New concept for syngas production: Microwave-induced cracking of pyrolytic tars coupled to microwave pyrolysis

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Abstract

Herein we propose a new process to produce a syngas-rich gas fraction (>80 vol% H₂+CO) from biowaste based on microwave heating within two differentiated steps in order to avoid tars production. The first step consists of the microwave pyrolysis of biowaste induced by a char-based susceptor at 400 – 800 °C; tars, char and syngas-rich gas fractions being produced. The tars are then fed into the second step where a portion of the char from the first step is used as a bed material in a 0.3:1 wt% ratio. This bed is heated up by microwaves up to 800 °C, allowing thermal cracking of tars and additional syngas (>90 vol% H₂+CO) being then produced. This new concept arises as an alternative technology to the gasification of biowastes for producing syngas, in addition to the provided advantages, such as the fact that neither catalysts nor gasifying reagents need to eliminate tars production.

Keywords

Microwave pyrolysis, Syngas production, Tar reduction, Emerging technologies, Energy consumption

1. Introduction

Fossil fuels continue to be the primary source for power generation despite the social concern on the climate change. The development of competitive technologies based on renewable sources have then become imperative to partially satisfy the production of sustainable fuels and chemicals (Lee & Den, 2016; Scarlat et al., 2015). Gasification technology is going to play a key role in the development of this strategy in the short and medium term. This technology is based on a complex physiochemical transformation of biomass which begins with a pyrolysis step - thermal degradation of the organic matter yielding a solid fraction (char), a liquid fraction (tar) and a gas fraction - that is then followed by the gasification of char and the reforming and cracking of tars and light hydrocarbons from the gas fraction by using a gasifying component, such as steam or oxygen. As a consequence, gasification yields a gaseous fraction with a high content in syngas ($H_2 + CO$) and a residual solid stream mainly formed by inorganic ashes.

One of the main problems this technology faces when processing biomass is the generation of a large amounts of tars. This fraction is a complex mixture of organic chemicals often containing hazardous compounds for health and the environment which can cause fouling in downstream units and the deactivation of catalysts in subsequent processes in which syngas is used (Beneroso et al., 2015a; Devi et al., 2003; Han & Kim, 2008). The removal of tars is undoubtedly one of the biggest challenges for biomass gasification, since its cost can knock down a whole project (Balat & Kırtay, 2010; Bermúdez & Fidalgo, Forthcoming; Huber et al., 2006; Navarro et al., 2007). Consequently, research efforts in this field are being focused on the exploration of

processes tackling the problem of tars production. A number of studies have proposed different possibilities for reducing the production of such tars or even processing them (Anis & Zainal, 2011; Neubauer, 2011). Generally, tar reduction can be accomplished using primary or secondary measures (Bermúdez & Fidalgo, Forthcoming). Primary measures are based on *in-situ* operations, i.e. by reducing tar generation in the reactor itself; for instance, by using staged gasification systems, catalytic active bed materials or applying extremely high temperatures (entrained flow gasification or plasma gasification). Secondary measures are based on downstream tar removal procedures; e.g., catalytic reformer reactors, gas washing operations or adsorption.

Microwave pyrolysis has emerged as an alternative to gasification of biomass and biowastes without the need for gasifying reagents as demonstrated within a large number of studies in the literature (Beneroso et al., 2016; Beneroso et al., 2015b; Beneroso et al., 2015c; Beneroso et al., 2014; Bhattacharya & Basak, 2016; Xie et al., 2014; Zhang et al., 2016; Zhao et al., 2010). The control of key parameters (mainly, the microwave power and temperature) has made possible to produce a high purity syngas fraction with low amounts of tars.

Nevertheless, yet presence of tars can be realised. In this work, we propose a new integrated approach for the removal of undesired tars produced during biomass pyrolysis. This approach allows the complete conversion of these tars into a rich-syngas fraction (from now on, syngas) by using a fixed-bed process in which the bed material is rapidly heated by microwave radiation up to 800 °C. To the best of our knowledge, there is no work in the literature using a similar method to convert such tars.

2. Experimental

The basis of this new process design is a series of batch experiments carried out at lab scale with 5 g of biowaste per batch. The biowaste used for this study was an organic fraction from municipal solid waste, obtained from a landfill in Seville (Spain). The waste was dried, partially cleaned of inerts such as glass or metals and size-reduced to 1-3 mm. The biowaste properties are reported in Table 1. A schematic diagram of the lab device is represented in Figure 1. Microwave-Induced Pyrolysis (MIP from now on) of biowastes was performed at a controlled temperature of 400 or 800 °C during 30 min. This system consists of a microwave magnetron with a maximum output power of 2 kW operating at 2450 MHz and a unimode cavity where the sample is placed into a quartz reactor, coupled to a condenser, where tars are collected, and a Tedlar bag for collecting the gas produced. Nitrogen was used as carrier gas to ensure an oxidising-free atmosphere. It was necessary to use a microwave susceptor material to reach the pyrolysis temperature because of the low capacity of organic wastes to absorb microwaves. To this end, the char obtained from previous pyrolysis was used in a 0.3:1 wt% ratio susceptor:biowaste ratio. Details of the tars and gas collection and analysis as well as the fraction yields calculation have been previously reported (Beneroso et al., 2015b).

TABLE 1

MIP of tars was performed at 800 °C in the same experimental device as MIP of biowastes during 15 min. The char obtained from previous pyrolysis was used as bed

material (approx. 10 cm height). In this case, 4 g of tar were deposited at the bottom of the quartz reactor and the bed material was placed on top of it, ensuring a 0.3:1 wt% tar:char ratio. Additional 0.4:1 and 0.6:1 ratios were also tested. The same system for collecting the gas applied in these experiments.

FIGURE 1

3. Results and Discussion

3.1. Process flowsheet proposal

The results from batch experiments were used to propose a new process flowsheet where syngas and carbonaceous char are the only products (Figure 2). Essentially, this process has two key steps: (i) MIP of biowaste, where biowaste (S-1) and char (S-7) are fed into a microwave cavity and different fractions are produced (char (S-2) and volatiles (S-3)). Volatiles are then passed through a condenser to separate condensables, known as tars (S-5), and incondensable syngas (S-4), i.e. > 80vol% H₂+CO; and (ii) MIP of tars, where tars (S-5) are thermally cracked into deposited coke and another syngas fraction (S-6) by the action of microwaves within a char fixed bed coming from the first step of the process (S-9). As a result, two different gas fractions (*gas1* and *gas2*) which could be further mixed (*gas3*) are obtained. Furthermore, two different char fractions (*solid1* and *solid2*) which could be further mixed (*solid3*) are also obtained. This approach enables the complete removal of tars at the time that the syngas production is increased without the need for catalysts or external gasifying agents, such as oxygen, air or steam. Of special interest is this second step of the MIP-MIP process as no previous works have been performed for processing tars through microwave-

1 heated fixed-bed technology to date. Only a study on toluene cracking as tar model
2 compound has been performed (Li et al., 2016). In that study, biomass-derived char was
3 utilised as a catalyst for toluene cracking. At 750 °C, toluene microwave cracking
4 approached the highest conversion of 92.8%, reaching a difference of 15.6% over
5 conventional heating.

6 7 **FIGURE 2**

8 9 **3.2. Mass balances of the MIP-MIP process**

10 Two different scenarios are then proposed depending on the pyrolysis temperature
11 during the first step: Scenario 1 (400 °C) and Scenario 2 (800 °C). All streams have been
12 normalised to 1 kg basis of processed biowaste. The mass balances are shown in Figure
13 3. These were calculated on the basis of the experimental yields from MIP of biowaste
14 and MIP of tars subject to the constraints detailed in the previous section. Tar:char
15 ratios higher than 0.3:1 wt% ratio lead to the incomplete cracking of tars as observed
16 during additional experiments using 0.4:1 and 0.6:1 ratios (not shown), so it is of
17 extreme importance to keep this ratio at its minimum as this will ensure enough
18 residence time for the tar-derived vapours along the fixed bed to be cracked.

19 20 **FIGURE 3**

21
22 Both scenarios highlight the possibility of efficiently treating biowaste for producing
23 syngas without any oily tars as subproduct. Nevertheless, Scenario 2 maximises the
24 production of syngas due to the more intense biomass degradation and gasification

reactions taking place at higher temperature (800 °C) (Beneroso et al., 2015b; Beneroso et al., 2015c; Beneroso et al., 2014). It is well known that microwave heating of carbonaceous materials at such temperatures promotes the appearance of *microplasmas* (Menéndez et al., 2011). These plasmas have a *pseudo*-catalytic effect within the bulk and favour the heterogeneous reactions (i) between the char and evolved gases, such as the *Boudouard* equilibrium $C + CO_2 = 2 CO$ or the water gas reaction $C + H_2O = H_2 + CO$; and (ii) hydrocarbon decomposition, such as $CH_4 = C + H_2$. This is the reason why higher amounts of H_2 and CO are produced at a higher temperature. Furthermore, such temperature reduces the production of tars from 0.13 kg to 0.08 kg, so that a lesser amount of syngas is generated in the second step as compared to that from Scenario 1. Regardless of the scenario, the gas stream from the second step, *gas2*, yields larger quantities of H_2 and minimised hydrocarbon concentrations compared to *gas1*.

3.3. Energy Costs for Syngas Production

Table 2 shows the energy expenditure to perform MIP of biowaste and MIP of tars at lab-scale along with the estimated values during the scale-up of the specific process. To this end, a simple method to estimate the energy consumption from lab-scale experiments, wherein low amounts of sample are generally used, has been applied (Bermúdez et al., 2015). Particularly, the model for high temperature heating of carbon materials was chosen as this is the most appropriate for pyrolysis processes. This corrective calculation is imperative in order to avoid overestimated energy values for driving the process owing to the larger heat losses to the environment and reflected power at low sample mass.

TABLE 2

To determine the energy consumption of the whole MIP-MIP process to produce 1 m³ of syngas, the production and composition of the *gas3* stream was determined from the density and composition of *gas1* and *gas2* streams and results are shown in Table 3. Figure 4 depicts the trade-off between the energy consumption of the two steps of the MIP-MIP process to produce 1 m³ of syngas and the volumetric energy contained within the produced gas fraction, which has been calculated taking into account the heat of combustion of every single gas component. Both scenarios provide a gas with approximately the same energy content (ca. 3.75 kWh/m³). However, the energy consumption is 14% higher if Scenario 2 is used as the energy necessary to achieve 800 °C for MIP of biowaste in the first step is much higher, although the production of syngas is 1.5 times higher.

FIGURE 4

TABLE 3

Besides, Scenario 1 provides a gas whose energy content is 85% of the energy consumption but Scenario 2 provides a gas whose energy content is 75% of the energy consumption. Nevertheless, considering the energy contained in the char produced can compensate the energy consumption of the whole process. This enables to establish the optimum operational conditions, between 400 °C, as MIP of biowaste began to take place at temperatures nearly to 400 °C; and 800 °C, as the energy cost would be extremely high.

Table 4 shows the energy consumption of the MIP-MIP process in comparison with other syngas generation technologies. Conventional like steam reforming, autothermal reforming or partial oxidation of methane present energetic consumptions quite lower than MIP-MIP. Moreover, in the case of autothermal reforming and partial oxidation, the energy consumption is one and two orders of magnitude lower. However, this is not an even comparison. Reforming and partial oxidation use methane (or other hydrocarbons) as feedstock. These feedstocks need to be previously produced from biomass (once discarded fossil fuels like natural gas). The generation of these hydrocarbons entails an energy cost that can vary a lot depending on the technology applied. In addition, both reforming and partial oxidation need the use of external agents such as oxygen or steam and, especially, catalysts. Furthermore, an exhaustive care must be taken to avoid catalyst deactivation; for instance, a higher steam/C ratio is usually required to drive the steam-methane reforming in order to avoid coke deposition onto the catalyst surface. In addition, char combustor and reformer reactors are usually required (Han & Kim, 2008; Neubauer, 2011). Very few studies have focused on the energy consumption of microwave pyrolysis of biomass as an alternative to conventional syngas production technologies. X. Zhao *et al.* reported such outcome from microwave pyrolysis of wheat and corn straw (see Table 4) (Zhao et al., 2010). In spite of producing large amounts of syngas at a lower energy consumption than that found out within the MIP-MIP process, yet the tar yield was large (between 32 - 35 wt.%). Comparable outcomes to those from microwave pyrolysis of straw can be derived from the data in Table 2 and are also shown in Table 4. These hurdles are removed when it comes to the MIP-MIP process, as no operating costs regarding to pre-

treatment steps, gasifying reagents (nor additional capital expenditure if air separation units are required to produce O₂) nor expensive catalysts are envisaged. For instance, J-L. Shie *et al.* reported that 43% of the total input energy for downdraft gasifier is spent within the pre-treatment processes (Shie et al., 2011). This leaves some room to the higher energy consumption reported for the MIP-MIP process, as microwave pyrolysis does not require such an intensive pre-treatment of biomass because only partial grinding and sieving of the feedstock would be required.

TABLE 4

4. Conclusion

A new approach to biowaste processing has been established to maximise syngas production based on microwave heating. An additional step consisting of a fixed-bed after microwave pyrolysis of biomass has been proposed to remove tars. Char has been used as bed material to achieve high enough bed temperatures to fully convert tars from pyrolysis into syngas, being possible to turn up to 54% of the biowaste mass into syngas after the whole process.

This process can have direct implications within other industries, such as coke or hydrocarbons processing, whereby tars can be processed to yield valuable chemicals, such as syngas.

5. Acknowledgements

The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2007-2013) under Grant Agreement No. 311815

(SYNPOL project). D. Beneroso also acknowledges the financial received from the PCTI and FICYT of the Government of the Principado de Asturias (Spain).

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1

2 **Figure captions**

3 **Figure 1.** Lab-scale equipment for microwave-induced pyrolysis

4 **Figure 2.** MIP-MIP process flowsheet

5 **Figure 3.** Mass balances of the MIP-MIP process for (a) Scenario 1 and (b) Scenario 2.

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2 **Table 1.** Proximate and ultimate analyses of the biowaste.

Proximate analysis (wt%)	Moisture	2.8
	Ash ^(a)	27.7
	Volatile matter ^(a)	61.1
	Fixed carbon ^(a)	11.2
Ultimate analysis (wt%)^(a)	C	45.1
	H	5.4
	N	2.1
	S	0.4
	O	19.3

3 ^(a) Dry basis

Table 2. Energy consumption values for MIP of biowaste and MIP of tars and estimated values after the scale-up of the processes. Consumed energy takes into account the magnetron efficiency.

Process	Lab-scale		Large-scale	
	<i>Emitted energy</i>	<i>Consumed energy</i>	<i>Emitted energy</i>	<i>Consumed energy</i>
MIP of biowaste at 400 °C	11.0 Wh/g _{biowaste}	16.5 Wh/g _{biowaste}	0.55 Wh/g _{biowaste}	0.83 Wh/g _{biowaste}
MIP of biowaste at 800 °C	40.0 Wh/g _{biowaste}	60.0 Wh/g _{biowaste}	2.00 Wh/g _{biowaste}	3.00 Wh/g _{biowaste}
MIP of tars at 800 °C	13.2 Wh/g _{bed}	19.8 Wh/g _{bed}	2.11 Wh/g _{bed}	3.16 Wh/g _{bed}

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Table 3. Characterisation of the *gas3* stream.

Gas components concentration (vol%)	Scenario 1	Scenario 2
H ₂	47.49	50.56
CH ₄	4.30	3.07
C ₂ H ₄	3.99	2.44
CO	34.06	35.86
CO ₂	10.16	8.07
Gas density (kg/m³)	0.75	0.70
Production (m³_{STP}/kg_{biowaste})	0.49	0.77

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Table 4. Energy consumption of different technologies for producing syngas.

Process	Energy consumption (kWh/m³syngas)	Reference
Steam-methane reforming	1.46	(Seo et al., 2002)
Partial oxidation of methane	0.01	(Seo et al., 2002)
Autothermal reforming of methane	0.14	(Seo et al., 2002)
Microwave assisted dry reforming of methane	2.20	(Fidalgo & Menéndez, 2012)
Pyrolysis-gasification of municipal solid waste	0.38	(Khoo, 2009)
Gasification of refused-derived fuel	0.41	(Khoo, 2009)
Microwave pyrolysis of straw bale	1.88	(Zhao et al., 2011)
Microwave pyrolysis of biowastes	1.63 – 3.89	This work
MIP-MIP process of biowaste	4.42	This work

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