# AMPERE NEWSLETTER

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EDITORIAL

I am truly glad to act in this 79th issue as the new editor of AMPERE newsletter. I would like in first place to express my profound gratitude to Prof. A. C. Metaxas for his incredible work and tireless dedication to this publication. I hope I can count on his wise advice while I am acting at this position. Also, I would like to invite all AMPERE members and people related to high-frequency heating techniques to contribute to this newsletter with technical papers, descriptions of related events and any information close to microwave and RF-heating fields.

This issue is delighted to present a contribution from Daniel Beneroso and J. Ángel Menéndez from the Group of Microwave and Carbons Applied to Technology at the Consejo Superior de Investigaciones Científicas (CSIC) in Spain about the use of microwave-assisted pyrolysis of wastes for the production of bioplastics.

Also coming from Spain, Professor Alejandro Díaz-Morcillo from Universidad Politécnica de Cartagena writes about the just finished research project entitled “Nanomicro: Integration in Micro-manufacturing” that aims to develop a high resolution and high productivity machine for the manufacturing of small metallic and cermet parts (few millimetres in size) by sintering layer-by-layer a powder stream from a capillary.

The Afterthought piece in this issue, written as usual by Prof. A.C. Metaxas, reviews the potential use of microwave-heating and ultrasound technology for biofuel production, microwave assisted oil synthesis and microwave assisted transesterification.

Editor
Prof. Juan Monzó-Cabrera
ETSI Telecomunicación
Universidad Politécnica de Cartagena (Spain)

BIOPLASTICS VIA MICROWAVE PYROLYSIS OF WASTES

Daniel Beneroso
Group of Microwaves and Carbons Applied to Technology (MCAT)
Consejo Superior de Investigaciones Científicas (Spain)

J. Ángel Menéndez
Group of Microwaves and Carbons Applied to Technology (MCAT)
Consejo Superior de Investigaciones Científicas (Spain)

The need for alternative materials is generally accepted because of the finite sources of fossil reserves. For that reason, bioplastics production is a industry niche that is being developed in an attempt to rise above the non-degradability problem of petrol-derived plastics. In this sense, plastic solids are produced globally to a level of 245 MT every year from oil and gas; therefore, it is evident that new alternative synthesis routes to petrol-based plastics are necessary, such as the microwave pyrolysis of biomass to produce syngas (CO + H2), as discussed below, followed by its microbial fermentation as depicted in Fig. 1. Such process has become a promising industrial procedure [1].

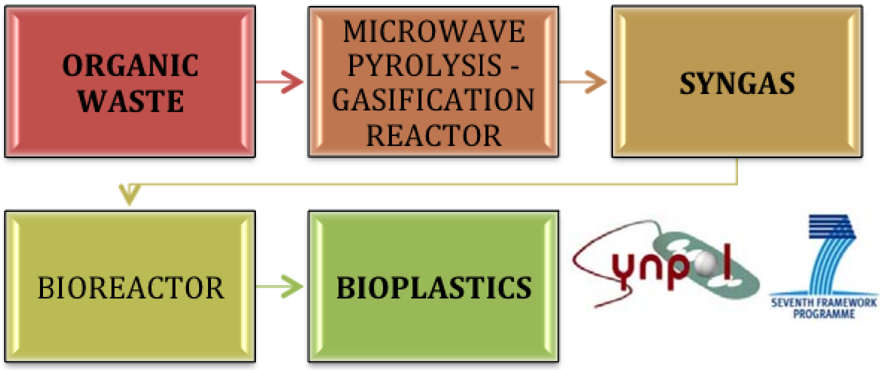

Figure 1. Schematic platform of organic waste pyrolysis integrated with syngas fermentation to bioplastics developed by the EU-funded SYNPOL project (http://www.synpol.org)

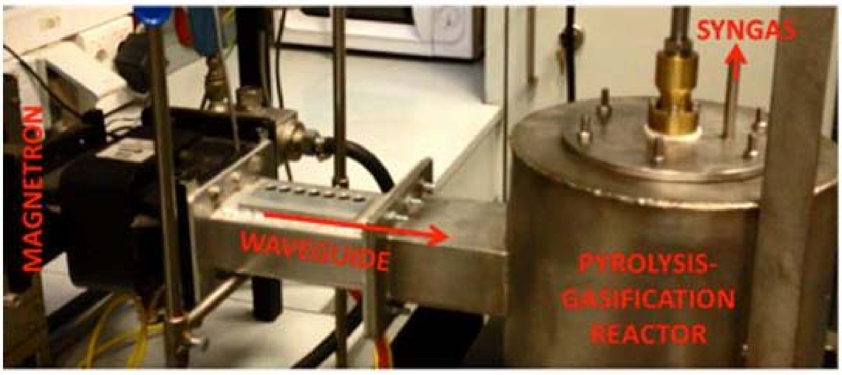

Figure 2. Microwave pyrolysis technology developed by MCAT (http://www.incar.csic.es/mcat)

In order to make the production of bioplastics a competitive process, organic waste streams could have the potential of reducing drastically the cost associated to the process by a 30-50% if they are used instead of refined feedstock [2]. The SYNPOL project is currently working on this way and will enable the EU to lead worldwide the syngas fermentation technology for waste valorization and sustainable biopolymer production.

Microwave induced pyrolysis has the potential to convert, in a very effective way, the organic waste feedstock into syngas (Fig. 2). Microwave heating mechanism is volumetric; thus it is clear that it should yield quite different products. The microplasmas phenomenon, which takes place when microwaves irradiate a carbonaceous residue, let the temperature rise up to 1000 °C in very confined and tiny spaces within the bulk and last for a fraction of second. However, the bulk temperature remains at much lower temperature depending on the microwave power. Hence, this pseudo-catalytic effect allows a significant thermal cracking of the volatiles given off, leading to thermodynamically more stable compounds in those conditions, such as CO and H2 instead of CO_2 or light hydrocarbons [3].

Furthermore, due to the volumetric nature of microwave heating, this may favour heterogeneous reactions between the gas released and the carbonaceous waste, which in turn might well increase the concentration of valuable products for bioplastics production such as CO. Likewise to conventional pyrolysis, different product fractions are obtained in the microwave pyrolysis as depicted in Fig. 3.

Figure 3. Products from the microwave pyrolysis: a) oil, b) solid char and c) syngas

In fact, our process allows recycling of carbonaceous solid char from the pyrolysis of the biowastes, as is mixed with the biowaste to be pyrolysed. This is because organic residues are known to be transparent to microwaves but the char is microwave absorbent, so that it easily reaches high temperature when irradiated with microwaves (Fig. 4). The biowaste is, then, heated up by conduction.

In addition, the char also acts as reactant since this can be gasified with CO_2 and H_2O, resulting from the biowaste volatiles evolved, to yield more syngas. This reaction pathway may be promoted by the ash metallic content existing in the char, such as K, Na, Ca, Fe or Mg.

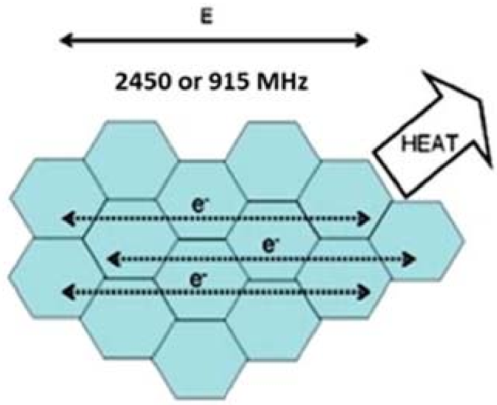

Figure 4. Delocalised π-electrons in carbon materials cannot couple to the changes of phase of the electric field and energy is dissipated in the form of heat [4]

Using this technology, developed in our research group MCAT, we have been able to exploit the potential benefits of microwave heating applied to the pyrolysis of a municipal solid waste. For instance, Fig. 5 compares the fraction yields resulting from this process at a relatively low temperature.

Gas yield is well improved by means of microwave pyrolysis at 400 °C; this result has been found to be similar at higher temperatures. Regarding to the gas production per biowaste feedstock, conventional pyrolysis at 400 °C leads to 0.08 m^3kg^{-1} (0.36 m^3kg^{-1} at 800 °C), whereas microwave pyrolysis gives 0.40 m m^3kg^{-1} (0.68 m^3kg^{-1} at 800 °C), which evidences the superiority of the last one to be taken into account in the production of bioplastics by the process mentioned above.

In addition, it is important to note that there is a significant decrease in the oil yield, which may indicate that these oils from the pyrolysis might have been cracked into incondensable gas. As the solid yield also decreases, gasification of the char could be taking place.

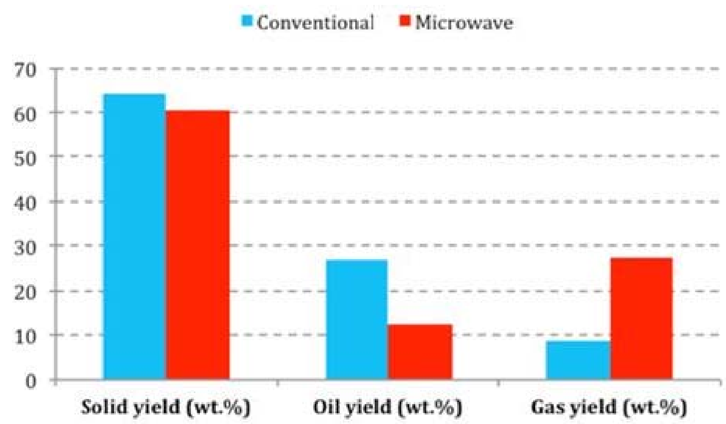

Figure 5. Fraction yields from the pyrolysis of municipal solid waste at 400 °C

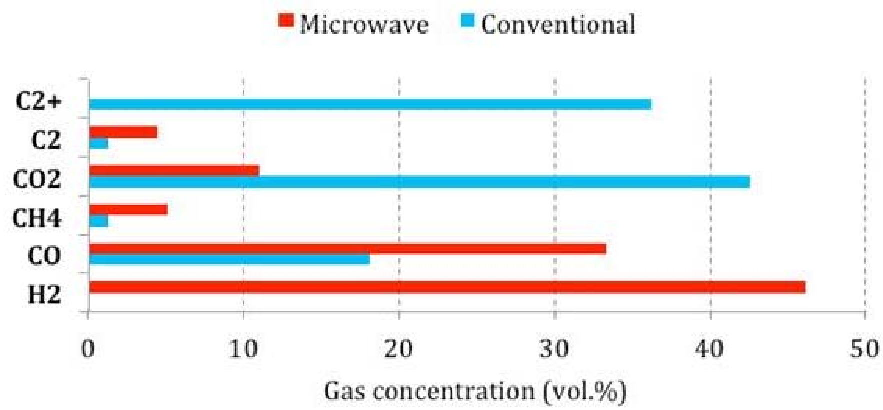

Figure 6. Influence of the heating method on the gas fraction composition at 400 °C

Conversely, Fig. 6 shows the gas fraction composition when this residue is subjected to both microwave and conventional heating at 400 °C. No hydrogen production is detected by conventional pyrolysis at 400 °C. Nevertheless, its concentration reaches 46 vol.% if microwave radiation is used.

Moreover, CO concentration from microwave heating is nearly two times higher and C_2+ hydrocarbons are not produced. Regarding to the production of bioplastics by means of syngas fermentation, maximizing both gas and syngas production would be the target to cope with and this is undoubtedly achieved with microwave pyrolysis as previously reported in countless studies [5, 6].

To sum up, since biocatalyst used to produce bioplastics do not seem to require a fixed CO/H_2 ratio [7] coupled with the fact that microwave heating seems to provide much better energy efficiencies at higher scale [8], microwave induced pyrolysis could be the way forward to be considered for sustainable bioplastics production from waste.

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NANOMICRO PROJECT: MICROWAVES IN THE 3D PRINTING INDUSTRY

Dr. Alejandro Díaz-Morcillo

Head of the Electromagnetics and Matter Group (GEM)

Universidad Politécnica de Cartagena

The Electromagnetics and Matter Group (GEM) at the Universidad Politécnica de Cartagena (UPCT) has since the very beginning dedicated numerous efforts towards microwave heating research as an alternative to conventional energy use. Nowadays industries employ traditional technologies that, in many cases, may be substituted and/or combined with more efficient microwave energy techniques.

GEM is confident of the enormous possibilities of microwaves and therefore has focused its main research line towards industrial application processes where microwaves could mean a competitive alternative to more conventional heating sources. Some examples of our research interest in this line are:

- Energy efficiency optimization of microwave heating ovens.
- Analysis and optimization techniques for obtaining uniform electric field patterns within the dielectric sample.
- Microwave-assisted drying modeling.
- Analysis and optimization of all kind of industrial applications of microwave energy such as:
  - Microwave-assisted curing of rubber.
  - Microwave-assisted drying of leather and clay.
  - Microwave-assisted packaged food sterilization.
  - Microwave-assisted curing of marble resin coatings.
  - Microwave manufacturing of abrasive pieces for marble polishing.
  - Rice and soil microwave disinfection.
  - Micro-manufacturing of metallic and cermet parts.

GEM offers consulting services for analysis and design of microwave heating systems, for static, batch or continuous processes, with the aim of joining minimization of energy cost and optimal quality in the final product.

Within its activities in micro-manufacturing, GEM is the coordinator of the European project NANOMICRO (Nanomicro Integration in Micro-manufacturing), granted with 3,900,000€ by the European Commission within the 7th Framework Program. The Consortium of the project is composed of three universities and eight companies from six different countries of the European Union (see figure 1).

Figure 1. NANOMICRO consortium partners' location

This project aims to develop in four years a high resolution (10µm) and high productivity machine for the manufacturing of small metallic and cermet parts (few millimetres in size) by sintering layer-by-layer a powder stream from a capillary. Whilst the final sintering of the powders on the substrate is realised by means of a laser beam, an on-flight pre-heating of the powder stream is needed for a better performance of the system. The realization of this platform requires the combination of different tasks, as figure 2 shows: production of nano-structured metallic or cermet powders, capillary feeding, laser sintering, microwave pre-heating and powder focusing, among others.

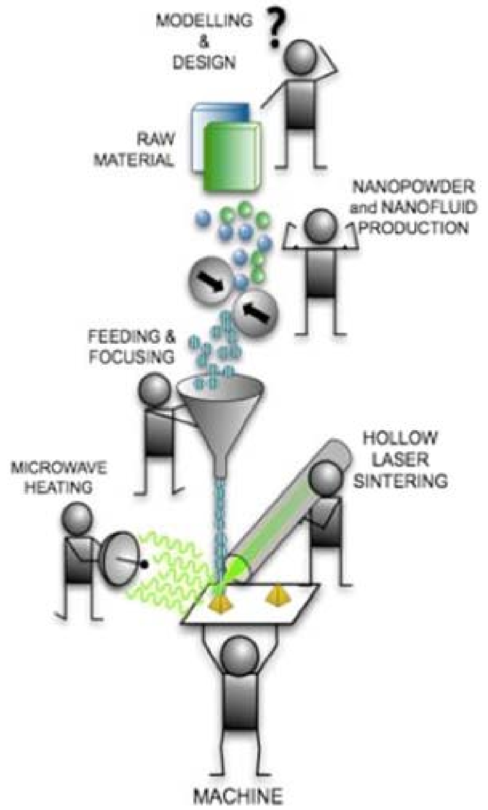


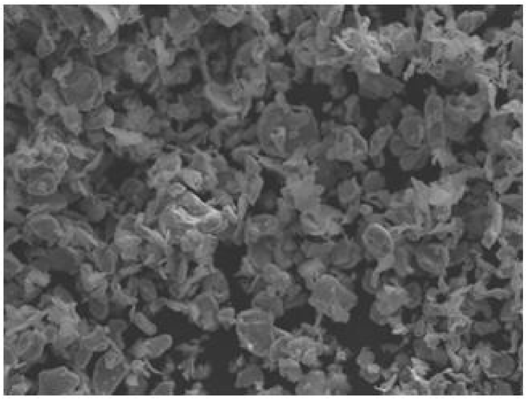
Figure 2. Nanomicro platform concept

The on-flight pre-heating is realized in the platform by means of microwaves. Past experiences with metal powders, although in a static scenario, have shown that microwave radiation can obtain a rapid heating of the metal when the powder particle size is less that 100µm. These experiences have easily reached sintering temperature ranges between 1100ºC and 1300ºC. For the NANOMICRO powders, a lower temperature is necessary for obtaining the pre-heating and even a partial melting of the particles. Moreover the particle size is much less than 100µm.

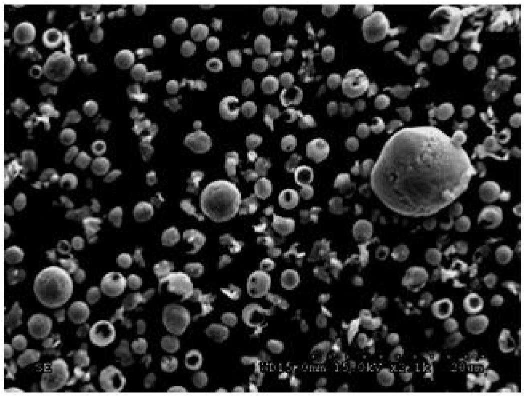
The design of this pre-heating system is really challenging since several constraints hinder it. First, the heating zone is relatively small in order to avoid interferences with the capillary system (composed by piezo-electric actuators) and the laser devices. In this sense, an electromagnetic compatibility among the different systems must be assured. Moreover, the critical issue for the on-flight microwave radiation is the rate of heating necessary to increase the temperature from room temperature to 800 – 1000ºC in a very small time. Finally, the small amount of material in the applicator produces a very sharp resonance and, therefore, difficulties in tuning.

After designing and testing different applicators, a final solution, which obtains very high heating rates with a 1kW magnetron, has been developed. Figure 3 compares the original powder with 5µm flake-shaped particles and the result after the on-flight microwave treatment. This picture shows that, not only the pre-heating is obtained, but a more rounded shape is obtained, which improves the flowability of the particles inside the capillary.

In this way, microwaves show that they can have its niche as well in the recent 3D-printing technology and in the manufacturing of metallic parts, historically a realm of induction and laser technologies.



a)



b)

Figure 3. SEM pictures of the processed powder: a) original, b) after microwaves

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Contact information:
Email: alejandro.diaz@upct.es
Websites: www.upct.es/gem
www.nanomicro-project.eu

EVENTS

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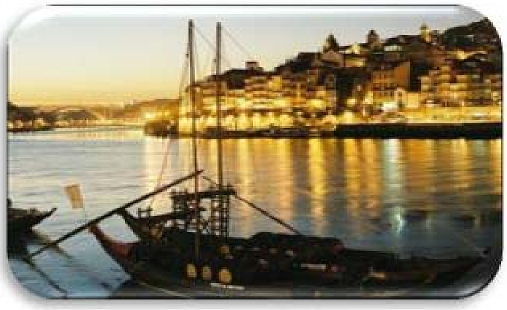

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AN AFTERTHOUGHT : MICROWAVES AND BIOFUEL

A. C. Metaxas
AC Metaxas and Associates
Cambridge UK

There is quite a lot of activity in the production and use of biofuels in terms of funding for understanding the technology with the aim of producing fuels that can replace the diminishing supplies of oil used worldwide. Government legislation points to increasing the percentage of energy that emerges from renewables and this contributes to the surge for finding better and more cost effective ways of producing such fuels. However, although proponents of this form of energy claim that such use reduces the emissions of greenhouse gases, some environmentalists have suggested that some biofuels could produce twice the carbon emissions of the fuels they replace. Be that as it may, the argument will go on for a few years until evidence points to savings or otherwise.

Having said that could microwaves be used in the production of some biofuels? A recent article entitled, "Microwave energy potential for biofuel production" has reviewed the principles and practices of microwave energy technology as applied to biodiesel feedstock preparation and processing. Having outlined the current conventional production of biofuels, this article goes on the review of microwave based biofuel production, microwave assisted oil synthesis and microwave assisted transesterification. The review article concludes that hybrid systems of ultrasonics and microwaves may offer improved reaction performance.

It is interesting to point out that the possibility of combining ultrasound and microwaves, showing wide range benefits, was the subject of a recent summer school held at the University of Turin in June 2013 and sponsored by ESS and AMPERE. Two of the organisers of this summer school our President Prof.ssa Leonelli and Prof. Mason are included in this review citing a paper published in 2010 highlighting the use of microwaves and ultrasound for industrial processing. The most impressive part of this review is its breadth and literature survey which extends to over 230 papers listed in the reference section.

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