Microwave Induced Pyrolysis (MIP) of organic waste for producing Syngas

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http://www.incar.csic.es/mcat
Two thoughts and an open question.
In 1964 Penzias and Wilson (Nobel Prize in Physics in 1978) discovered the Cosmic Microwave Background Radiation (CMBR). Since then we know that the Universe started with the Big Bang and that microwaves fill the whole Universe.

So microwaves are "the most natural thing" that you can find everywhere anytime.

A few percent (ca., 1%) of the "static" on analog TV is noise caused by CMBR.
We are filling our planet of garbage.

So residues are becoming “the most unnatural thing” that you can find everywhere anytime.
Why people fear microwaves but don't fear garbage?
Let's see how Microwave Induced Pyrolysis (MIP) can help us to get rid of organic wastes and convert them into syngas with which we can produce lots of valuable goods.
First principle of circular economy: “Waste is food” ... or money

The circular economy is a generic term for an industrial economy that is producing no waste and pollution.
An old concept

“Back to the Future” (1985)
**Pyrolysis** is a thermochemical and irreversible decomposition of organic materials at elevated temperatures in the absence of oxygen. It involves the simultaneous change of physical phase and chemical composition.
Early investigations in MIP

1969 - Pyrolysis of coals in a microwave discharge. Fu, V.C.; Blaustei, B.D. Industrial & engineering chemistry process design and development, 8, 257

1973 - Microwave pyrolysis of coal and related hydrocarbons. bodily, dm; che, sc; wiser, wh. abstracts of papers of the american chemical society, 30.

1987 - Pyrolysis of discarded vehicle tyres by direct internal heating esp. by microwave radiation to recover hydrocarbon(s) and carbon black. Apffel, F. Patent: US4647443-A


1999 - Microwave high pressure thermochemical conversion of sewage sludge as an alternative to incineration. Bohlmann, JT; Lorth, CM; Drews, A; et ál.. Chemical Engineering & Technology. 22, 404-409.

2002 - Microwave-induced pyrolysis of sewage sludge. J.A. Menéndez*, M. Inguanzo, J.I. Fis Instituto Nacional del Carbón (HCAR) C.S.I.C., Avenida JF, 38008 Santiago, Spain. Received 13 July 2001; accepted 17 December 2001

Abstract
This paper describes a new method for pyrolysing sewage sludge using a microwave furnace. It was found that if just the raw sewage sludge is mixed with a small amount of a suitable microwave absorbent such as the clay produced in pyrolysis at temperatures of up to 800°C, can be achieved, so that pyrolysis takes place rather than drying. Microwave treatments were also compared with those carried out by conventional electric furnaces, as well as the characteristics of their respective combustion solid residues. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Sewage sludge; Drying; Pyrolysis; Domestic heating; Microwave:

1. Introduction
The disposal of sewage sludge produced by urban and industrial wastewater treatment plants is a matter of great concern [1]. Handling of this waste is not easy and invariably gives rise to some collateral problems. The most common alternatives of treatment and/or disposal of sewage sludge are sludge handling, centralized application, incineration and anaerobic digestion, none of which are exempt of drawbacks [2]. Another method of disposal which is being investigated at the moment is pyrolysis [2-4]. This technique appears to be less polluting than incineration, as it concentrates the heavy metals in a solid carbonaceous residue so that the leaching of these metals is not as important as in the ashes from incineration [5]. The pyrolysis of sewage sludge also gives rise to oils and gases, which can be used as fuels.

In addition, microwars are used in various technological and scientific fields, to heat electronic materials [6]. Microwave heating has also been considered as an alternative to carry out the pyrolysis of biomass [7], coal [8], oil shales [9] and different organic wastes [10]. These are, in general, poor receptors of microwave energy, so they cannot be heated directly up to the high temperatures usually required in conventional pyrolysis. However, microwave-assisted pyrolysis is possible if the raw material is mixed with an effective absorber of microwave energy such as carbon (9-11) or contain metal oxides [9].

The aim of this work was to compare sewage sludge pyrolysis using a microwave with that of a conventional electric furnace, and to compare also the characteristics of the char (combustion residue) resulting from these pyrolysis experiments. The study of the characteristics of the fuel gases and liquids produced in the pyrolysis experiments does not come within the scope of this paper and will be carried out in a future work.

2. Experimental
An anaerobic sewage sludge, which was produced in a Spanish urban wastewater treatment plant, was used as starting material. Detailed chemical characteristics and the heavy metal content of this material are given in Table 1.

Microwave experiments were carried out by placing samples of the wet sludge mix, 20 g in a quartz reactor, which in turn was placed inside a medium microwave cavity. Microwave treatments consisted in
Why syngas from MIP?
Char fractions often contain an important amount of inorganic matter (ashes) and heavy metals making difficult their industrial use.

MIP minimizes the solid fraction (part can be reticulated as microwave susceptor and catalyst).

The liquid oil fraction needs to be upgraded to lower the oxygen content and to remove moisture, heavy metals and other undesirable compounds.

Oil fraction may also contain hazardous compounds such as polycyclic aromatic hydrocarbons (PAHs).

MIP minimizes the oil fraction.

MIP reduces the hazardous compounds content of oils.

Gas fraction

The gas fraction collected from pyrolysis can be used directly as fuel.

It contains a high proportion of syngas (H₂ + CO) that can be used in the synthesis of ammonia, methanol and the Fischer-Tropsch derived products, hydrocarbons, biopolymers, etc.

**MIP for syngas production needs of higher temperature/power.**

<table>
<thead>
<tr>
<th></th>
<th>Microalgae</th>
<th>MSW</th>
<th>Straw</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIP Gas Yield (wt%)</td>
<td>57.2</td>
<td>48.3</td>
<td>55.9</td>
</tr>
<tr>
<td>Conv. Gas Yield (wt%)</td>
<td>34.7</td>
<td>36.1</td>
<td>37.6</td>
</tr>
<tr>
<td>Increment</td>
<td>64.8%</td>
<td>33.8%</td>
<td>48.7%</td>
</tr>
<tr>
<td>MIP Syngas vol%</td>
<td>94.0</td>
<td>94.6</td>
<td>95.2</td>
</tr>
<tr>
<td>Conv. Syngas vol%</td>
<td>53.0</td>
<td>72.5</td>
<td>79.8</td>
</tr>
<tr>
<td>Increment</td>
<td>77.4%</td>
<td>30.5%</td>
<td>19.3%</td>
</tr>
</tbody>
</table>


The production of syngas by **High Temperature MIP** can be compared with “classical” gasification processes rather than with “conventional” pyrolysis:
"Houston, we've had a problem here"

The **dielectric properties of the dried biomass** (and organic wastes, in particular) **are very poor**, i.e., it is very difficult to heat it, up to the high temperatures needed, by microwave radiation, unless very high power is used... One way to overcome this problem is to use a microwave susceptor.

The resulting char from MIP is a good microwave-absorbent material because of the delocalized $\pi$-electrons, which cannot couple to the changes of phase of the electric field, and so the accumulated energy dissipates in the form of heat. Eventually electrons may jump out of the material ionizing molecules of the surrounding atmosphere and forming microplasmas.
How microwave susceptors work?

Evolution of the organic particles (white circles) and microwave susceptor particles (black circles) during MIP, where it is shown the creation of second, third, etc. generation of microwave receptors (gray circles).

Y. Fernandez, A. Arenillas, J.A. Menéndez. “Microwave heating applied to pyrolysis” in Advances in Induction and Microwave Heating, S.Grundas Ed. INTECH 2011, Ch.31, pp. 723-752.
How much susceptor should I put?

There is a minimum concentration of the microwave susceptor below which MIP does not take place unless a very high power is used.

This is also the optimum concentration, since at higher concentrations the pyrolysis progresses in an uneven way due to a decrease of the penetration of microwaves, because of the formation of an outer layer of good microwave absorber char that hinders the penetration of microwaves.

Triple role of the char as: susceptor, reactant and catalyst

Heterogeneous \((g/s)\) endothermic gasification reactions

\[
\begin{align*}
\text{CO}_2 + C &= 2\text{CO} \\
\text{H}_2\text{O} + C &= \text{CO} + \text{H}_2
\end{align*}
\]

Heterogeneously Catalyzed \((g/s)\) endothermic gasification reactions

\[
\begin{align*}
\text{CO}_2 + (-\text{CH}_2^-) &= \text{(Char)}\Rightarrow 2\text{CO} + \text{H}_2 \\
\text{H}_2\text{O} + (-\text{CH}_2^-) &= \text{(Char)}\Rightarrow \text{CO} + 2\text{H}_2
\end{align*}
\]

Heterogeneously Catalyzed \((g/s)\) endothermic methane decomposition

\[
\begin{align*}
\text{CH}_4 &\stackrel{\text{(Char)}}{\Rightarrow} \text{C} + 2\text{H}_2
\end{align*}
\]

Heterogeneously Catalyzed \((g/s)\) exothermic water-gas shift reaction

\[
\begin{align*}
\text{CO} + \text{H}_2\text{O} &= \text{(Char)}\Rightarrow \text{CO}_2 + \text{H}_2
\end{align*}
\]

Direct heating of the char (reactant or catalyst) favors the heterogeneous (or heterogeneously catalyzed) gasification reactions because the reactant (or the catalyst) is at higher temperature than the surrounding atmosphere.

Different species in microplasmas

Recombination favors the formation of simple molecules like CO and H₂

The occurrence of microplasmas have a pseudo-catalytic effect that selectively favors the production of syngas.

Ok, cool!... but is this scalable?
Most of the data available are obtained from lab experiments. However, a rough approximation based in an extrapolation of several microwave heating processes can be done to estimate the energy consumption to scale up a MIP process.

The problem of scaling up MIP

At present, there are not commercially available microwave equipments able to process several tons of wastes in a reasonable time.

<table>
<thead>
<tr>
<th>Process</th>
<th>Processing Capacity</th>
<th>Energy Consumption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scandinavian Biofuel (Norway)</td>
<td>70 T/day</td>
<td>0.15 kWh/kg</td>
</tr>
<tr>
<td>Payakkawan et al. (Thailand)</td>
<td>1 T/day</td>
<td>1.5 kWh/kg</td>
</tr>
<tr>
<td>Rotawave Ltd. (UK)</td>
<td>3-12 kg/load</td>
<td>0.5-1.3 kWh/kg</td>
</tr>
</tbody>
</table>

Torrefaction

http://www.sbiofuel.com/
doi:10.1016/j.renene.2013.10.042

http://www.rotawave.com
# Energy costs of producing syngas by MIP

<table>
<thead>
<tr>
<th>Process</th>
<th>kWh/m³ of syngas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steam-CH₄ reforming</td>
<td>1.46</td>
</tr>
<tr>
<td>Partial oxidation of CH₄</td>
<td>0.01</td>
</tr>
<tr>
<td>Autothermal reforming of CH₄</td>
<td>0.14</td>
</tr>
<tr>
<td>Microwave-assisted dry reforming of CH₄</td>
<td>2.20</td>
</tr>
<tr>
<td>Pyrolysis-gasification of MSW</td>
<td>0.38</td>
</tr>
<tr>
<td>Gasification of refused-derived fuel</td>
<td>0.41</td>
</tr>
<tr>
<td>MIP of straw</td>
<td>1.88</td>
</tr>
<tr>
<td>MIP of biowastes</td>
<td>1.63 – 3.89</td>
</tr>
</tbody>
</table>

Comparatively, the energy cost for producing syngas from MIP processes is higher than the energy consumed in other conventional processes.

But...

✓ Syngas is produced from residues instead of coal, CH₄, HC, alcohols...
✓ MIP does not need of a catalyst.
✓ MIP does not need of a gasification agent (steam, air, oxygen...).

Concluding remarks

✓ Syngas production by MIP of organic wastes and other biosolids is an attractive technology from an environmental point of view, giving that hazardous and pollutant materials are converted into a clean and valuable gas.

✓ Collateral pollution released in the oil and solid subproducts is lower as compared to other alternatives.

✓ The high degree of cracking of the organic molecules due to the use of the char as susceptor-reactant-catalyst and to the microplasmas occurring during MIP gives rise to a high syngas production.

✓ The viability of this technology will be linked to the evolution of the waste management cost and to the development of new microwave equipment capable of operating on a large scale.
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Thanks for your attention

Now you can clap and make easy questions

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