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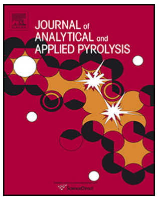

Comparing the composition of the synthesis-gas obtained from the pyrolysis of different organic residues for a potential use in the synthesis of bioplastics

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ABSTRACT

In this article we propose the possibility of obtaining syngas from very different and complex organic wastes, such as municipal solid wastes, agricultural residues or sewage sludge, through microwave-induced and conventional pyrolysis at 400 and 800 °C. Microwave heating has proved to be an appropriate way to produce a syngas with $CO + H_2$ concentrations as high as 90 vol% and in large yields (up to $0.83\,L\,g^{-1}{}_{waste}$). In addition, the potential of the syngas produced by this technology as fermentation substrate for the production of bioplastics is discussed. Microwave pyrolysis seems to serve as a novel route into biorefineries to produce valuable biobased products.

1. Introduction

Plastics are widely used in almost all industries, especially in the packaging and building sectors, due to their great versatility, low weight and excellent electrical and thermal insulation properties. Although the production of plastics has grown worldwide since 1950, in the European Union, this production has remained practically constant at 55–60 million tons per year since 2000. The production process leads inevitably to the generation of large amounts of plastic waste. The slow degradation rate, the potential risk of accidental fire and the heavy metals content in plastic additives have been proposed as the potential reasons for the search for alternative means of disposal to landfill, such as re-extrusion, mechanical recycling, chemical recycling or energy recovery [1,2]. The increasing use of these technologies has led to a decrease in the amount of waste plastic sent to landfill sites since 2008. Alternatively, because of the finite sources of fossil reserves, bioplastics production is a niche industry that is being developed in an attempt to overcome the non-degradability problem of fossil-based plastics, and to help reduce the carbon footprint of products [3,4]. According to European Bioplastics (http://en.european-bioplastics.org/), bioplastics are economically innovative and have great potential for further economic growth along the value added chain.

Of special interest are those plastics that are biobased and biodegradable, such as polyhydroxyalkanoates [5] (PHA), which can be employed for short-life applications such as packaging [6], certain agricultural applications [7] and bags suitable for organic recycling, although more sophisticated uses of PHA have also recently been reported (tissue repair and regeneration, drug delivery systems or heart tissue engineering) [8,9]. Since PHA are polyesters with a highly versatile structure, their potential is immense. Their thermo-mechanical properties can even be tailored to make them comparable to those of conventional plastics [10,11]. PHA can be made by causing microorganisms to accumulate them. High-value substrates such as sucrose, methanol or vegetable oils can then be subjected to fermentation and converted into PHA. However, the cost of these carbon sources, which may amount to as much as 50% of the total production cost of PHA, is the main reason for the slow growth of the PHA industry [12]. For this reason, the use of cheaper renewable resources as substrates such as wastes from biodiesel production [13], waste plant oils [14], paper industry wastewater [15] or dairy wastewater activated sludge [16], is essential to ensure the commercial viability of the process. Another attractive alternative would be to use syngas, defined for this particular application as $CO + H_2 + CO_2$. Syngas fermentation has been

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Abbreviations: EF, electric furnace; MIP, microwave-induced pyrolysis; MWS, municipal solid waste fraction; MSWd, dried municipal solid waste fraction; PHA, polyhydroxyalkanoates; PLA, plastic solid waste fraction; SSd, dried sewage sludge fraction; STP, standard conditions for temperature and pressure; STR, straw fraction.

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Table 1
Advantages and drawbacks of using syngas in biocatalytic processes.

Organic waste to produce syngas: abundantly available, does not require additional production costs and is a substrate that does not compete with human nutrition [37]	Mass-transfer limitations of syngas components to the fermentation medium due the low solubilities of CO and H_2 [48], although various attempts to overcome this have been reported [49]
Syngas fermentation needs low operating temperatures and pressures, reducing energy and operating costs	Relatively low volumetric productivity [49]
Biocatalysts usually show a sulphide tolerance of $\geq 2\%$ H_2S or COS [46,47]	Some components might be inhibit the metabolism of bacteria, such as tars, SO_x and NO_x; syngas cleaning may be necessary [35,50,51]
Allows the bioreactor hydraulic retention time to be uncoupled from the substrate supply, making it possible to control substrate inhibition and product formation [42]	
Biological fermentation does not require a fixed H_2/CO ratio due to the specificity of enzymatic reactions [39]	
Advantages	Drawbacks

proposed as a conversion route to produce bulk chemicals such as ethanol [17], acetate [18] or butyrate [19]. The use of syngas fermentation affords significant advantages over conventional processes for producing such chemicals as shown in Table 1.

Even though more than 300 microorganisms are known to synthesize PHA [20], few of them are able to process the syngas components [21]. For instance, autotroph microorganisms can use single-carbon compounds (CO and/or CO_2) as their sole carbon source and CO and H_2 as their energy source; whereas, unicarbonotroph microorganisms are only able to use CO directly as their sole source of both carbon and energy. The use of syngas as substrate to produce PHA is a truly novel research area, and this explains why so little information is available. Do et al. studied the growth of *Rhodospirillum rubrum* on seed corn-derived syngas containing 8.8% H_2, 17.2% CO and 16.3% CO_2, which resulted in a mixture of two types of PHA (β-hydroxybutyrate and β-hydroxyvalerate) [22]. According to these authors, small quantities of H_2S in the syngas may have been responsible for increased growth rates. The results of their research were used to develop a techno-economic model to demonstrate the feasibility of PHA production from biomass-derived syngas fermentation [23]. It is with this aim that the SYNPOL project (http://www.synpol.org) is currently being developed and is expected to enable the European Union to lead the way in the field of syngas fermentation technology for waste valorization and sustainable biopolymer production.

We propose a new potential bioprocessing scheme in Fig. 1 for the production of biodegradable polyhydroxyalkanoates. As shown, the syngas stream can be obtained from renewable feedstock. The microwave pyrolysis of biomass has demonstrated its potential to maximize both the gas yield and syngas concentration, and so is the most appropriate heating method to obtain syngas for fermentation [24–29]. This process prevents the generation of wastes, e.g., by recirculating part of the solid char to the reactor as a microwave receptor material [28]. The microwave heating mechanism is volumetric and yields quite different product distributions by favoring heterogeneous reactions between the volatiles released and the carbonaceous waste. This makes it possible to increase the concentration of valuable products, such as CO, for bioplastics production. In short, microwave pyrolysis offers an excellent opportunity for diverting organic waste away from the traditional disposal methods such as landfill and incineration and the possibility of recovering commercially valuable products from wastes. Besides, the use of microwave pyrolysis to produce syngas on a large scale will probably contribute to a more environmentally sustainable and energy-efficient process compared to conventional heating processes, as has been demonstrated in a recent study in which energy efficiency of microwave pyrolysis of wheat straw was 1.5 times higher than the energy efficiency achieved by a conventional pyrolysis process [30]. Although this technology has been widely studied, it has never been previously proposed for the production of syngas for use in fermentation processes. Moreover, no studies have yet explored the possibility of applying microwave-induced pyrolysis to the biopolymer production process through syngas fermentation. Once the syngas is fermented by bacteria, PHA can be recovered by using a solvent extraction; e.g., using chloroform and methanol [31] or combining surfactant addition to break down the cell wall followed by solubilization of cell material with sodium hypochlorite [23]. This stage should be followed by the separation of the PHA-containing phase from the residual cell material by sedimentation.

In this article we offer an extensive comparative study of organic wastes and their pyrolysis-derived syngas at different temperatures and in two different heating systems for their subsequent use as feedstock for bioplastics production by means of syngas fermentation. Of particular interest is the innovative use of microwaves to achieve this goal, as this possibility to the best of our knowledge has never been considered before in the literature.

2. Material and methods

2.1. Samples preparation

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

1. An organic fraction from a municipal solid waste, obtained from a landfill in Seville (Spain). This fraction was subjected to a size reduction of 1–3 mm. This sample will be labelled as MSW.
2. An organic fraction from a municipal solid waste, dried and partially cleaned from inerts. This fraction was taken from the previous fraction (MSW) and subjected to removal of moisture and inert solids, such as glass or metals. After this pre-treatment, the fraction size was reduced to 1–3 mm. This sample will be labelled as MSWd.
3. A plastic fraction from a municipal solid waste. This sample, a complex mixture of plastic residues, was obtained from the same landfill in Seville. The fraction was milled to 1–3 mm and will be labelled as PLA.
4. 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 to a size range of 1–3 mm. This sample will be labelled as STR.
5. 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 to a size range of 1–3 mm. This sample will be labelled as SSd.

2.2. Analysis of the samples

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 micro-analyzer provides carbon, hydrogen, nitrogen, and sulfur percentage composition. The oxygen content was determined from the LECO-TF-900 furnace. The content of metals from the ashes was determined by means of atomic absorption spectroscopy using an Agilent 7700x. The