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HYDROGEN PRODUCTION FROM BIOMASS AND PLASTIC MIXTURES BY PYROLYSIS-GASIFICATION

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ABSTRACT

The addition of plastics to the steam pyrolysis/gasification of wood sawdust with and without a Ni/Al_2O_3 catalyst was investigated in order to increase the production of hydrogen in the gaseous stream. To study the influence of the biomass/plastic ratio in the initial feedstock, 5, 10 and 20 wt. % of polypropylene was introduced with the wood in the pyrolysis reactor. To investigate the effect of plastic type, a blend of 80 wt. % of biomass and 20 wt. % of either polypropylene, high density polyethylene, polystyrene or a mixture of real world plastics was fed into the reactor. The results showed that a higher gas yield (56.9 wt.%) and a higher hydrogen concentration and production (36.1 vol.% and 10.98 mmol. H_2 g^{-1} sample, respectively) were obtained in the gaseous fraction when 20 wt. % of polypropylene was mixed with the biomass. This significant improvement in gas and hydrogen yield was attributed to synergetic effects between intermediate species generated via co-pyrolysis. The Ni/Al_2O_3 catalyst dramatically improved the gas yield as well as the hydrogen concentration and production due to the enhancement of water-gas-shift and steam reforming reactions. Very low amounts of coke (less than 1 wt. % in all cases) were formed on the catalyst during reaction, with the deposited carbonaceous material being of the filamentous type. The Ni/Al_2O_3 catalyst was shown to be effective one hydrogen production in the co-pyrolysis/gasification process of wood sawdust and plastics.

Keywords: Hydrogen; Biomass; Waste; Plastic; Pyrolysis; Gasification

1. Introduction

Although hydrogen does not naturally exist in its elemental form on earth, it can be considered as a renewable, versatile and sustainable energy. Hydrogen is a clean fuel that can be easily used in both fuel cells and hydrogen fuelled turbines for generation of electricity or as a fuel for transportation, where it is directly combusted in internal combustion engines [1, 2]. At present, hydrogen is usually produced from fossil fuels (natural gas, naphtha or coal) or via water electrolysis, photolysis or thermolysis. To establish the sustainability of hydrogen production, alternative sources for the hydrogen, such as renewable biomass, are being investigated.

Biomass is the fourth largest source of energy in the world, and it is also a renewable, abundant and potentially sustainable source of energy. Accordingly, it has been considered as a possible major source for hydrogen production in the future [3, 4]. Biomass can be processed in numerous ways including several thermochemical and biological processes, such as gasification, pyrolysis, hydrolysis and fermentation to produce gases, liquids and solids. Pyrolysis and gasification are two effective conversion methods to produce hydrogen-rich gas from biomass, which can be also steam-reformed or passed through a catalyst to obtain higher-purity streams of gas [5-9]. Moreover, pyrolysis and gasification process conditions can be optimized to maximize the yields of gas, liquids or chars [10, 11]. However, single-stage gasification tends to generate low quality gas, which is commonly used for direct thermal use [12]. Two-stage reaction systems have been used in the gasification process in order to increase the hydrogen concentration in the product stream [13, 14]. These kinds of reaction systems improve the contact between pyrolysis products and the catalyst. Furthermore, process temperature can be easily controlled in each step.

Nevertheless, the yield of hydrogen that can be produced from biomass is relatively low, at about 5-8 wt.% based on dry biomass [15]. In order to increase the amount of hydrogen in the gaseous stream, the addition of plastics to biomass wastes is an interesting alternative, in that they contribute to increasing the content of hydrogen in the feed. Furthermore, since the availability of biomass wastes is subject to seasonal changes, the addition of another material would help to maintain a steady supply of the feedstock during off-season of a given biomass. Polypropylene (PP), polyethylene (PE) and polystyrene (PS) are the three main plastics present in municipal solid wastes. Adding PE, PP or PS to biomass wastes can lead to an increase in the gas and hydrogen yield since polyolefinic plastics are an excellent hydrogen source. Furthermore, these materials can also be very useful for the selective production of higher value added products, such as light olefins [16].

Papers on co-conversion [17-21] report synergetic interactions between intermediate species derived from both plastic and biomass when co-pyrolysis or co-gasification are performed, thus improving the properties and quality of the final products. An explanation is the lower stability of biomass compared to plastics, which affects the radical degradation mechanism by promoting the degradation of polymers [22]. In other words, the decomposition temperature of the plastics is lowered due to interactions between the volatiles and the char formed from the biomass. These kinds of interactions have been commonly studied with the aim of increasing the liquid yield. In fact, these synergetic effects have also given way to a clear decrease in the amount of water present in the oils [23]. However, few studies deal with the objective of improving the properties of the gaseous fraction. Pinto et al. [18] investigated steam gasification of biomass and polyethylene and concluded that plastic contents up to 20 wt.% in the feed favoured the release of hydrogen, with its concentration being at around 50 vol.%, with decreased CO yield in the final gas. For higher plastic concentrations in the feed, the H_2 and CO concentrations remained steady. Ruppolo et al [24] performed the gasification of a mixture of plastics and biomass pellets in a catalytic fluidized bed and achieved hydrogen concentrations of up to 32 vol. %. In addition, Liu et al. [25]

carried out the vapour-catalyzed co-pyrolysis of pubescens and low density polyethylene and obtained a H_2 concentration of 61.8 vol.% in the gaseous mixture using a combination of Ni and Pd in a Al-MCM-41 catalyst.

In order to maximise the hydrogen yield, the use of catalysts is considered a key factor in the gasification process [26, 27]. Ni-catalysts have been widely used for biomass steam gasification due to their low cost, high activity for C–C bond rupture and H_2 formation from H atoms with a high rate in the water gas shift reaction. Ni catalysts usually are deactivated due to carbon (coke) deposition on catalytically active sites and sintering effects on the catalyst surface. Alumina-based material (Al_2O_3) is generally used as a support due to its chemical and physical stability and suitable mechanical properties. Hydrogen and gas yields have also been found to increase by increasing the Ni content in the catalytic system [14, 28]. Nevertheless, 10-15 % Ni loading has been reported [29] to provide the optimum catalytic activity for tar gasification since higher Ni contents did not produce a significant increase in the product yields. Moreover, high Ni contents can cause significant deactivation due to the stronger interaction between NiO and the support, given that the latter restrains the loss and sintering of nickel [30, 31].

In this paper, the co-pyrolysis/gasification of biomass and plastics has been studied with the aim of exploring the synergetic effects between these two materials in order to increase hydrogen concentration and production in the gaseous fraction. Therefore, this paper deals with the influence of plastic content and plastic type in the feed and the presence of a Ni/Al_2O_3 catalyst on the yield and composition of the final products. In order to achieve a higher hydrogen content, steam was used as the gasifying agent in the process.

2. Materials and methods

2.1. Materials

The biomass used in this research was wood sawdust and represented a range of different wood types. The wood sawdust was obtained from Liverpool Wood Pellets, Liverpool, UK. It was milled and sieved to a particle size of less than 0.2 mm. The results of the ultimate (thermogravimetric analyser) and elemental analysis (CE Instrument CHNS-O analyser) of the biomass sample are summarized in Table 1. As observed, one of the main characteristics of this type of biomass, which makes it appropriate for thermal processing, is the low amount of ash and nitrogen, at 1.2 and 0.1 wt.%, respectively.

Four different kinds of plastics were used for co-processing with the biomass: polypropylene (PP), high density polyethylene (HDPE), polystyrene (PS) and a mixture of real world plastics (RP) previously collected and recycled. HDPE and PS (both about 2 mm) have been supplied by ACROS Organics UK, whereas PP was obtained as 2 mm virgin polymer provided by BP Chemicals UK. The real world plastics were recovered from municipal solid waste and were obtained from Fost Plus, Belgium, the details of the sample have been reported in a previous work [34]

The Ni/Al_2O_3 catalyst was prepared by an impregnation method, in which the γ-Al_2O_3 support was impregnated with an aqueous solution of $Ni(NO_3)_2.6H_2O$. The loading of Ni in the catalyst was 10 wt.%. The mixture was stirred for an hour followed by drying at 105 ˚C overnight. The catalyst was then calcined in an air atmosphere at 750 ˚C for 3 h. Finally, the prepared catalyst was ground and sieved to a size between 50-180 μm, and reduced in-situ by the process gases such as H_2 and CO, which were generated during the reaction.

2.2. Methods

The co-pyrolysis/gasification of wood sawdust and different kinds of plastics was carried out in a two stage fixed bed reactor. 2 g of a biomass and plastic mixture were placed in a sample holder in the first stage pyrolysis reactor and this blend was pyrolyzed at 600 ˚C. Experiments were performed with the biomass alone or binary mixtures with PP, varying the plastic content from zero to 20 wt. % in the initial feedstock. In addition, the influence of plastic type was studied feeding a blend of 80 wt. % of biomass and 20 wt. % of HDPE, PS or RP into the reactor. The vapours generated in the first stage were then passed directly to the second stage gasification reactor, where the temperature was maintained at 800 ˚C. Water, which was converted into steam, was used as the gasifying agent in the process, and was introduced into the second stage reactor using a syringe pump. The injection rate of water was 4.74 ml h^{-1}. 1 g of the prepared Ni/Al_2O_3 catalyst was placed in the second reactor supported on quartz wool. When the experiment was carried out without catalyst, only quartz wool was placed inside the gasification reactor. During the entire process, nitrogen was used as carrier gas with a flow rate of 80 ml min^{-1}. A schematic diagram of the pyrolysis/gasification unit has been described in a previous paper [13].

The experimental procedure consisted of the following steps. First, the gasification reactor was heated to 800 ˚C and once the temperature was stabilised, the first stage pyrolysis reactor was heated to 600 ˚C with a heating rate of 40 ˚C min^{-1}. Since the biomass decomposition profile showed that the release of volatile compounds started around 220 ˚C, the injection of water was started when the pyrolysis reactor reached 200 ˚C in order to ensure the gaseous products derived from the biomass degradation were gasified with steam. Then, once the pyrolysis reactor reached 600 ˚C, it was kept constant for 30 min. The products generated in the co-pyrolysis/gasification process were cooled passing through two condensers. The first condenser was cooled with air and the second one with dry ice in order to gather the liquid products. All the non-condensable gases were collected using a 10 L $Tedlar^{TM}$ gas sample bag. After finishing each experiment, the gases were collected for a further 20 min to ensure the reaction was completed. When the reactor was cooled, the sample holder, the condensers and the syringe were weighted to determine the amount of char, condensed liquid and injected water, respectively. Each experiment was repeated to ensure the reliability of results.

The gases collected in the gas sample bag were analysed off-line by gas chromatography. Hydrocarbon gases (from C_1 to C_4) were determined by a Varian 3380 chromatograph with a flame ionisation detector (GC/FID), 80-100 mesh Hysep column and using nitrogen as carrier gas. Permanent gases, i.e., CO, O_2, N_2 and H_2, were determined by a Varian 3380 chromatograph with a 60-80 mesh molecular sieve column and argon as carrier gas with a thermal conductivity detector, whereas CO_2 was analysed by another Varian 3380 GC provided with a Hysep 80-100 mesh column and using argon as carrier gas and a thermal conductivity detector.

In order to determine the amount of coke deposited on the catalyst, temperature-programmed oxidation (TPO) was performed on the used catalyst in a Stanton-Redcroft thermogravimetric analyser (TGA and DTG). Around 10 mg of the catalyst recovered after the reaction were heated in an atmosphere of air at 15 °C min^{-1} to a final temperature of 800 °C, with a dwell time of 10 min.

High resolution scanning electron microscopy (SEM) (LEO 1530) was used to study the surface morphology of the used catalyst. The system used was a Gemini Field Emission Gun SEM, FEGSEM LEO 1530, manufactured by Zeiss, Oberkochen, Germany. The SEM used an accelerating voltage of 3KV, at a working distance of 3-8 mm from the electron gun and an 80 mm X-Max SDD detector.

3. Results and discussion

3.1. Influence of biomass/plastic ratio

3.1.1. Mass balance closure with and without catalyst

The co-pyrolysis/gasification with wood sawdust and polypropylene was carried out with and without catalyst to determine the influence of the plastic content on hydrogen production and the contribution of the catalyst. The mass balances and the product yields for different biomass/plastic ratios are shown in Table 2. The residue or char obtained after pyrolysis was calculated by difference between the initial and final weight of the sample placed in the sample holder. In order to increase the hydrogen production in the process, steam is known to be very effective to promote steam reforming and water gas shift (WGS) reactions [13].

$$CO + H_2O \longleftrightarrow CO_2 + H_2 \tag{1}$$

$$C_nH_m + nH_2O \longleftrightarrow CO + (n + m/2)\ H_2 \tag{2}$$

As observed in Table 2, the results showed a reasonable mass balance closure in the range of 92-95 wt.% in all cases. The mass of the sample (mixture of biomass and plastic) and that of the water injected are considered in the mass balance. The total liquid retained in the condensers was a mixture of mostly water and a brown coloured oil.

Table 2 shows that the addition of polypropylene in the non-catalytic process appears to increase the gas and hydrogen yields. Polypropylene, as a polyolefinic plastic, represents a significant source of hydrogen. The gas yield based on the mass of sample and water injected increased from 15.5 to 17.9 wt. % when the amount of polypropyelene was increased from 0wt.% to 20 wt.% when the reaction was carried out without the catalyst. This increase may be due to the higher H/C molar ratio caused by the higher amount of plastic in the feed. Thus, more H and OH radicals are released and they act as hydrogen donor species, promoting the cracking of the aromatic compounds in the biomass [32]. In addition, the char and the liquid generated decreased with increasing plastic content, suggesting that the suppression of secondary reactions, such as condensation and repolymerization reactions, leads to a reduction in char and oil formation [33]. The hydrogen released by the polyolefinic polymer in the co-pyrolysis reaction (first pyrolysis stage) is responsible for the inhibition of recondensation reactions forming the char [34].

As shown in Table 2, when 1 g of Ni/Al_2O_3 catalyst was introduced in the gasification reactor, the gas yield increases slightly from 51.6 wt.% to 53.6 wt.% by mass unit of the sample when no plastic was added to the biomass. However, when the plastic/biomass ratio was increased in the presence of the catalysis, the gas and hydrogen yields increased considerably compared to the process without the catalyst. Thus, the gas yield corresponding to the mass of biomass and plastic increases from 56.9 to 85 wt.% for a biomass/plastic ratio of 80/20, from 55.1 to 69.8 wt.% for a ratio of 90/10 and from 51.5 to 59.5 wt.% for a ratio of 95/5. Furthermore, an increase in gas yield in the catalytic process was much more pronounced than in the non-catalytic system, indicating that the Ni catalyst plays a significant role when more plastic was present in the mixture. The effect of Ni catalysts in the pyrolysis/gasification processes has been extensively studied by several researchers for plastics and biomass separately [13, 34, 35]. The differences in the catalytic process for the mixture of biomass and polypropylene suggest the existence of synergetic effects on the product distribution when the Ni/Al_2O_3 is used. This synergy is probably related to secondary cracking reactions involving tars and heavy gas compounds in the gasification step. Furthermore, the contact time of the products formed in the catalyzed reaction is higher than in the non-catalytic process, which is essential for the occurrence of synergy [36].

3.1.2. Gas composition and hydrogen production with and without catalyst

The gaseous fraction was mainly composed of carbon monoxide, carbon dioxide and hydrogen, but there are also small amounts of C_1-C_4 hydrocarbons (Fig. 1). When more polypropylene was present in the feed mixture, the total oxygen content available would be lower. Hence, the yields of CO and CO_2 in the non-catalytic process are higher than those when 20 wt.% PP is added, i.e., 35.5 vol.% compared to 27.5 vol.% and 15.7 vol.% compared to 11.2 vol.%, respectively. In the presence of 5 wt.% of PP in the waste mixture, the release of CO is slightly higher than that of H_2. When higher amounts of PP are added (10 and 20 %), the H_2 content was always higher than the CO concentration. The composition of light hydrocarbons (C_1-C_4) was considerably increased when the plastic content was higher, from 18.4 vol.% to 25.3 vol.% in the non-catalytic pyrolysis/gasification process. This is because the olefinic pyrolysis products provided by polypropylene are decomposed by thermal cracking reactions at 800 ºC forming more light species. Pinto et al. [18] confirmed that bond fracture occurs across the molecule and olefinic polymers (such as PP and HDPE) decompose into small molecular fractions.

The highest hydrogen yield (10.98 mmol H_2 g^{-1} sample) and concentration (36.1 vol.%) in the non-catalytic gasification of the mixture was obtained for a biomass/plastic ratio of 80/20. According to the literature [13, 18], the main reactions controlling hydrogen concentration in the biomass gasification process are decomposition of hydrocarbons and water gas shift reactions. When polypropylene was introduced with the wood sawdust, high hydrogen concentrations were obtained due to PP cracking. However, Pinto et al. [18] predicted that an increase in the plastic beyond 20 wt.% will not result in an increase in H_2 concentration in the gas. Fig. 1, shows that the presence of polyolefinic plastics in the uncatalyzed biomass pyrolysis/gasification process increases hydrogen production in the gaseous stream. However, the concentration of H_2 in the gas is hardly affected by the plastic content in the non-catalytic process, since it only increases slightly from 30.3 to 36.1 vol. %.

Once the catalyst is introduced in the second stage and steam is fed, hydrogen production and concentration are greatly improved. As observed in Fig. 1, H_2 concentration increases from 36.1 vol.% (without catalyst) to 52.1 vol.% (with catalyst) for 20 wt.% of PP in the feedstock. Likewise, H_2 production increases from 10.75 to 27.27 mmol H_2 g^{-1}, respectively. These differences between H_2 concentration and H_2 production in the catalytic and non-catalytic process suggest that the catalyst promotes water gas shift and steam reforming reactions (Eq (1) and Eq (2)). The increase in the concentration of CO_2 and the decrease in CO and light hydrocarbons (C_1-C_4) confirm that the water gas shift and hydrocarbon decomposition reactions are the main reactions responsible for producing more hydrogen. When the experiments were carried out with a catalyst, synergetic effects take place influencing hydrogen production, resulting mainly from the promotion and the strong ability of Ni to catalyse H_2 production [25]. The increase in active H radicals due to plastic addition and the significant role of Ni in the reforming process remarkably improve hydrogen generation in the process.

3.2. The influence of different types of plastics

3.2.1. Mass balance closure with and without catalyst

The effect of different kinds of plastics in the initial feedstock on the two-stage reaction system with and without catalyst is discussed in this section. The selected plastics were PP, HDPE, PS and a mixture of real world plastics (RP). In all the experiments to study this influence, a biomass/plastic ratio of 80/20 was used.

Table 3, shows that in the uncatalyzed reaction, gas yield was the highest at 18.6 wt.% when HDPE was used as the co-pyrolysis raw material, which is probably because the aliphatic molecular structure allows the production of lighter intermediate radicals. The results obtained with polypropylene/biomass were very close to those obtained with high density polyethylene/biomass. This is most probably due to the similarity between these two polymers, whose carbon and hydrogen contents are very similar. The lowest gas yield was obtained for the polystyrene/biomass mixture, with a value of 15.9 wt.% by mass unit of sample and water. Wu and Williams [34] have suggested that the gaseous products derived from polystyrene require a higher reaction energy to be cracked compared to other plastics, and therefore more liquid product (73.7 wt.%) is obtained compared to the other plastics. The real world waste plastics produced a high gas yield (18.1 wt.%), probably because they consist of mainly high density polyethylene and polypropylene. The char yields in the catalytic and non-catalytic processes for the real world plastic/biomass mixture were the highest of the plastic/biomass samples, i.e., 18.7 and 18.0 wt. %, respectively. This may be due to the presence of other kinds of plastics, such as polyethylene terephthalate (PET), whose chemical structure and associated thermal behaviour are different, thus increasing the final amount of solid residue.

Table 3 shows that the addition of the catalyst in the gasification stage produces high gas yields for the different types of plastics/biomass. Although the gas fraction increased in all the catalytic experiments, this effect was more pronounced when using polypropylene than for the other plastics, with the gas yield reaching a maximum value (28.1 wt. % by mass unit of sample and water). Apparently, the decomposition products from biomass and polypropylene in the presence of Ni/Al_2O_3 catalyst promote reforming reactions, thereby increasing the overall gas yield. Therefore, the synergetic effect is more pronounced when biomass and polypropylene are used in the feedstock. The lowest gas yield was obtained in the catalytic process for the sample containing 20 wt.% of polystyrene. This low yield with polystyrene may be caused by the intermediate radicals generated in the course of the pyrolysis reaction, producing high molecular weight species [37]. Furthermore, a lower gas yield (21.4 wt.%) and a higher liquid yield (67.9 wt.%) was obtained for the catalytic steam pyrolysis/gasification of biomass and real world plastics compared to the results with polypropylene/ biomass and high density polyethylene/biomass.

There are few reports on the influence of different types of plastics on the pyrolysis/gasification of biomass with steam and catalyst for hydrogen production. Most of the research studying the influence of plastic polymers focus only on the pyrolysis stage, in which the bio-oil is usually the major fraction. Brebu et al. [22] carried out the co-pyrolysis of pine cone with PP, PE, PS and a mixture of these three polymers and they also obtained the lowest gas yield and the highest char and tar yields when PS was added in the feedstock. Likewise, Sharypov [19] showed that the type of both biomass and polymer plays an important role in the liquid product distribution of co-pyrolysis of beech and medium density polyethylene, atactic polypropylene and isotactic-polypropylene. The influence of different kinds of biopolymers, such as polylactic acid (PLA), polyhydrobutyrate (PHB), Bioperals or Eastar, has also been studied by Cornelissen et al. [23] in the flash co-pyrolysis with willow. Their results showed a significant decrease in the water content in the bio-oil and a remarkable increase in the gaseous fraction when biopolymers where fed into the reactor, especially PHB.

3.2.2. Gas composition and hydrogen production with and without catalyst

This section discusses the gas composition and the hydrogen production for the non-catalytic and catalytic co-pyrolysis/gasification of wood sawdust with PP, HDPE, PS and RP. Fig. 2 shows the volumetric concentrations of gaseous compounds as well as the production of H_2 from the experiments with and without catalyst. When the experiments were carried out without catalyst, the highest hydrogen production was obtained for polypropylene (10.98 mmol H_2 g^{-1}). For the remaining plastic/biomass experiments (HDPE, PS and RP) the hydrogen yield values were quite similar in the 9.6-9.9 mmol H_2 g^{-1} range. The highest H_2 concentration in the non-catalytic co-pyrolysis gasification was obtained when polystyrene was used in the feedstock (37.1 vol.%). These results are consistent with those obtained in previous work [34], in which the highest H_2 concentration was obtained also for polystyrene in the non-catalytic pyrolysis-gasification of different plastics. Furthermore, the highest concentration of CO and CO_2 (32.9 and 14.7 vol.%) and the lowest concentration of light hydrocarbons (10.9 vol.% of CH_4 and 4.5 vol.% of C_2-C_4) was obtained with polystyrene and wood sawdust. The explanation lies in the chemical structure of polystyrene, which during the pyrolysis stage forms more stable free radicals than with other plastics and interacts faster with steam, promoting water gas shift and steam reforming reactions in the gasification process [22, 38].

As observed in Fig. 2, the use of a catalyst plays a significant role in the increase of hydrogen production in the gasification process. Furthemore, H_2 and CO_2 concentration increases, whereas those of CO and light hydrocarbons decrease in the catalytic steam co-pyrolysis/gasification of PP, HDPE, PS and RP. The excellent performance of Ni/Al_2O_3 catalyst in the gasification process apparently efficiently promotes water gas shift and steam reforming reactions, and therefore more H_2 and CO_2 are produced in the gaseous fraction. In the presence of Ni/Al_2O_3 catalyst, the highest hydrogen production was obtained with PP, and then with HDPE and RP (27.27, 25.48 and 21.76 mmol H_2 g^{-1} sample, respectively). The lowest hydrogen yield (19.95 mmol H_2 g^{-1} sample) was achieved when the biomass was mixed with polystyrene. This is attributed to more alkanes and alkenes derived from the co-pyrolysis of biomass with PP, HDPE and RP than with PS. These compounds are easier to reform in the gasification stage in the presence of Ni catalysts than those derived from the co-pyrolysis of wood sawdust and polystyrene, which are mainly aromatic compounds [34].

3.3. Used Ni/Al_2O_3 catalyst

The deposition of coke on the Ni/Al_2O_3 catalyst used in the pyrolysis/gasification of biomass and plastics was determined by temperature-programme oxidation (TPO). This coke blocks the pores and poisons the active sites, which gives way to a loss of activity in the catalyst, and consequently hydrogen production is reduced. Figs. 3 and 4 display the results of TGA-TPO for the catalysts used with different polypropylene/biomass ratios and different types of plastics. In both cases, the overall coke deposition is very low (less than 1 wt. %). Fig. 3 and 4 reveal that there is a mass loss between 0 and 150 ºC in all cases. This is likely to be due to the vaporization of the moisture contained in each coked catalyst, with mass loss being in all the cases of around 2-3 wt. %. The mass loss around 350-400 ºC is due to coke combustion. The addition of steam during the gasification stage as well as the high temperature in the second reactor (800 ºC) reduce the final coke deposition on the catalyst because the carbon atoms generated react with the steam introduced at that temperature.

The TGA-TPO results for different biomass/polypropylene ratios (Fig. 3) reveal that the lowest coke deposition in the catalyst was obtained when only biomass was present in the reactor. Coke deposition on the catalyst is hardly affected by the plastic content in the plastic/biomass mixture since all the coke percentages are similar and low.

Fig. 4 shows the TGA-TPO mass loss results for the different types of plastics/biomass mixtures. The lowest coke formation was observed for the catalyst used in for the pyrolysis/gasification of biomass and polypropylene. The amount of coke increased slightly when other plastics were introduced in the pyrolysis stage. However, the amount was so small in all cases that catalyst deactivation was not observed.

Several researchers have reported the deactivation of Ni/Al_2O_3 catalysts by coke in the steam gasification of biomass and plastics [39, 40, 13]. For example, Kimura et al. [34] obtained a maximum of 5 wt. % coke deposition on a Ni/Al_2O_3 catalyst (12 wt.% Ni) by operating with a temperature between 600 and 650 ºC in the steam gasification process. Wu et al. [13] investigated a Ni/Al_2O_3 catalyst (10 wt.% Ni) in the steam pyrolysis/gasification of polypropylene and showed that the catalyst was effective for the production of hydrogen even though a high coke deposition occurred (11 wt.%). However, no studies have been carried out on the catalyst deactivation in the co-pyrolysis/gasificaction of biomass and plastics.

Fig. 5 shows the scanning electron micrographs (SEM) of the used catalysts used for the pyrolysis/gasification of biomass, a mixture of 90 wt.% biomass and 10 wt.% of polypropylene and for 80 wt.% biomass and 20 wt.% polypropylene. The SEM analysis confirmed the presence of filamentous type carbon deposits on the catalyst surface. As observed in Fig. 5, when plastic was introduced to the biomass/plastic feed, hydrogen production was increased and coke deposition on the catalyst increased slightly. These results are consistent with those obtained in the TPO (Fig 3 and 4), in which the lowest hydrogen and coke yields have been obtained for the pyrolysis/gasification of 100 wt.% biomass. Hence, when the percentage of plastic in the mixture was increased to 10 wt.% of polypropylene, coke deposition also increased. However, when 20 wt.% of polypropylene was added to the biomass, the coke yield in the catalyst remains almost constant.

4. Conclusions

Different amounts and types of plastics have been added to biomass using a two-stage pyrolysis/gasification process, with and without catalyst, in order to determine the influence of mixing on hydrogen production. The main conclusions are as follows:

(1) The addition of polypropylene markedly increased the yield of the gaseous fraction and hydrogen since the presence of hydrogen in the feedstock was higher tha with biomass alone. Moreover, a reduction in CO and CO_2 yields and concentrations was obtained when the amount of polypropylene was increased from 0 to 20 wt. % in the initial feedstock mixture.

(2) The presence of a Ni/Al_2O_3 catalyst in the steam co-pyrolysis/gasification of different plastics at different ratios in the feed mixture produced a sharp increase in gas yield and hydrogen production compared to non-catalytic co-pyrolysis/gasification. The Ni/Al_2O_3 catalyst seems to be suitable for this process due to its high activity for C–C

bond rupture and H_2 formation with a high efficiency of the water gas shift reaction and a low coke deposition.

(3) The results obtained from the mixture of plastics and biomass showed that polypropylene produced the highest hydrogen production compared to high density polyethylene and polystyrene. However, high density polyethylene produced the highest gas yield in the process, whereas the highest oil and char yields were obtained with polystyrene. This may be attributed to the higher reaction energy required to crack polystyrene in the pyrolysis stage.

(4) Catalyst deactivation was low, which was consistent with the low coke deposition on the catalyst. Most of the carbon deposited appeared to be of the filamentous type and increased when the amount of plastic in the plastic/biomass mixture was increased.

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TABLES

Table 1. Proximate and elemental analysis of the wood sawdust.

Elemental analysis* (wt. %)	
Carbon	47.1
Hydrogen	5.9
Nitrogen	0.1
Oxygen	46.9
Proximate analysis (wt. %)**	
Moisture	6.4
Volatile	74.8
Fixed carbon	18.3
Ash	1.2

* Oxygen content was calculated by mass difference

**On wet basis

Table 2. Mass balance and main product yields for different biomass/plastic ratios.

	Without Catalyst				Ni/Al_2O_3			
Wood (wt.%)	100	95	90	80	100	95	90	80
Polypropylene (wt.%)	0	5	10	20	0	5	10	20
Mass balance based on the sample + water (wt. %)								
Gas	15.5	15.9	16.1	17.9	15.4	19.0	20.3	28.1
Liquid	71.0	72.0	70.6	68.6	74.0	65.0	67.1	61.6
Char	6.3	6.1	5.5	5.4	5.9	6.3	5.6	5.5
Mass Balance (wt.%)	92.8	94.1	92.2	91.9	95.2	90.3	93.0	95.7
Mass balance based on the sample (wt. %)								
Gas	51.6	51.5	55.1	56.9	53.6	59.5	69.8	85.0
Char	20.9	19.9	18.7	17.3	20.6	19.8	19.3	16.9

Table 3. Mass balance closure and main product yields for different types of plastics.

	Without Catalyst				**Ni/Al_2O_3**			
Type of plastic	PP	HDPE	PS	RP	PP	HDPE	PS	RP
Mass balance based on the sample + water (wt. %)								
Gas	17.9	18.6	15.9	18.1	28.1	25.7	24.6	21.4
Liquid	68.6	67.5	73.7	69.2	61.6	65.2	69.7	67.9
Char	5.4	5.2	5.6	5.9	5.6	5.6	6.3	5.6
Mass Balance (wt.%)	91.9	91.2	95.2	93.2	95.8	96.5	100.6	94.9
Mass balance based on the sample (wt. %)								
Gas	56.9	59.9	50.9	57.2	85.0	77.5	68.1	68.6
Char	17.3	16.7	17.8	18.7	16.9	16.9	17.5	18.0

FIGURE CAPTIONS

Figure 1. **Gas composition and hydrogen production for different biomass/plastic ratios.**

Figure 2. **Gas composition and hydrogen production for different types of plastics.**

Figure 3. **TGA thermograms for the coked catalyst after pyrolysis-gasification of wood sawdust with different polypropylene ratios.**

Figure 4. **TGA thermograms for the coked catalyst after pyrolysis-gasification of wood sawdust with different types of plastics.**

Figure 5. **SEM micrographs for the catalysts used with different mixtures of biomass and polypropylene. (a) 100 wt. % of biomass; (b) 90 wt. % of biomass and 10 wt. % of PP; (c) 80 wt. % of biomass and 20 wt.% of PP.**

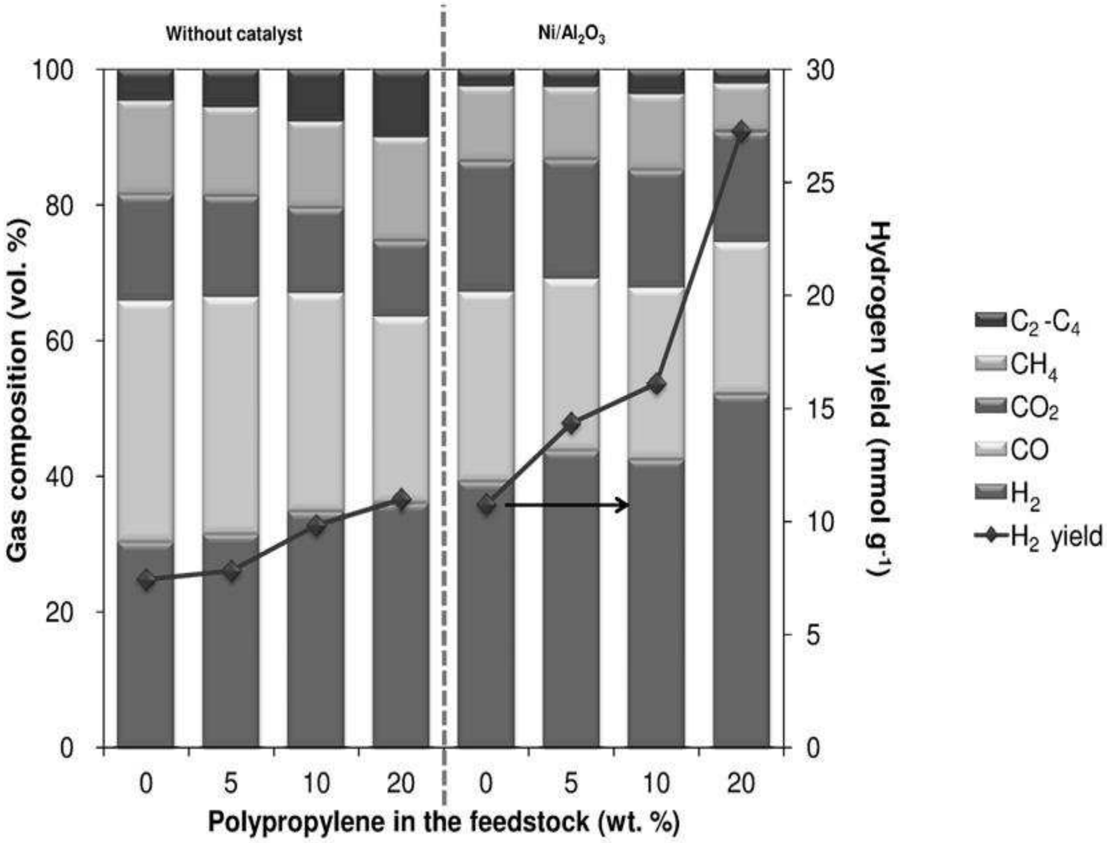
Without catalyst
Ni/Al2O3
Gas composition (vol. %)
Hydrogen yield (mmol g-1)
Polypropylene in the feedstock (wt. %)
0
20
40
60
80
100
0
5
10
15
20
25
30
0
5
10
20
0
5
10
20
C2-C4
CH4
CO2
CO
H2
H2 yield

Figure 1.

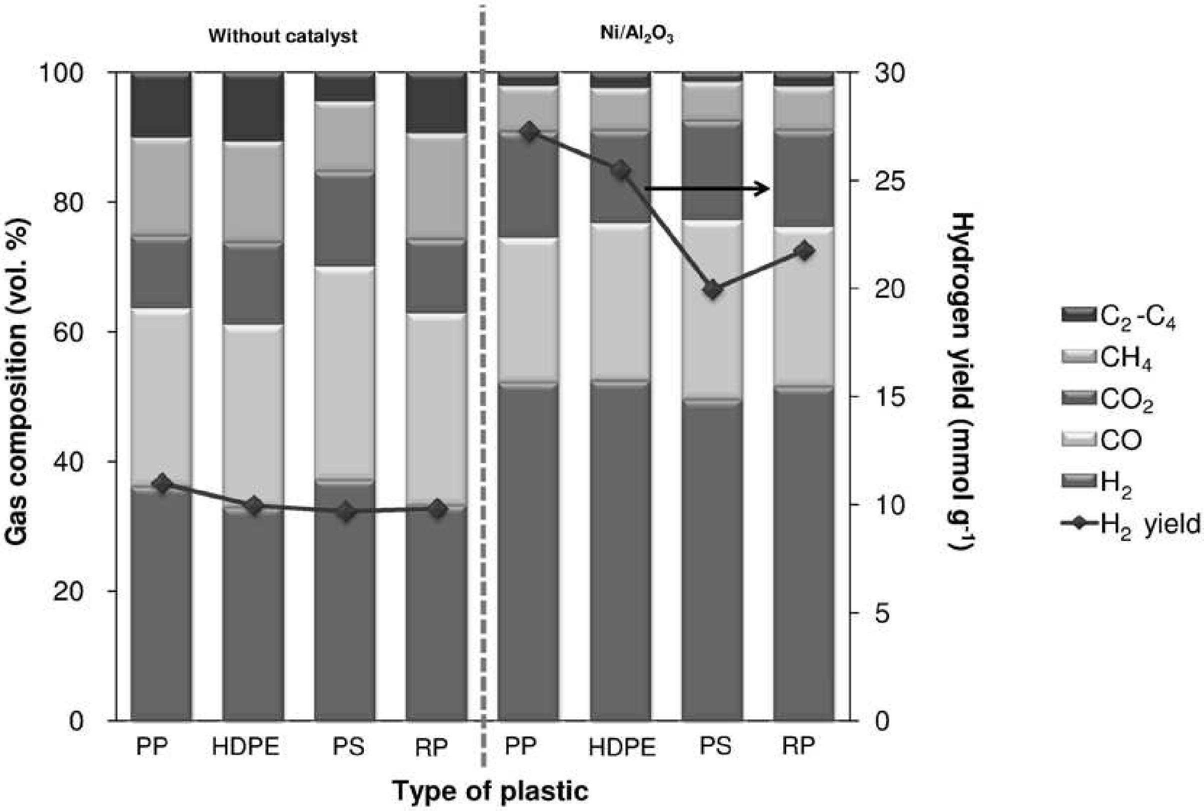
Without catalyst
Ni/Al_2O_3
Gas composition (vol. %)
0
20
40
60
80
100
Hydrogen yield (mmol g^{-1})
0
5
10
15
20
25
30
PP
HDPE
PS
RP
PP
HDPE
PS
RP
Type of plastic
C_2-C_4
CH_4
CO_2
CO
H_2
H_2 yield

Figure 2.

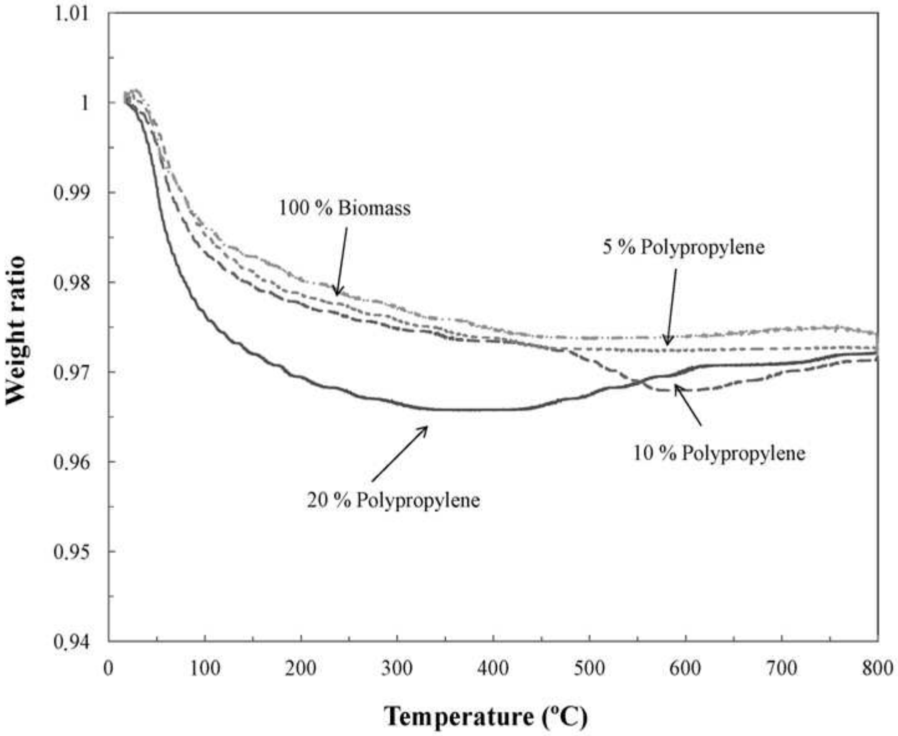
1.01
1
0.99
0.98
0.97
0.96
0.95
0.94
Weight ratio
0
100
200
300
400
500
600
700
800
Temperature (ºC)
100 % Biomass
5 % Polypropylene
10 % Polypropylene
20 % Polypropylene

Figure 3

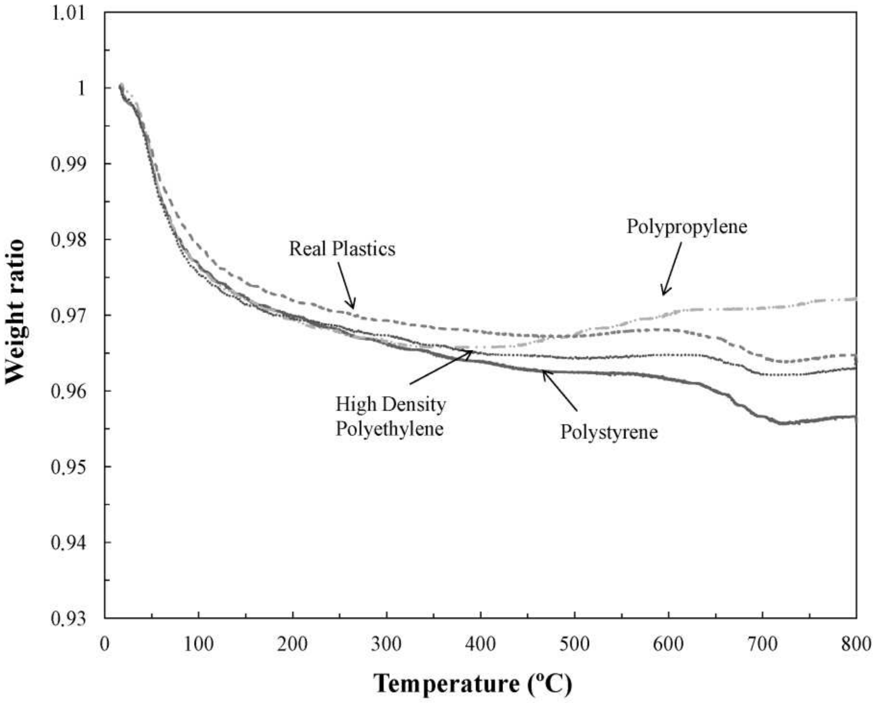
Weight ratio
1.01
1
0.99
0.98
0.97
0.96
0.95
0.94
0.93
0
100
200
300
400
500
600
700
800
Temperature (ºC)
Real Plastics
Polypropylene
High Density
Polyethylene
Polystyrene

Figure 4

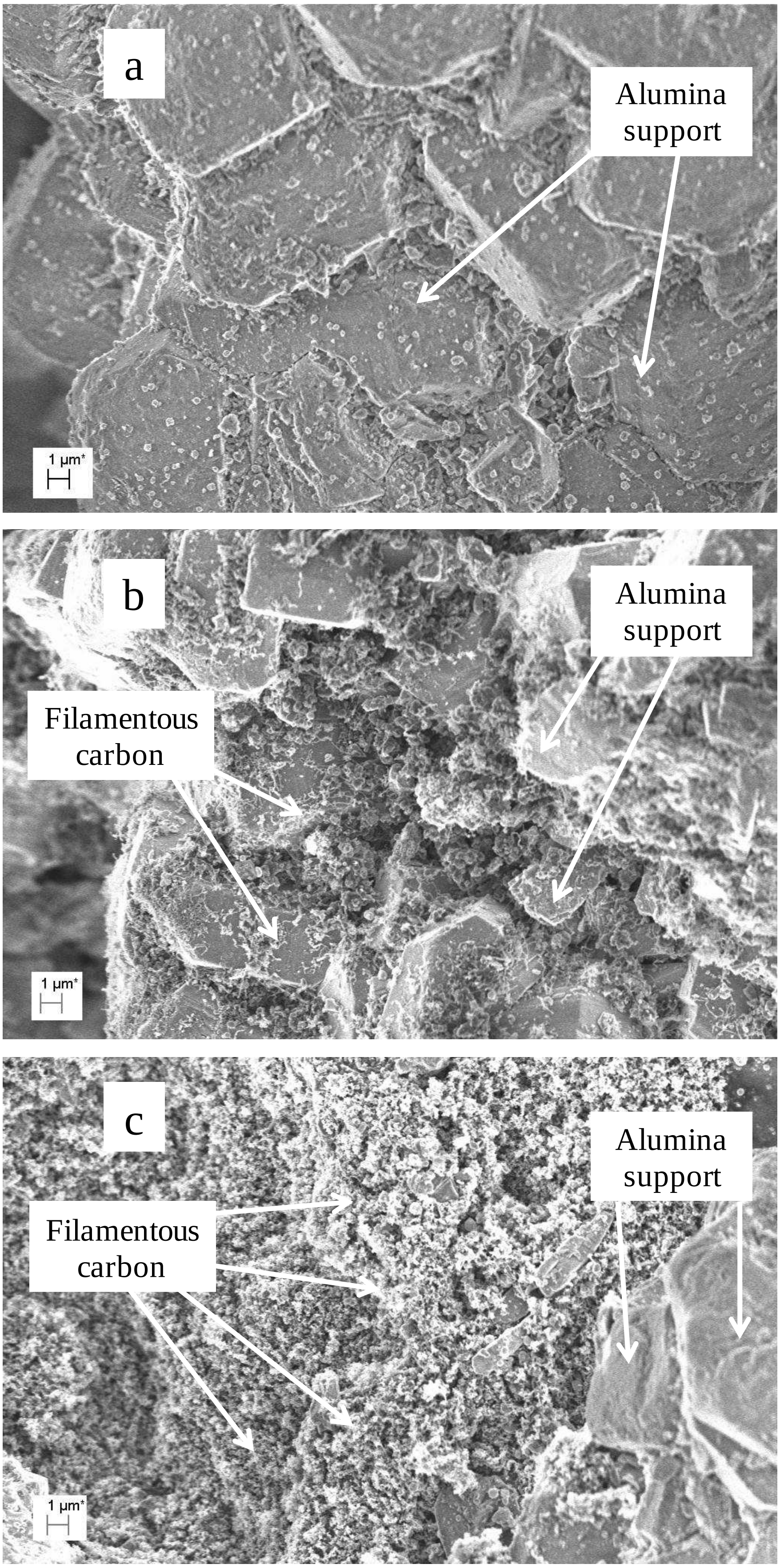
a
Alumina support
1 µm*
b
Alumina support
Filamentous carbon
1 µm*
c
Alumina support
Filamentous carbon
1 µm*

Figure 5.