



# Oil fractions from the pyrolysis of diverse organic wastes: The different effects of conventional and microwave induced pyrolysis

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## ABSTRACT

Several studies have dealt with the microwave-induced pyrolysis of organic residues as an effective technology for maximizing the production of syngas at the expense of the production of oily tars. This liquid fraction is composed of a complex mixture of organic compounds making it difficult to upgrade for use as a biofuel and containing hazardous compounds such as polycyclic aromatic hydrocarbons (PAH). In this study the effect of the type of residue (municipal solid wastes, sewage sludges, plastic wastes and agroresidues) and the heating mechanism on the product distribution within the oil fraction has been investigated by means of GC–MS technique. Two different approaches have been performed: direct GC–MS analysis and methanolysed-oils GC–MS analysis, the later determining the non-volatile compounds. In general, quite different distributions are attained when microwave pyrolysis is conducted, providing lighter compounds. In some cases, such as the plastic-derived oil, microwave pyrolysis lead to a potential source of chemicals such as benzene, toluene and xylenes.

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## 1. Introduction

Climate change and its relationship with CO<sub>2</sub> emissions has become an issue of major concern in recent years [1]. Although several efforts are being made to bring this phenomenon under control, the problem continues to grow. According to the World Energy Outlook of the International Energy Agency, the energy demand is expected to increase until 2035 and the associated CO<sub>2</sub> emissions to rise by 20% [2]. Indeed, fossil fuels will continue to be the primary source of energy generation in the short to medium term. However, in the same report this organization states that government policies can influence the pace of fossil fuel consumption. Governments have already taken concrete decisions to reduce the risks associated with fossil fuel emissions. Some examples are the Climate Action Plan in USA or the European Strategic Energy Technology Plan of the European Union [3,4]. In the case of the EU plan, one of its objectives is that 14% of the European energy mix should come from cost-competitive and sustainable bioenergy by 2020. Accordingly, technologies such as pyrolysis or gasification are going to play a

key role in the development of this cost-competitive bioenergy in the near future [4].

Pyrolysis is a process in which organic matter is thermally decomposed without the use of oxidizing agents to yield three different fractions: a solid residue commonly known as char, a liquid oily fraction (tar) and a gaseous fraction. Gasification is a process which begins with a pyrolysis step that is then followed by the gasification of char and the reforming and cracking of tars and light hydrocarbons by a gasifying component, such as steam or oxygen. As a consequence, gasification usually yields higher amounts of gas than pyrolysis [5].

One of the main problems with both technologies is the production of a large amount of tars [6]. This liquid fraction is a complex mixture of organic chemicals largely composed of aromatic and polycyclic aromatic hydrocarbons that can be hazardous for health and the environment. Moreover, they can cause problems that affect the process itself including the fouling of engines and the deactivation of catalysts [7,8]. For these reasons, research into biomass pyrolysis and gasification is looking for ways to decrease the production of tars or, at least to improve their quality, by keeping the proportions of complex compounds like polycyclic aromatic hydrocarbons (PAH) down to a minimum.

For this reason, the use of microwave heating is seen as an appealing alternative since the main feature of microwave-induced

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pyrolysis (MIP) is its ability to maximize the production of gas and minimize that of tars [9]. This tendency has been tested with many different types of residues, including algae, municipal solid wastes, agricultural wastes, sewage sludge and automotive wastes [10–13]. However, so far the effect of microwaves upon the quality of the tars has not been given serious consideration. Some studies have pointed out that, while MIP could serve to minimize the production of PAH [14], the type of residue used might also be an influential factor. In this regard, the gaseous composition from the MIP seems to be very similar regardless of the residue pyrolysed with few exceptions [12,13,15,16], syngas ( $H_2 + CO$ ),  $CO_2$  and light hydrocarbons being the most common gaseous species found. On the other hand, the influence of the type of residue on oil composition is much more prominent. For this reason, the trends observed in the production of PAH by MIP in the study of Domínguez et al. [14] cannot be generalized without carrying out a deeper study of the process with several types of wastes. It is the aim of the present study to make up for this shortcoming by gaining further insight into the influence of microwave heating on the composition of the tars produced during the pyrolysis of different types of organic residues as a continuation of a previous study in which the suitability of several organic wastes was examined in order to maximize the production of syngas for further bioplastics production [17].

## 2. Experimental

### 2.1. Materials

Four different samples, provided by BEFESA Gestión de Residuos Industriales S.L. (Seville, Spain), were selected for this study:

- An organic fraction from a municipal solid waste, dried and partially cleaned from inerts, such as glass and metals. After this pre-treatment, the fraction size was reduced to 1–3 mm. This sample has been labelled MSWd.
- Dried sewage sludge. This sample was collected from a wastewater plant in Seville. The sludge, after being subjected to secondary treatment, was dried to facilitate transportation. After being dried, the sample was milled down to a size range of 1–3 mm. This sample has been labelled SSd.
- A plastic fraction from a municipal solid waste. This sample, a complex mixture of plastic residues, was obtained from the same landfill site in Seville. The fraction was milled to 1–3 mm and has been labelled PLA.
- An agricultural residue. This sample was obtained from a biodiesel production plant located in Salamanca (Spain) and is composed of straw. The sample was also milled down to a size range of 1–3 mm. This sample has been labelled STR.

The moisture, ash content and volatile matter data of the residues were obtained by means of a LECO TGA-601. To perform the ultimate analysis, a LECO-CHNS-932 micro-analyzer and a LECO-TF-900 furnace were used. The metallic content of the ashes was determined by means of ICP-MS analysis. First, the samples were dissolved in inorganic acids ( $HNO_3$  4N and concentrated HCl) and digested using microwave heating in a MILESTONE ETHOS 1 oven at 600 W during 35 min. Identification of the elements was carried out on an Agilent 7700x using a Ar plasma. An external calibration method between 0 and 1000 ppb internal standard (Sc) and a collision cell of He (to eliminate possible matrix interferences) was used to determine the concentration of metals. The results of this characterization are presented in Table 1.

### 2.2. Pyrolysis techniques

Conventional pyrolysis (CP) was performed at 800 °C in an electric furnace. Approximately 4 g of sample was introduced into a quartz reactor. First, the reactor was placed outside the furnace and purged with  $N_2$  for 30 min at a flow rate of  $50 mL min^{-1}$  to ensure an oxygen-free atmosphere. Meanwhile, the furnace was heated up to 800 °C. Once the reactor had been purged and the electric furnace had reached the desired temperature, the  $N_2$  flow was reduced to  $10 mL min^{-1}$  and the reactor was introduced into the furnace for pyrolysis, the duration of which was 1 h. The use of such a low flow rate favours secondary reactions of tar allowing for a maximum syngas production [17,18]. The volatiles evolved during pyrolysis were forced to pass through a condensing system (cooled by a cryogenic solution of water and NaCl) where the condensable compounds were removed from the gaseous fraction. Both the reactor and the condensing system were weighed before and after the pyrolysis experiment to determine the solid and liquid yields (respectively). The gas yield was determined by difference. Each experiment was performed in duplicate to check the repeatability and the errors came to less than 6% both for the yields and the gas composition [17].

Microwave-induced pyrolysis (MIP) was performed using a microwave oven consisting of a microwave magnetron with a maximum output power of 2 kW operating at 2450 MHz and a single mode cavity where the sample-containing quartz reactor was placed. As in conventional pyrolysis, the reactor was purged with  $N_2$  for 30 min at a flow rate of  $50 mL min^{-1}$ . The flow rate was then reduced to  $10 mL min^{-1}$  and the microwave irradiation was switched on and regulated until a temperature of 800 °C was reached. The reflected power was regulated by means of tuning screws until it reached zero. The same system as that used in CP was used to collect the liquid fraction.

Owing to the poor capacity of organic wastes used in this study to absorb microwaves, it was necessary to use a microwave receptor material to induce the pyrolysis [12]. For the purpose of this study, the char obtained from a previous pyrolysis at the same temperature (hence, very unlikely to release any volatiles at 800 °C) was employed as a microwave receptor at a receptor-to-feedstock mass ratio of 0.3:1.

### 2.3. Characterization of the oil fractions

To characterize the oils, a semi-quantitative study was carried out by calculating the percentage of area of the chromatographic peaks. Two different sample preparations were performed before the GC-MS analysis:

- In the first, anhydrous sodium sulfate ( $Na_2SO_4$ ) was added to the condensed oil fraction to remove all traces of water, and injected directly into the GC-MS in order to identify the volatile compounds.
- In the second, the following methanolysis step was included. 2 mL of methanol containing 15% sulfuric acid and 0.5 mg/mL of 3-methylbenzoic acid (internal standard), was introduced, after dehydration of the oil with  $Na_2SO_4$ , followed by an incubation period of 7 h at 80 °C. After cooling, 1 mL of demineralized water and 1 mL of chloroform were added and the organic phase was analyzed by GC-MS. During the methanolysis step, the non-volatile compounds (mainly fatty acids) were turned into methyl ester derivatives, which are volatile compounds and can be easily identified by GC-MS.

All the samples were analyzed by GC-MS using an Agilent 7890A gas chromatograph (Agilent Technologies, Palo Alto, California, USA) coupled to an Agilent 5975C mass detector (electron ioniza-

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