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

D. Beneroso, J.M. Bermúdez, A. Arenillas, J.A. Menéndez*

Instituto Nacional del Carbón, CSIC, Apartado 73, 33080 Oviedo, Spain

* Corresponding author. Tel.: +34 985 118972; Fax: +34 985 297672

E-mail address: angelmd@incar.csic.es

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 + H₂ 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.

Keywords

Bioplastics, Polyhydroxyalkanoates, Syngas fermentation, Microwave pyrolysis, Waste valorization

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

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 $\text{CO} + \text{H}_2 + \text{CO}_2$. Syngas fermentation has been 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 H₂S 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.

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

Advantages	Drawbacks
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 ₂ S 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]	

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.

Fig. 1. Integrated microwave pyrolysis for the polyhydroxyalkanoates production process through syngas fermentation.

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 1. An organic fraction from a municipal solid waste, obtained from a landfill in
2 Seville (Spain). This fraction was subjected to a size reduction of 1-3 mm. This
3 sample will be labelled as MSW.
- 4 2. An organic fraction from a municipal solid waste, dried and partially cleaned
5 from inerts. This fraction was taken from the previous fraction (MSW) and
6 subjected to removal of moisture and inert solids, such as glass or metals. After
7 this pre-treatment, the fraction size was reduced to 1-3 mm. This sample will be
8 labelled as MSWd.
- 9 3. A plastic fraction from a municipal solid waste. This sample, a complex mixture
10 of plastic residues, was obtained from the same landfill in Seville. The fraction
11 was milled to 1-3 mm and will be labelled as PLA.
- 12 4. An agricultural residue. This sample was obtained from a biodiesel production
13 plant located in Salamanca (Spain) and is composed of straw. The sample was
14 also milled to a size range of 1-3 mm. This sample will be labelled as STR.
- 15 5. Dried sewage sludge. This sample was collected from a wastewater plant in
16 Seville. The sludge after being subjected to secondary treatment was dried to
17 facilitate transportation. After being dried, the sample was milled to a size range
18 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 results from this characterization are presented in Table 2. The TGA and DTGA profiles were obtained using a SDTQ600 Thermobalance (provided by TA Instruments) using a flowrate of N₂ of 20 mL/min with a heating rate of 10 °C/min up to 1000 °C. The thermogravimetric behavior of the residues is shown in the Supplementary Data (see Fig S1-S5).

Table 2. Proximate and ultimate analyses of the different residues. Content of metals of the ashes.

Residue		Municipal solid waste - Organic fraction	Municipal solid waste – Dried&Clean organic fraction	Municipal solid waste - Plastic fraction	Straw	Sewage sludge (dried)
Label		MSW	MSWd	PLA	STR	SSd
Proximate analysis (wt.%)	Moisture	46.3	2.8	1.3	11.5	3.4
	Ash ^a	22.6	27.7	8.9	6.3	15.4
	Volatile matter ^a	68.0	61.1	88.9	76.2	74.5
Ultimate analysis (wt.%)	C	36.0	45.1	70.9	45.0	43.8
	H	5.8	5.4	9.7	5.0	6.1
	N	1.6	2.1	1.2	1.6	9.7
	S	0.2	0.4	0.5	0.0	0.1
	O	33.8	19.3	9.1	42.0	24.9
Content of metals (ppm)	Cu	24.6	44.8	50.8	0.00	153.4
	Cd	<0.1	<0.1	<0.1	0.41	2.0
	Mn	13.5	83.0	18.8	18.3	40.4
	Zn	100.5	182.9	73.2	6.6	459.8
	Fe	4880.1	8896.3	1098.8	286.9	2984.6
	Pb	17.1	30.8	4.7	<0.1	1.6
	Cr	32.0	58.7	72.5	0.0	11.7
	Ni	9.6	17.6	24.7	<0.1	2.8
	Tl	<0.1	<0.1	<0.1	0.0	0.0

^a Dry basis

2.3 Conventional pyrolysis of samples

Conventional pyrolysis was performed at two different temperatures (400 and 800 °C) in the electric furnace (EF) shown in Fig. 2a. Approximately 4 g of sample was introduced into a quartz reactor. First, the reactor was placed outside the EF and was purged with N₂ for 30 minutes at a flow rate of 50 mL_{STP} min⁻¹ to ensure an oxygen-free atmosphere. Meanwhile, the EF was heated up to the pyrolysis temperature. Once the reactor had been purged and the EF had reached the desired temperature, the N₂ flow was reduced to 10 mL_{STP} min⁻¹ and the reactor was introduced into the EF for pyrolysis, the duration of which was 1 hour. The gases 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. Then, the gaseous fraction was collected in a Tedlar® bag and analysed by means of a Varian-CP3800 gas-chromatograph equipped with a TCD detector and two columns connected in series. The first column was 80/100 Hayesep Q (2 m x 1/8 in. x 2mm) and the second column was a 80/100 Molesieve 13X (1.5 m x 1/8 in. x 2 mm). The second column was bypassed by a six-port valve for the analysis of the CO₂ and hydrocarbons. The carrier gas flow (He) was 30 mL/min. The initial oven temperature was set at 40 °C, which was maintained for 1.2 min. It was then programmed to rise from 40 to 65 °C at 50 °C/min with an isothermic step of 3.3 min. The temperature was then lowered from 65 to 55 °C at 20 °C/min and held for 2.6 min. The injector and detector temperatures were fixed at 150 °C. The TCD was calibrated using a standard gas mixture.

Fig. 2. Experimental set-up used: a) Conventional pyrolysis; b) Microwave-induced pyrolysis.

2.4 Microwave-induced pyrolysis of samples

Microwave-induced pyrolysis (MIP) was performed using the microwave oven shown in Fig. 2b. This system provided by MES (*Microondes Énergie Systèmes*) consists 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 the conventional pyrolysis, the reactor was purged with N_2 for 30 minutes at a flow rate

of 50 mL_{STP} min⁻¹. Then, the flow rate was reduced to 10 mL_{STP} min⁻¹ and the microwave irradiation was switched on during 1 h. The reflected power was regulated by means of tuning screws until it reached zero. The same system as that used in conventional pyrolysis, was used to collect the liquid and gaseous fractions. Owing to the low capacity of organic wastes used in this study to absorb microwaves, it was necessary to use a microwave receptor to induce the pyrolysis [27]. After the microwaves started to pass through the sample, they are absorbed by the receptor and the temperature increases. This allows the heat to be conducted to the waste until a temperature high enough to start the pyrolysis is reached. As the pyrolysis proceeds, the waste is carbonized and is then able to absorb microwaves, so that from that point on it can be directly heated by microwave radiation. The most appropriate material for use as microwave receptor is the char obtained from the previous pyrolysis, since it is a product of the process itself and does not contain any strange material that might influence the composition of the fractions. Nevertheless, other microwave receptor materials, such as SiC, CaO or activated carbons, could be used influencing pyrolysis reactions [32]. For this study, a *receptor – to – dry feedstock* mass ratio of 0.3:1 was selected. This ratio was selected after several preliminary experiments, which showed that this was the lowest ratio that would allow the biomass to be heated to the desired temperature while avoiding the thermal runaway effect which could result from microwave heating [27]. The experiments were performed in duplicate to check the repeatability. The errors came to less than 3% for the gas composition and less than 6% for the yields.

3. Results and Discussion

3.1 Conventional vs. Microwave-induced pyrolysis

Fig.3 shows the specific yields from the three fractions obtained in the pyrolysis at 400 and 800 °C by conventional and microwave-induced pyrolysis. Some general trends can be clearly observed, although they are more pronounced at 400 °C than at 800 °C.

Fig. 3. Fraction yields (wt.%) from the conventional (EF) and microwave-induced (MW) pyrolysis of the different residues at: (a) 400 °C; and (b) 800 °C.

Table 3. Composition of the gaseous fraction (vol.%) obtained in the conventional and microwave-induced pyrolysis of the different residues.

400 °C										
	MSW	Conventional				MSW	Microwave			
		MSWd	PLA	STR	SSd		MSWd	PLA	STR	SSd
H ₂	0.0	0.0	0.0	0.0	0.0	51.4	46.2	9.1	32.4	21.3
CO	20.3	16.3	7.3	30.1	6.6	23.3	33.3	8.8	23.6	15.4
CO ₂	48.8	37.9	28.2	48.5	47.0	19.0	11.0	14.8	33.2	22.4
Syngas	69.1	54.2	35.5	78.6	53.6	93.7	90.5	32.7	89.2	59.1
CH ₄	1.2	1.1	1.2	2.2	3.0	3.9	5.1	14.1	8.6	12.9
C ₂	1.0	0.7	3.2	0.9	1.7	2.4	4.4	23.8	2.3	8.1
Other*	28.7	44.0	60.1	18.3	41.7	0.0	0.0	29.5	0.0	20.0
H ₂ /CO	0.00	0.00	0.00	0.00	0.00	2.21	1.39	1.03	1.37	1.38
CO/CO ₂	0.42	0.43	0.26	0.62	0.14	1.23	3.03	0.59	0.71	0.69

800 °C										
	MSW	Conventional				MSW	Microwave			
		MSWd	PLA	STR	SSd		MSWd	PLA	STR	SSd
H ₂	22.4	21.4	9.2	19.8	15.8	47.6	50.4	26.6	49.1	48.2
CO	24.3	25.6	9.6	31.1	18.1	33.7	36.2	11.5	37.4	22.6
CO ₂	23.9	25.5	11.3	28.9	17.6	13.6	8.0	8.1	8.7	15.2
Syngas	70.6	72.5	30.1	79.8	51.5	94.9	94.6	46.2	95.2	86.0
CH ₄	11.2	12.7	20.3	13.0	20.7	3.1	3.3	20.0	3.7	8.1
C ₂	8.9	8.5	26.0	2.9	12.3	2.0	2.3	17.5	1.2	5.9
Other*	9.2	6.3	23.7	4.2	14.4	0.0	0.0	16.3	0.0	0.0
H ₂ /CO	0.92	0.84	0.96	0.64	0.87	1.41	1.39	2.31	1.31	2.13
CO/CO ₂	1.02	1.00	0.85	1.08	1.03	2.48	4.53	1.42	4.30	1.49

* Higher hydrocarbons (C₃, C₄, >C₄) and aromatics

MIP enhances the gas production whereas the production of liquid is reduced in almost all cases. At 400 °C, MIP gives rise to greater gas yields than conventional pyrolysis. These consist of a percent increase from 42% in the case of SSd to more than 100% in the case of MSW and MSWd. The liquid yields are lower from MIP, with the exception of SSd and PLA. These wastes contain a larger amount of volatiles that are released at temperatures slightly higher than 400 °C compared to the other residues (see Fig. S1-S5 of ESI). Such volatiles can be removed from SSd and PLA by means of microwave heating but not by conventional heating and hence the liquid yield is increased. This ability of microwave heating to promote processes occurring at temperatures higher than the operating temperature is due to the presence of microplasmas [33,34]. These microplasmas are sparks or hot spots that last just a fraction of second and reach temperatures considerably superior to the mean temperature of the material, which remains at the operating temperature. However, temperature measurement of microplasmas is a very complex issue, although this temperature must be high enough to allow for such high H₂ and CO concentrations observed in the gas fraction during MIP as shown in Table 3. This phenomenon resembles what occurs in a *lightning storm*, where the rays achieve an extremely high temperature without affecting the mean temperature of the atmosphere. For this reason, microwave heating is able to extract higher amounts of volatiles [24,25,27]. These volatiles are recovered in the liquid fraction since temperatures are not high enough for further cracking into gaseous products. In the case of the MSW, although there is a small decrease in liquid production when microwave heating is used, the liquid yields are very similar in both heating devices and considerably higher than in the other wastes. This is due to the high moisture content, which mainly accumulates as water within the liquid fraction. Finally, the solid yields are lower in the MIP than in the conventional pyrolysis in all the wastes

[26]. As previously mentioned, the reason for this is that at 400 °C microwaves are able to extract more volatiles than conventional heating, but cracking reactions are only slightly promoted, as a result of which only a small amount of coke is produced (Table 4, reactions 1 and 2).

Table 4. Main chemical reactions involved in pyrolysis.

Number	Reaction	$\Delta H_{298\text{ K}}$ (kJ mol ⁻¹)
1	$\text{CH}_4 \leftrightarrow \text{C} + 2 \text{H}_2$	76
2	$\text{C}_n\text{H}_m \leftrightarrow n \text{C} + (m/2) \text{H}_2$	
3	$\text{C}_2\text{H}_6 \leftrightarrow \text{C}_2\text{H}_4 + \text{H}_2$	136
4	$\text{CH}_4 + \text{CO}_2 \leftrightarrow 2 \text{H}_2 + 2 \text{CO}$	247
5	$\text{CH}_4 + \text{H}_2\text{O} \leftrightarrow 3 \text{H}_2 + \text{CO}$	205
6	$\text{C}_n\text{H}_m + n \text{H}_2\text{O} \leftrightarrow n \text{CO} + (n + m/2) \text{H}_2$	
7	$\text{C}_n\text{H}_m + n \text{CO}_2 \leftrightarrow 2n \text{CO} + (n/2) \text{H}_2$	
8	$\text{C} + \text{CO}_2 \leftrightarrow 2 \text{CO}$	173
9	$\text{C} + \text{H}_2\text{O} \leftrightarrow \text{CO} + \text{H}_2$	131
10	$\text{C} + 2 \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + 2 \text{H}_2$	90

At 800 °C, the differences between both heating devices are not as great and, in some cases, the yields do not follow the same trends as in the experiments at 400 °C. In the case of the gas yields, some of the wastes show similar levels of gas production in both devices (MSW and SSd), which may even be lower in the MIP than in conventional pyrolysis (PLA). From the results in Table 3, it can be seen that in these cases (MSW, SSd and PLA), the gases produced in the electric furnace have considerable amounts of hydrocarbons (CH_4 , C_2 and $>\text{C}_2$). These compounds, under microwave heating, can be easily cracked into smaller hydrocarbons and coke (Table 4, reactions 1 and 2). Thus, a large amount of the gases that are produced in the EF, especially from these hydrocarbons, is deposited as coke, but to a much lesser extent than with microwave

heating, which favors the formation of light gases (especially H_2 and CO). As a result, coke production from these cracking reactions leads to higher solid yields. However, the increase in the solid yield is also a consequence of the cracking of the liquid fraction compounds, so that the liquid fraction yield decreases in all cases. Only MSW (due to its high water content) and SSd show similar levels of liquid productions in MIP and conventional pyrolysis (Fig. 3). However, it is important to bear in mind that these yields are expressed in mass terms. Nevertheless, gas volumetric production (which depends on the gas yield and composition) increases in the MIP regardless of the residue and the temperature used.

The most remarkable differences between MIP and conventional pyrolysis are to be seen in the composition of the gas fractions (Table 3). Conventional pyrolysis does not produce H_2 at low temperatures (400 °C), whereas MIP is able to produce it in high concentrations at both of the temperatures. Moreover, in conventional pyrolysis, the maximum H_2 concentration achieved is ca. 20% in the case of MSW and MSWd at 800 °C. In the case of MIP, the lowest H_2 value achieved is slightly higher than 20%, in the pyrolysis of SSd at 400 °C (with the exception of PLA, which gave the worst results irrespective of the temperature and heating device used to produce the syngas; being this due to the nature of this substrate, which is mainly composed of polymeric carbon chains with lower H/C and O/C molar ratios compared to the other residues). In terms of syngas concentration (being the sum of H_2 , CO and CO_2 concentrations, which are the gases involved in fermentation processes), the results are even more favorable to MIP. As can be seen, MIP gives rise to syngas concentrations above 90 vol.% in many cases, even at 400 °C. Only in the case of plastics pyrolysis, is the syngas concentration value really low for both heating devices (30-35% in the case of conventional pyrolysis

and 32-46% in the case of MIP). Furthermore, owing to the high proportions of other compounds (CH_4 , C_2 , higher hydrocarbons and aromatics) which may damage the bacteria and inhibit the fermentation process [35], the plastic fraction from municipal solid waste can be discarded as substrate for this process. Here, MIP offers a significant advantage over conventional pyrolysis, since it is able to minimize the presence of these compounds within the gas fractions, which will favour a higher quality syngas available for fermentation with the exception of using plastic waste.

The H_2/CO and CO/CO_2 ratios of the gas fractions obtained are also shown in Table 3. The values of these parameters reveal that MIP promotes the generation of H_2 and CO over CO_2 . As can be seen, these ratios are higher in microwave heating than in conventional heating.

Nevertheless, it is not only necessary to consider the composition of the gas fraction in applying pyrolysis to bioplastics production via syngas fermentation [23], but also the production of the key gases (H_2 , CO , CO_2) for it is one of the parameters that determines the effectiveness of these materials as substrates for the pyrolysis. The results of the specific productions ($\text{L}_{\text{STP}} \text{g}^{-1}$ of residue pyrolysed) of H_2 , CO , CO_2 , syngas and total gas (including all the gaseous compounds) are shown in Table 5. As mentioned above, the volumetric production of gas in MIP is higher than in conventional pyrolysis in all cases. This is due to the fact that MIP favors the production of lighter gases, such as H_2 and CO , due to cracking reactions, dehydrogenating reactions (Table 4, reaction 3), reforming reactions (Table 4, reactions 4-7) and gasification processes (Table 4, reactions 8-10), where CH_4 , CO_2 , the carbonaceous matter and steam are converted to lighter products. As already mentioned,

the differences between MIP and conventional heating are apparent even at 400 °C, the production of syngas in MIP being as much as ten times higher than in the case of conventional heating. This is mainly due to the large amounts of H₂ produced by means of MIP, even at low temperatures. At 800 °C, the gap, although still wide, narrows, the syngas production in MIP being between 75 and 180% higher than in conventional heating.

In view of these results, it is clear that microwave-induced pyrolysis is a quite good technique for generating syngas from wastes without the need of a gasifying agent, as would be necessary in the case of other technologies such as gasification. This method is bound to increase the production of the key gases necessary for syngas fermentation (H₂, CO and CO₂) and PHA production.

Table 5. H₂, CO, CO₂, syngas and total gas productions (on a dry basis) in the conventional and microwave-induced pyrolysis of the different residues.

400 °C											
		Conventional					Microwave				
		MSW	MSWd	PLA	STR	SSd	MSW	MSWd	PLA	STR	SSd
Productions (L _{STP} /g _{waste})	H ₂	0.00	0.00	0.00	0.00	0.00	0.07	0.17	0.02	0.16	0.05
	CO	0.00	0.01	0.00	0.05	0.01	0.03	0.12	0.02	0.11	0.03
	CO ₂	0.01	0.02	0.01	0.08	0.04	0.03	0.04	0.04	0.17	0.05
	Syngas	0.01	0.03	0.02	0.13	0.04	0.13	0.33	0.09	0.44	0.13
	Total gas	0.02	0.04	0.05	0.16	0.08	0.14	0.36	0.26	0.50	0.22
800 °C											
		Conventional					Microwave				
		MSW	MSWd	PLA	STR	SSd	MSW	MSWd	PLA	STR	SSd
Productions (L _{STP} /g _{waste})	H ₂	0.08	0.07	0.04	0.07	0.05	0.23	0.34	0.13	0.43	0.21
	CO	0.09	0.08	0.04	0.11	0.06	0.16	0.25	0.06	0.33	0.10
	CO ₂	0.09	0.08	0.05	0.10	0.05	0.07	0.05	0.04	0.08	0.07
	Syngas	0.26	0.24	0.13	0.30	0.16	0.46	0.64	0.23	0.83	0.37
	Total gas	0.36	0.32	0.43	0.40	0.31	0.48	0.68	0.50	0.88	0.43

3.2 Applicability of syngas to bioplastics production

Great efforts are being made to metabolically engineer bacteria to produce a broad variety of bulk chemicals, bioplastics and biofuels [36,37] and to extend the use of substrates in the area of R&D bacterial fermentation. Researchers are strongly in favour of syngas fermentation for bioplastics production [21,38], but to date very few studies on syngas-derived biopolymers have been published. It has been widely claimed that, even though biological catalysts use a wide range of syngas H_2/CO ratios, they retain their product specificity [39]. Therefore, the syngas production process needs to be focused on the most effective means of conversion in terms of energy efficiency and production.

From the point of view of energy efficiency, it has been observed that the scaling-up of microwave-heated processes from lab to kilogram scale can be more energy efficient than conventionally heated systems [30,40]. In particular, high-temperature processing, such as pyrolysis, using powerful magnetrons over an optimized frequency range appears to be very promising. Indeed, *Scandinavian Biofuel Company* has already taken out a patent to perform microwave-induced pyrolysis on an industrial scale [41].

From the point of view of production, Fig. 4a evidences the superiority of MIP in terms of syngas yield, especially in the case of the STR and MSWd substrates, whose maximum values are 0.83 and 0.64 $L_{STP} g^{-1}_{waste}$ respectively. Moreover, MIP offers a wider variety since the conventional pyrolysis yields only range from 0.01 to 0.26 $L_{STP} g^{-1}_{waste}$. Although conventional pyrolysis yields a syngas composition that is richer in carbon (i.e., low values of $H_2/(CO+CO_2)$ ratio), it is important to note that the largest part is CO_2 , whereas CO is normally the preferred substrate for fermentation [21,22,42].

In this respect, MIP improves CO production and the $H_2/(CO+CO_2)$ ratio may even get to be higher than 1, so that the H_2 production would be greater than that of carbon oxides, except in the case of STR. However, neither of the organic fractions from municipal solid waste (MSW and MSWd) produce more carbon substrate ($CO+CO_2$) than H_2 in MIP.

As can be seen from Fig. 4b, microwave pyrolysis offers a wider range of syngas compositions, although it is not possible to produce syngas with H_2/CO ratios lower than 1. If necessary, conventional pyrolysis can be employed despite the serious drawback of undesired compounds (hydrocarbons and aromatics). In fact, if H_2/CO ratios greater than 1 are used for syngas fermentation, as in microwave-induced pyrolysis, an excess of hydrogen may be the result. This, however, is a highly valuable chemical that does not greatly affect the fermentation process. Indeed, in a study by *Do et al.*, *Rhodospirillum rubrum* was cultivated on syngas to produce PHA (with ratios of $H_2/CO = 0.5$ and $CO/CO_2 = 1.1$) [22]. This gas composition was based on a typical stream from an air-blown gasifier, and therefore had not been optimized for PHA production. *R. rubrum* metabolized CO as the only substrate and produced H_2 via the biocatalytic water-gas shift reaction ($CO + H_2O \rightleftharpoons CO_2 + H_2$) in addition to the H_2 from the syngas fed to the bioreactor. However, this should be considered an advantage, as H_2 produced by a biorefinery is a co-product that has a high market value [23].

In spite of the repeated calls in the literature for a syngas H_2/CO ratio independent of biocatalytic processes, there is some controversy surrounding this issue. *Heiskanen et al.* studied the effect of the syngas composition on *Butyribacterium methylotrophicum* [43]. The addition of hydrogen was reported to increase the formation of useful chemicals, such as butyric acid from *B. methylotrophicum*. In their study, they used a

mixture of $H_2/CO/CO_2$ in ratios of $H_2/CO = 1.1$ and $CO/CO_2 = 1.4$, and found that *B. metylotrophicum* preferentially uses most of the CO before consuming hydrogen as reported in another study with *Eubacterium limosum* [44]. This suggests that CO_2 was not indispensable to the growth of bacteria on CO, but increased the initial growth rates of *B. metylotrophicum*, and was converted to valuable organic products in the presence of H_2 once the CO concentration reached a low enough level. Thus, the subsequent uptake of these gases should be taken into account when designing the fermentation process. In addition, Vega *et al.* reported the growth of *Peptostreptococcus productus* (strain U-1) on CO and CO_2/H_2 to produce acetate and found that its growth on CO_2/H_2 could not be sustained, but when CO_2 and H_2 were fed together with CO, with the resulting change in H_2/CO ratio, they contributed to the production of acetate [45]. This suggests that the composition of the syngas has an effect on the growth rate and on the products obtained from fermentation.

Whatever the case, CO is by far the most important carbon source from syngas to be used by bacteria [21] and, clearly, microwave-induced pyrolysis can provide the level of CO required by offering CO/CO_2 ratios from 0.6 to 4.5, whereas conventional pyrolysis can only offer a range of 0.1 to 1.1 (Fig. 4b). Furthermore, as previously indicated, the use of microwaves allows the potential destruction of components that may be toxic to the bacteria. This is a very important advantage, since the need to remove these compounds prior to syngas use will increase the production costs that can be avoided with microwave-induced pyrolysis.

Fig. 4. (a) Syngas production versus H₂/(CO+CO₂) ratio and (b) CO/CO₂ ratio versus H₂/CO ratio of the gas produced in the conventional (EF) and microwave-induced (MW) pyrolysis of the different wastes studied.

Therefore, optimization of the syngas composition should be evaluated on a case-by-case basis by metabolic engineers for possible further bioplastics synthesis, bearing in mind that microwave-derived syngas offers overwhelming advantages over traditional methods of syngas production.

4. Conclusions

Syngas fermentation is attracting widespread interest for implementation in biorefineries and great efforts are being made to metabolically engineer microorganisms for the production of specifically targeted chemicals. Organic waste has been demonstrated to have the potential for producing a high quality syngas when microwave-induced pyrolysis is used as the main thermochemical route. CO has been found to be the main carbon substrate for fermentation by bacteria and the microwave heating to be the most efficient means of producing a syngas with high CO/CO₂ ratios, which are even greater than 4 when straw and the organic fraction of municipal solid waste (dried and partially cleaned of inert solids) are used. The plastics fraction of the municipal solid waste has been found to be unsuitable for syngas production, since its fossil-based nature leads to significant amounts of hydrocarbons and aromatics in the composition of the gas produced, which can be highly damaging to the bacteria. Except in this case, microwaves have been demonstrated to drastically reduce the hydrocarbons and aromatics content of the syngas produced. Furthermore, the gas obtained from microwave pyrolysis contains exceptionally high H₂ concentrations, which amount to 49 vol.% in the case of straw pyrolysis. This H₂ could be used by bacteria as an energy source or remain as a valuable by-product for future use. To sum up, microwave-induced pyrolysis has been confirmed to be a highly useful technology for producing

syngas for use as in the production of bioplastics, due to its high gas production potential, high syngas concentration and low proportion of toxic compounds.

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