	17.09	Unknown	29.08
Unknown	18.3	Unknown	29.8
Octadecane	19.57	Hexadecanoic acid	31.169
Acetosyringone	20.83	Octadecanoic acid	34.68
Unknown	21.18	Cholest-3-ene, (5.alpha)-	43.419
		Cholest-4-ene	44.08

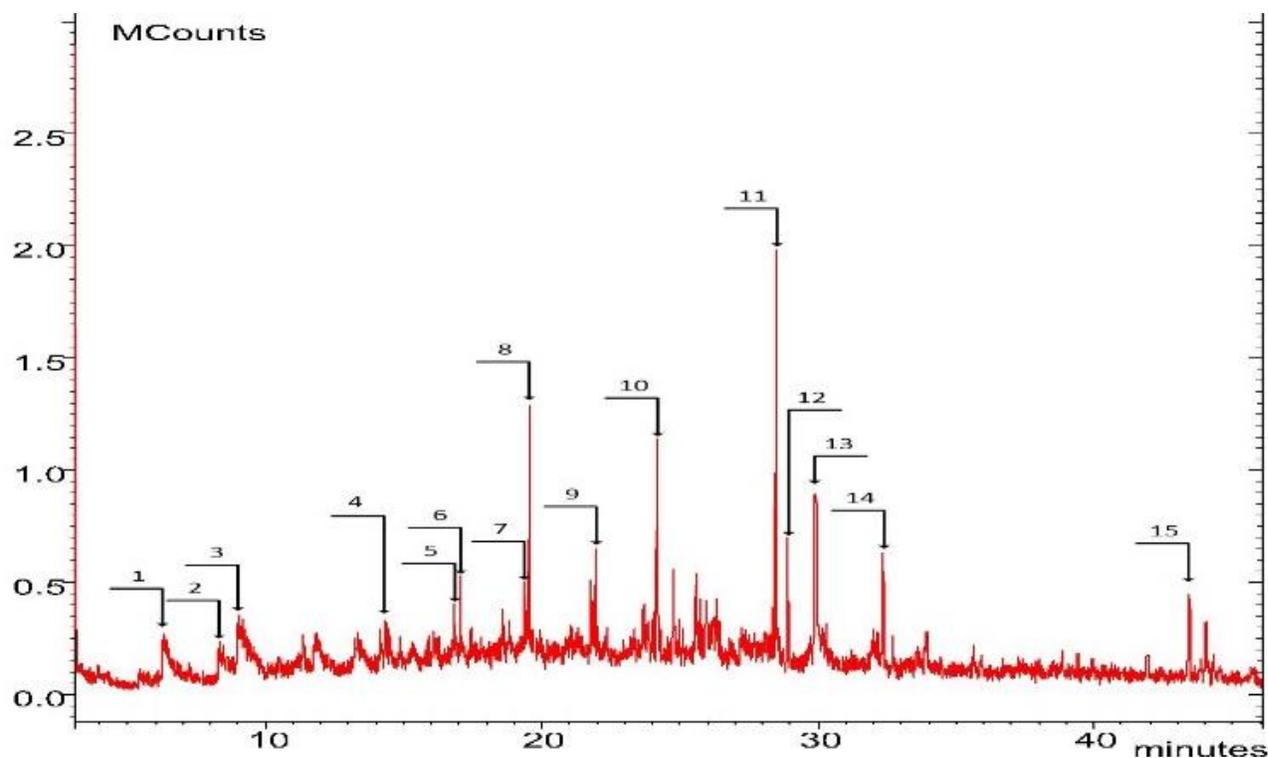


Figure 4: Example of mass spectrum from one of the bio-oil samples.

#### 4 Conclusion

Microwave pyrolysis of stabilised sewage sludge, also called biosolids, is quick, compared with conventional pyrolysis, and yields: biochar; bio-oil; and syngas. Biochar has important applications in

agricultural production and syngas can be used as a fuel. The bio-oil contained at least 45 chemicals, with about 40 % of the oil being phenols and carboxyl acids. These and other chemicals that were recovered in the oil fraction have important industrial applications and economic value.

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#### For further reading

1. LeBlanc, R. J.; Matthews, P. and Richard, R. P.; *Global atlas of excreta, wastewater sludge, and biosolids management: moving forward the sustainable and welcome uses of a global resource*
2. Pritchard, D. L.; Penney, N.; McLaughlin, M. J.; Rigby, H. and Schwarz, K.; Land application of sewage sludge (biosolids) in Australia: risks to the environment and food crops, *Water Science & Technology*, 2010, **62** (1), 48-57.
3. Kaudal, B. B.; Chen, D.; Madhavan, D. B.; Downie, A. and Weatherley, A.; Pyrolysis of urban waste streams: Their potential use as horticultural media, *Journal of Analytical and Applied Pyrolysis*, 2015, **112**; 105-112.
4. Corporation, M. W.; "Waste to resources", <http://www.melbournewater.com.au/whatwedo/liveability-and-environment/waste/pages/waste-to-resources.aspx>, 2015.
5. Aimin, J.; Yan, C.; Hongya, L. and Zuguo, Q.; A Review on Pyrolysis Technology and Characters of Products from Sewage Sludge, *Applied Mechanics and Materials*, 2013, **295-298**; 1419-1424.
6. Luo, S.; Zhou, Y. and Yi, C.; Syngas production by catalytic steam gasification of municipal solid waste in fixed-bed reactor, *Energy*, 2012, **44** (1), 391-395.
7. Kirubakaran, V.; Sivaramakrishnan, V.; Nalini, R.; Sekar, T.; Premalatha, M. and Subramanian, P.; A review on gasification of biomass, *Renewable and Sustainable Energy Reviews*, 2009, **13** (1), 179-186.
8. Brodie, G.; Destefani, R.; Schneider, P. A.; Airey, L. and Jacob, M. V.; Dielectric Properties of Sewage Biosolids: Measurement and Modelling, *Journal of Microwave Power and Electromagnetic Energy*, 2014, **48** (3), 147-157.
9. Antunes, E.; Schumann, J.; Brodie, G.; Jacob, M. V. and Schneider, P. A.; Biochar produced from biosolids using a

- single-mode microwave: Characterisation and its potential for phosphorus removal, *Journal of Environmental Management*, 2017, **196**, 119-126.
10. T.J. Buckley and E.S. Domanski; Evaluation of data on higher heating values and elemental analysis for refuse-derived fuels, *Division, C. T., US National Bureau of Standards*, 1988.
  11. Annamalai, K.; Sweeten, J.M. and Ramalingam, S. C.; Estimation of Gross Heating Values of Biomass Fuels, *American Society of Agricultural Engineers*, July-August 1987, **30** (4), 1205-1208.
  12. Harris, G. A.; Brodie, G. I.; Ozarska, B. and Taube, A.; Design of a Microwave Chamber for the Purpose of Drying of Wood Components for Furniture, *Transactions of the American Society of Agricultural and Biological Engineers*, 2011, **54** (1), 363-368.
  13. Brodie, G.; The influence of load geometry on temperature distribution during microwave heating, *Transactions of the American Society of Agricultural and Biological Engineers*, 2008, **51** (4), 1401-1413.
  14. Dominguez, A.; Menéndez, J. A.; Inguanzo, M. and Pis, J. J.; Investigations into the characteristics of oils produced from microwave pyrolysis of sewage sludge, *Fuel Processing Technology*, 86 (9), pp. 1007 -1020, 2005.

### About the authors



**Graham Brodie** is an electrical engineer with the Faculty of Veterinary and Agricultural Sciences at the University of Melbourne. His research interests include: microwave heating of bio-materials; using microwaves for sensing and communication in agriculture and forestry; improving water use efficiency in agriculture; producing renewable energy on farms; on-farm animal waste management; and applications of Geographic Information System (GIS) and Remote Sensing technologies in agriculture and archaeology. He obtained his PhD from the University of Melbourne, Australia, in 2005. He has over 35 years of professional experience in industry and academia.



**Dr. Augustine Doronila** engages with many industries, in particular small and medium enterprises (SME) which require analytical services and scientific consultation to enhance and value add their processes. This has resulted in productive and worthwhile contracts and partnerships with industry and government authorities and utilities (ca. 20 in 2 years), which harness the capabilities of SCAN and its collaborators. Augustine draws on many years of research and collaboration in environmental and analytical chemistry and ecology. He has been involved in post mining land rehabilitation with different mining and extractive industries. His expertise includes research on arsenic and

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**Dr Alex Duan** has a background in Chemistry (PhD) and research experience studying materials and surface chemistry, focusing on characterisation using X-ray photoelectron spectroscopy (XPS) and electron microscopy, particularly useful for contamination and unknown substance determination. Due to industry engagement and consultancy at SCAN, Duan has developed broader experience with materials analysis and investigation in the areas of construction, manufacturing, preservation and environmental science. His experience with interdisciplinary projects has given him expertise with understanding and comparing the advantages and disadvantages of a suite of analytical techniques including gas chromatography mass spectrometry (GCMS). He currently manages Trace Analysis for Chemical, Earth and Environmental Sciences (TrACEES) platform in aim to develop advanced analytical capabilities and capacities for multidisciplinary researches and technical supports.



**Elsa Antunes** obtained her PhD degree in Chemical Engineering from James Cook University in 2017. Elsa's PhD was focused on understanding the impact of microwave pyrolysis conditions on biochar properties produced from diverse biomass. She has recently joined James Cook University as a Chemical Engineering Lecturer. She is currently focused in materials engineering, such as biomedical implants, transparent ceramics and surface functionality of biochar through different modification techniques for water purification, resource recovery and desalination.



**Mohan Jacob** is a Professor in Electrical Engineering and Associate Dean Research Education at James Cook University. He received his PhD from University of Delhi in 1999. He is actively involved in non-destructive characterization of various materials at microwave frequencies and cryogenic temperatures. He is also involved in the development of sustainable, natural-resource-based environmentally friendly biomaterials and electronic and biomedical devices. He developed graphene from non-conventional sustainable sources using plasma enhanced chemical vapour deposition. He has published over 150 peer reviewed Journal papers and conference papers.