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Characterizaton of Thermochemical Conversion Processes in a Technical-Scale Fixed-Bed Reactor: Pyrolysis and Gasification

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Abstract

Consolidated industrial application of biomass thermochemical conversion processes, such as pyrolysis and gasification, requires the development and application of control and optimization techniques. To this end, on-line process characterization, regarding mainly product distribution and composition under similar conditions as the ones encountered in industrial applications is needed. In the present study, slow pyrolysis and updraft gasification of thermally thick particles in a technical scale fixed-bed reactor are carried out under several process conditions. Different raw materials are used: pine wood chips, beech-wood spheres and cellulose. In pyrolysis, the increasing influence of transport phenomena in the conversion process due to the use of a technical-scale reactor and thermally thick wood particles is analysed through the temperature distribution inside the bed during the process together with the char properties characterization taken from four different positions inside the bed. The influence of process conditions, such as the N_2 flow rate, on the products composition and distribution is also analysed. In gasification, the influence of the air to fuel ratio on the product gas composition is characterized, as well as the qualitative evolution of polycyclic aromatic hydrocarbons (PAH) representative species in the volatiles vapours by applying laser-induced fluorescence (LIF).

Keywords: technical-scale, fixed bed, updraft, pyrolysis, gasification, on-line, LIF.

Introduction

Fixed-bed thermochemical conversion processes, such as pyrolysis, combustion or gasification may be a possible solution for decentralized biomass energetic utilization and waste treatment due to its possible application at small scales with an acceptable high efficiency, as well as their good performance with high moisture content and big particle size.

Among these processes, pyrolysis is of particular interest because of its possible potential utilization for bio-oil and bio-char production, but also for being a key stage in other thermochemical conversion processes where the tar yield can be reduced by controlling the pyrolysis process [1]. Although plenty of information can be found in literature regarding pyrolysis characterization [1-3], the conversion mechanism is not yet fully understood and, consequently, neither is the influence of the different process conditions such as pressure or particle size on the process evolution and products composition. This is due to the high degree of complexity of the chemical evolution that the biomass structures undergo, together with the influence of the physical phenomena taking place, as well as the processes themselves and the wide heterogeneity of biomass feedstock available [1-6]. Despite this, some general trends can be outlined from the large range of experimental data available in literature [3] to establish the influence of some parameters on the product yields and composition. It is shown that the parameter with the greatest influence on the product distribution is temperature. Highest liquid yields are obtained in the temperature range of 500 to 550 ºC [4-6], independently of the process severity and the raw material. With higher temperatures homogeneous secondary reactions are strongly enhanced leading to a significant decrease in the tar yield benefiting the gas yield while high heating rates accompanied

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by fast removal of volatiles from the reaction zone benefit the liquid yield. On the other hand, low temperatures and high residence times favour the yield of solids. Other parameters affecting the product distribution are the particle and bed size, increasing the influence of heat and mass transport phenomena and leading to a possible enhancement of heterogeneous secondary reactions. Aguiar et al. [8] show that the particle size has a stronger influence on the product composition than on the product distribution, with a more valuable char from the calorific point of view and a higher presence of species such as CH_4 and H_2. Char yield decreases strongly until a temperature around 400 ºC due to the primary decomposition of the raw material. At higher temperatures it overcomes a much softer decrease involving char aromatization [9] and also secondary char is produced due to secondary reactions. The char yield is also very dependent on the raw material. It has been shown in the literature that a reduction of around 1% in the inorganics contained in the raw material causes a reduction in the char yield of 20% [10]. Char yield is also significantly increased when the lignin content in the biomass increases. The inorganic content together with the char structure at molecular level has a great influence on its reactivity. Also the presence of secondary char due to secondary reactions reduces the char reactivity [11]. The morphology and structure of char are also related to the parent material and the devolatilization conditions such as heating rate, maximum temperature and residence time. However, most of these experimental results from literature are obtained in small lab-scale facilities, reducing the complexity of the processes as well as the products characterization – for example for condensing the vapour phase for further analysis or closing the mass and energy balances – but also reducing the influence of physical phenomena and thus getting away from real applications. The objective of the present work is the development of an experimental set up allowing the study and characterization of slow pyrolysis and updraft gasification under conditions closer to real applications. Permanent gas composition, as well as qualitative evolution of PAH species will be measured on-line, as well as the axial and radial temperature profiles inside the bed. Analysis of the char fraction will also provide valuable information about the process.

This study constitutes an extension of a previous study by the authors [12]. In that previous work, focused was on a deep characterization of the solid product from pyrolysis, while in the present study characterization of the three product phases from pyrolysis and updraft gasification is performed.

Experimental

Sample Characterization

Several raw materials are used in the pyrolysis process: pine wood chips with average dimensions of 3 ×2 × 0.5 cm^3, beech wood spheres with a diameter of 2.5 cm and cellulose. The pine wood chips come as a residue from a timber merchant company outside Berlin, Germany, directly with the shape defined as big particle size. The beech wood spheres are provided by Meyer & Weigand GmbH (Nordlingen, Germany), and the cellulose material comes from disposable plates. The elemental analysis of the three materials is presented in Table 1, the proximate analysis in Table 2.

Table 1
Elemental analysis in dry ash free basis for pine wood chips, beech wood spheres and cellulose
(*: by difference)

	C(%)	H (%)	O (%)*	N (%)	S (%)
Pine wood	49.38	6.61	43.78	0.05	0.19
Beech wood	47.92	6.64	44.38	0.26	0.03
Cellulose	39.00	5.57	39.31	0.20	0.22

Table 2
Proximate analysis of the species used as feed-stock. The fixed-carbon content is obtained by difference.

	Volatiles (% daf)	Ash (% db)	Fixed carbon (% daf)
Pine wood	86.55	0.24	13.35
Beech wood	85.47	0.28	14.53
Cellulose	86.44	15.70	13.56

Experimental Setup

The experiments are carried out in a stainless steel fixed-bed reactor of 102.5 cm height and an internal diameter of 22 cm. The inert atmosphere is provided by a N_2 flow entering the reactor from the bottom through a stainless steel mesh to get a uniform flow distribution inside the bed. The biomass particles are placed inside the reactor in a stainless steel container of 21 cm of diameter and 56 cm height placed directly on the previously mentioned mesh. The reactor is externally heated with a wire heater with a power of 3.000 W placed on the external reactor wall. Both flanges in the reactor are also heated and insulated to reduce heat losses. The N_2 flow is preheated before entering the reactor as well. This preheater is operated at 600 °C. The line from the preheater to the inlet of the reactor is heated up to 800 °C. A scheme of the setup is shown in Fig. 1. The temperatures are measured inside the reactor at three different heights: 5, 10 and 30 cm from the bottom of the reactor, as well as at the reactor inlet (0 cm). At each height, three thermocouples are also placed at three radial positions: 0, 5 and 10 cm from the container wall. The pyrolysis temperature is taken as the temperature given by the thermocouple placed at 10 cm from the bottom of the reactor and in the centre of the bed. The heating rates are limited by the heat transfer inside the bed, and values between 1 and 10 K/min are achieved.

The gas outlet is at the top part of the reactor. From the main line, three sampling lines, heated to temperatures above 300 °C, leading to the analytical devices to characterize the volatiles: permanent gases and tar.

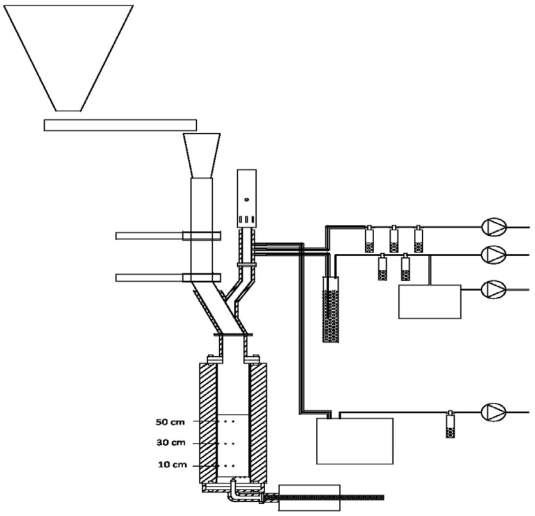

Fig. 1. Reactor set up: 1 – hopper, 2 – conveyor belt, 3 – feeding valves, 4 – burner, 5 – tar condensation line, 6 – GC-TCD, 7 – LIF system, 8 – Preheater.

The first sampling line is constituted by condensers in an iced bath filled with a solvent such as isopropanol to condense the volatiles vapour for off-line analysis in GC-MS/FID. The second line leads the gas after removal of condensable volatiles to a GC-TCD for on-line permanent gas analysis. The condensation system to clean the permanent gases from tar is formed by a condenser filled with water at ambient temperature, followed by a second one filled with isopropanol ice-cooled and silica gel to dry the gas. The third sampling line leads the vapour products to a LIF system for on-line tar characterization. The setup of this LIF system has been presented in previous studies of the authors [15, 16]. The volatile vapours enter the system at temperatures around 300 ºC. The measuring cell is also kept at this temperature to avoid condensation on the optical pathway. After the LIF system, the volatiles are condensed. At the end of each line a pump is placed to suck the gas from the reactor. After the pumps, a gas clock is attached to measure the flow rates.

Experimental Conditions

The pyrolysis experiments were carried out under different external conditions - maximum temperature and N_2 flow rate, material and bed density – to study the influence of these parameters on the process evolution itself and the product distribution and composition.

The feedstock was dried before each pyrolysis experiment. The reference temperature in these experiments was taken as the temperature measured at 10 cm from the bottom of the reactor at the centre line as specified in the reactor-setup description.

The gasification experiments were carried out using air as gasifying agent with air to fuel ratio varied. The influence of this parameter on the product gas composition is evaluated.

Results and Discussion

Pyrolysis Characterization

Temperatures Distribution

As previously stated, the main difference between the work presented in this paper and most of the studies found in literature for pyrolysis characterization is the size of the reactor, the quantity of used feedstock and the particle size, leading to a higher influence of the transport phenomena on the pyrolysis process.

For this reason, the temperatures distribution inside the bed is a key parameter to characterize the pyrolysis evolution, since it gives information about how the bed heating up takes place, the temperature homogeneity of the bed during the process under different conditions and also the endothermic and exothermic processes taking place at each moment and position. The bed is heated up with an external heat flux provided by a heating wire placed uniformly along the external reactor wall and a N_2 flow entering in the reactor preheated. Consequently, the temperature evolution will depend on the heat flux set in the heater, the N_2 flow and the inlet temperature of this flow, but also on the bed properties since it deter-mines the heat transfer inside the bed, including the particle properties and the inter-particle transfer mechanisms.

In Fig. 2 the temperature evolution in different parts of the reactor and for several external conditions are shown. The temperature of the N_2 entering the bed is given by "inlet" temperature. The temperature named "T 10 cm, wall" gives the temperature at 10 cm from the bottom of the reactor on the internal side of the reactor wall. The temperature named "T 10 cm, centre" gives the temperature evolution at the reference position as previously explained and the temperature "T 20 cm, average" gives the mean value of the three radial temperatures measured at a distance of 20 cm from the bottom of the reactor, i.e., the upper part of the bed.

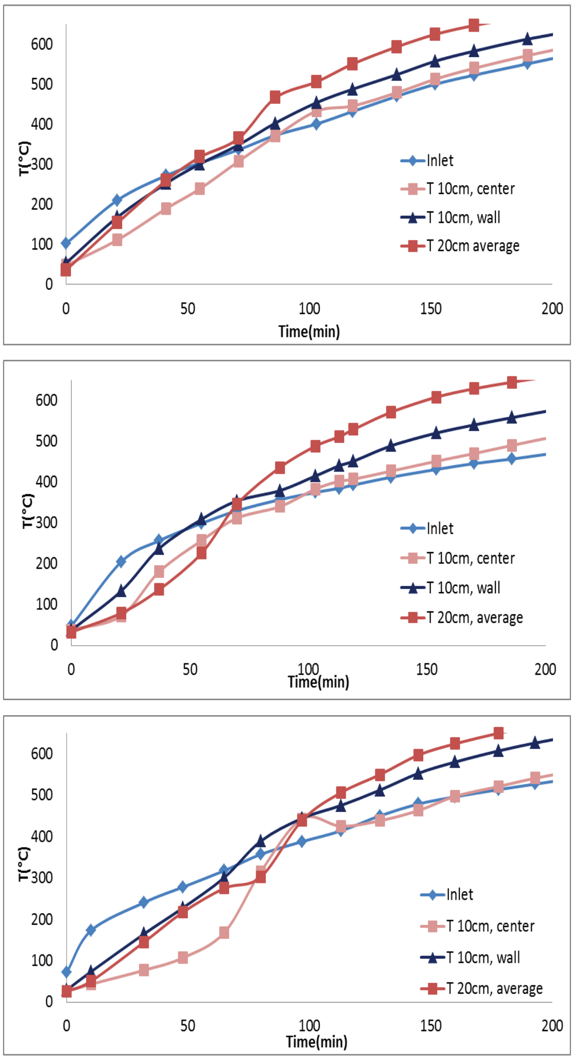

Fig. 2. Top – Comparison of temperatures evolution for wood chips with N_2 flow rates of 20 l/min. Middle – Comparison of temperatures evolution for pine wood chips with N_2 flow rates of 40 l/min. Bottom – Comparison of temperatures evolution for beech wood with N_2 flow rates of 20 l/min.

In the three experiments shown in Fig. 2 the external power applied to the bed is the same, i.e., 1.800 W and the same bed height, 25 cm. In the top and middle graphic in Fig. 2 the used raw material is wood chips, with a bed density of approximately 180 kg/m^3. In the bottom graphic of Fig. 2 the raw material used is beech wood and the particle size 2.5 cm. The bed height is 25 cm. The results from the top and middle graphics in Fig. 2 correspond to experiments with the same conditions except the N_2 flow rate, being in the first case (top) 20 l/min and in the second case (middle) 40 l/min. The third graphic corresponds to the results of the pyrolysis experiment with beech wood and the same conditions as the top graphic except the bed density being in this case 410 kg/m^3.

By comparing the two upper graphics in Fig. 2, it can be observed that at early stages of the pyrolysis process, i.e., with temperatures below 300 °C, higher flow rates seem to improve the heat transfer inside the bed, but not in the upper part of the bed. This can be seen by comparing the temperatures "T10 cm, centre" for both cases, being the slope of the temperature curve steeper for the case of 40 l/min. The same is observed in the inlet temperature. However, the temperature "T 20 cm, average" shows a completely different behaviour in both cases, being significantly lower in the case of 40 l/min. Between around 200 and 400 °C, where most of the pyrolysis takes place, a change in the temperature trend between both cases is observed. The heating rate for the case of 40 l/min is reduced while the temperature in the same position in the case of 20 l/min keeps increasing, reaching the wall temperature at this height, which would be considered as the maximum possible temperature that can be reached since the reactor heating takes place from the reactor wall and the inlet temperature at this stage of the pyrolysis is already lower than the wall temperature.

This change in trend in the temperature evolution in the centre of the bed for both cases, with the only difference between them regarding experimental conditions being the N_2 flow rate, may be related to the possible presence of exothermic secondary reactions, i.e., the lower flow rate gives results in higher concentration and higher residence time of volatiles inside the bed. This could lead to an enhancement of exothermic secondary reactions, such as clarification reactions leading to a temperature increase, observed in the temperature evolution. If the top and bottom graphics are now compared, it is observed that the inlet temperature follows the same behaviour but the rest of the temperatures are significantly lower and the bed gradients higher in the bottom graphic. This is due to the significantly higher bed density in the case of beech wood (bottom graphic). However, when pyrolysis starts already at temperatures below 200 °C, a significant change in the temperature evolution in the centre of the bed for the case of beech wood is observed, affecting even the temperature close to the wall at the same height and overlapping this temperature at around 400 °C. After this point, the temperature in the centre of the bed decreases slightly and follows the same behaviour as the inlet temperature. This may be considered as a validation of the presence of these exothermic secondary reactions, enhanced by the higher particle size and significantly higher concentration of volatiles (higher bed density) in the case of beech wood.

In Fig. 3 the temperature evolutions in the centre of the bed – the reference position for the previous cases – together with new experimental results are compared.

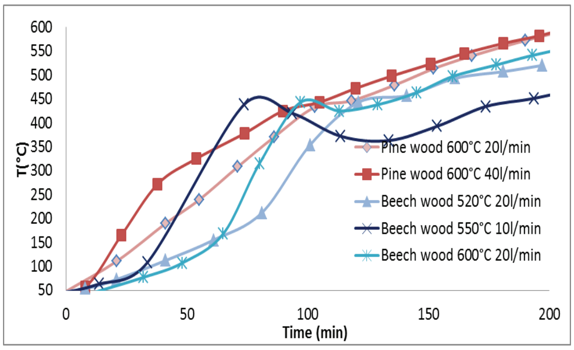

Fig. 3. Comparison of temperatures evolution in the reference position for several pyrolysis experiments.

As previously stated, comparing the two cases of pine wood, a higher flow rate leads to an improvement in the heat transfer at early stages of the process, but when most of the pyrolysis is taking place, between 200 and 400 °C, there is a change in the trend of the temperature evolution, increasing for the case of 20 l/min. If the cases of beech wood are compared, this change in the temperature evolution slope is much clearer, due most probably to the higher bed density, and it increases with the increase in volatiles concentration, being the most extreme case the experiment named "Beech wood 550 °C 10 l/min", with a bed density of 400 kg/m^3 and a flow rate of 10 l/min. In this case the volatiles concentration is the highest one, as well as the observed exothermicity.

Products Distribution and Composition

Product Yields

Different process conditions have a direct influence on products distribution and composition.

In Fig. 4 char, liquid and gas yields for pine wood and cellulose pyrolysis experiments are presented. For all cases the temperature is the same, the N_2 flow rate and the feedstock being the difference between the experiments. The char yield is measured by weighting the solid product once the experiment is finished and the solid cooled down. To determine the liquid and gas yields, part of the vapour products were sampled. The condensable volatiles were condensed in toluene at -20 °C and isopropanol at 0 °C. Then the gas stream was passed through silica gel to dry the gas and afterwards piped to a GC-TCD. The liquid yield is obtained by weighting the condensation system before and after the experiment. The total gas yield (H_2, CO, CH_4, CO_2) is obtained by deter-mining the N_2 percentage in the output gas and relating it to the N_2 fed into in the reactor. The flow through the GC-TCD is kept constant to be able to compare the results and the total flow through the sampling line after condensation is also measured to extrapolate the condensed mass to the total vapour mass produced in the reactor. However, in the case of pine wood pyrolysis the mass balance is not closed to 100%. This is most probably due to the fact that some very light volatile compounds are not being condensed. That is why the liquid yield per difference is also presented. It is observed that the difference between the liquid yield measured and the liquid yield obtained per difference is higher for the experiment with 10 l/min than for the experiment with 20 l/min.

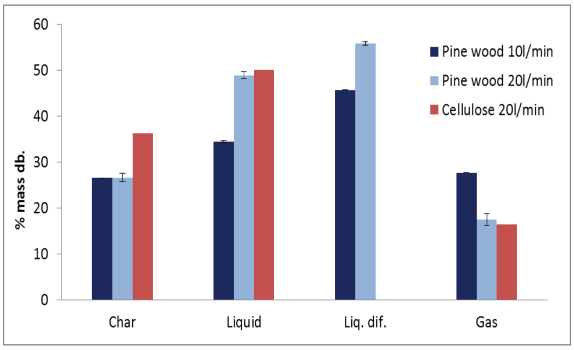

Fig. 4. Char, liquid, and gas yields of pyrolysis experiments. Liq. dif. corresponds to the liquid yield obtained by difference 100 – (% char + % gas).

The char yield from pine wood pyrolysis is very similar independently of the N_2 flow rate. The liquid yield is higher in the case of 20 l/min, while the gas yield is lower, being the maximum temperatures approximately the same in both cases. This could be due to the presence of secondary reactions increasing the gas yield. This is in agreement with the temperature evolutions described in the previous section, i.e., lower flow rates, giving place to higher volatiles concentration and residence time, lead to higher temperatures inside the bed, possibly due to the presence of exothermic secondary reactions. The observation that the difference between the liquid yield and the liquid yield obtained per difference is higher for the case of 10 l/min is also consistent with this, since these secondary reactions would give place as a product to light compounds not condensed under the conditions given.

In the case of cellulose, the char yield is higher than in the case of wood and the liquid and gas yields are similar to the yields from pine wood pyrolysis with 20 l/min.

Permanent Gas Composition

In Fig. 5 the permanent gas composition (H_2, CO, CO_2 and CH_4) from the experiments shown also in Fig. 4 is presented. It can be observed that lower flow rates lead to an increase in the CO and CO_2 content, with CO_2 being the one with the highest increase. Also the CH_4 and H_2 contents are increased.

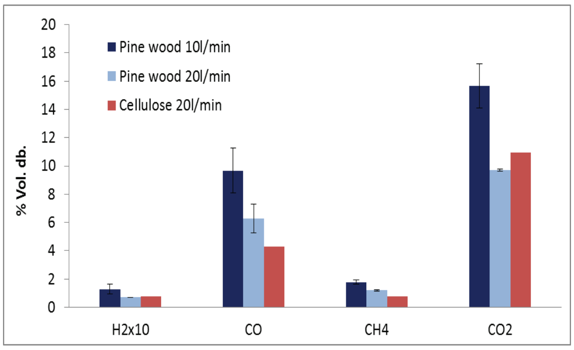

Fig. 5. Permanent gas composition for the experiments presented in Fig. 4.

Since the permanent gas composition is measured on-line, transitory evolution of the gases is also characterized. In Fig. 6 these results are presented.

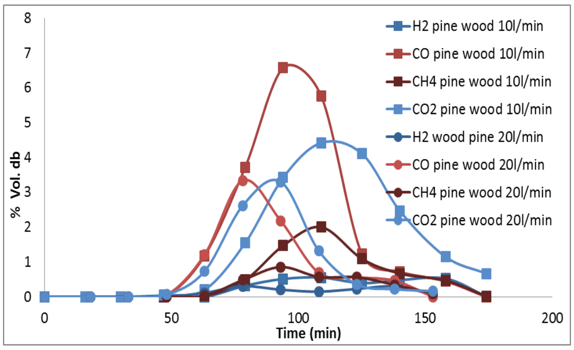

Fig. 6. Permanent gas evolution for the pyrolysis experiments of pine wood with 10 and 20 l/min.

For each experiment, it is observed that CO is the first gas produced while CO_2 and CH_4 appear delayed with time and with coinciding peak production. These two gases, together with H_2 may also be the product of secondary reactions.

Characterization of PAH in Volatiles Vapors with LIF

The presence of PAH in the pyrolysis volatiles is qualitatively characterized by applying Laser-Induced Fluorescence (LIF).

According to Asmadi et al. [13] PAH may be produced in secondary reactions of lignin primary products, while Hajaligol et al. [14] suggest the formation of PAH from direct decomposition of cellulose and hemicellulose. The formation of PAH during pyrolysis and its characterization has already been addressed in a previous work from the present authors [15], where it was observed that these species may be produced already during primary pyrolysis decomposition as well as due to heterogeneous secondary reactions of primary pyrolysis products, leading to a red-shift in the signal, i.e., to bigger PAH [16].

In Fig. 7 several fluorescence spectra obtained at different times of the pyrolysis process for pine wood with a flow rate of 20 l/min – corresponding with the temperature evolutions shown in the top graphic of Fig. 2 – are presented. It is observed that at early stages of the pyrolysis some compounds emitting fluorescence are already produced having been identified as extractives, containing probably carbonyl functional due to the fluorescence signal and the process temperature [15].

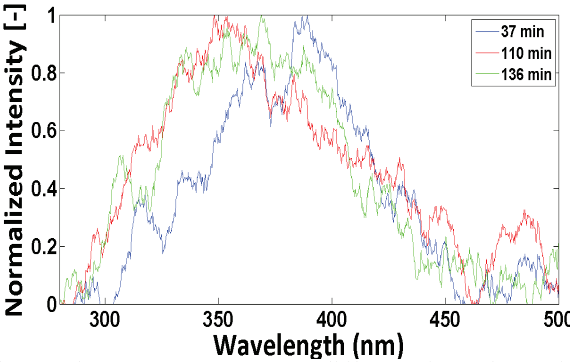

Fig. 7. Fluorescence spectra at different times from pine wood pyrolysis with a flow rate of 20 l/min [17].

In advanced stages of the pyrolysis process, fluorescence signals typical of 2 and 3 aromatic compounds appear while at higher temperatures a red shifting in the signal due to an increase in the number of rings is observed [16].

Char Characterization

Characterization of the solid product gives also information about the pyrolysis process, besides the possible applications of the char itself as a fuel or as biochar for soil amendment or other non-thermal applications.

In Figs. 8 and 9 the volatiles content in mass % dry basis as well as the carbon content, also in mass % dry basis, are shown respectively. Despite using the same maxi-mum temperature – measured at the reference position – the volatiles as well as the carbon content from the chars measured at four different positions inside the bed differ significantly from each other due to the different influence of transport phenomena caused by different bed properties.

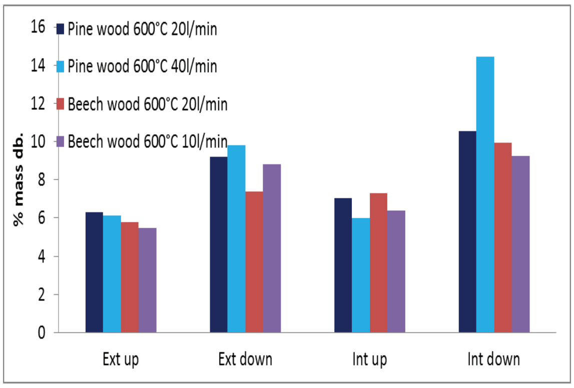

Fig. 8. Volatiles content in mass percentage in dry basis for pine and beech pyrolysis up to a maximum temperature of 600 °C measured in the reference position and with flow rates of 10, 20, and 40 l/min.

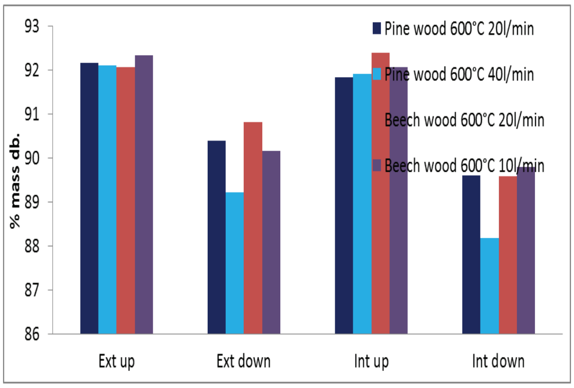

Fig. 9. Carbon content in mass percentage in dry basis for pine and beech pyrolysis up to a maximum temperature of 600 °C measured in the reference position and with flow rates of 10, 20, and 40 l/min.

The part of the bed with the highest volatiles content and lowest carbon content, i.e., the lowest degree of conversion is presented by the char in the internal bottom part of the bed, which is consistent with the temperature evolutions shown in Fig. 2, since the inlet temperature is the lowest one at the end of the experiment. However, the char in the external part is more evolved due to the heat flux from the reactor wall, leading to higher temperatures. Looking at the top part of the reactor, the conversion degree is quite similar for the external and internal parts, although slightly more evolved in the external part due to the same reason as in the bottom part. For the same position inside the bed, higher bed density gives in general place to higher carbon content (beech wood experiments in comparison with pine wood experiments) and higher flow rate leads to a lower carbon content (pine wood 20 l/min versus pine wood 40 l/min). These results could be in agreement with the presence of exothermic secondary reactions giving place to secondary char, which would have higher carbon content.

Gasification Characterization

This setup has been also used to characterize updraft gasification processes using air as gasifying agent.

In Fig. 10 the product gas composition for gasification of beech wood using three different air to fuel ratios (in kg) is presented. It is observed that the lower the air to fuel ratio the higher the H_2 and CO content and the lower the N_2 and CO_2 content, i.e., higher calorific value, as shown in Fig. 11.

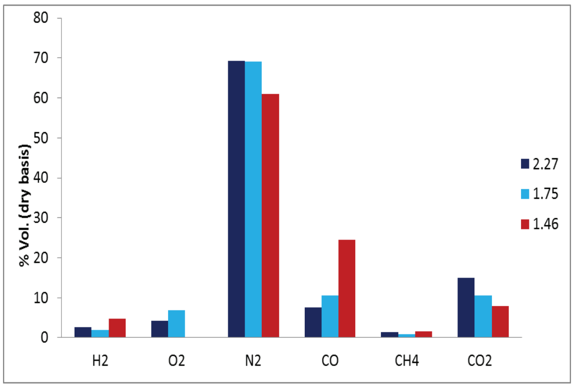

Fig. 10. Product gas composition of gasification process using three different air to fuel ratios in kg.

The same LIF system is also applied in gasification to characterize the PAH present in the volatiles vapours. In Fig. 12 a temporal evolution of the fluorescence spectra during gasification is shown. It is observed that as the process evolves, the spectra are shifted to higher wave-lengths, typical of 3 and 4 aromatic compounds and also to higher fluorescence intensities. If these spectra are fitted with representative pure species – guaiacol, naphthalene, phenathrene and pyrene – as already introduced by this group in previous works [15, 16], a qualitative evolution of these species during the gasification process is obtained.

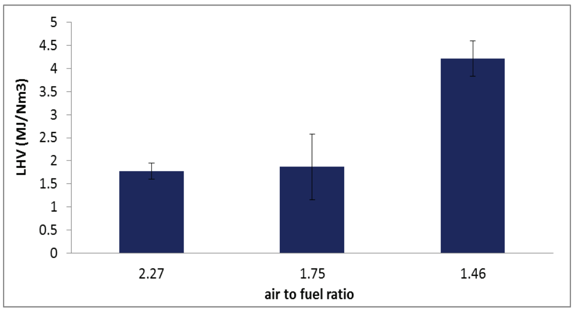

Fig. 11. Low heating value of the product gas for the three different process conditions presented in Fig. 10.

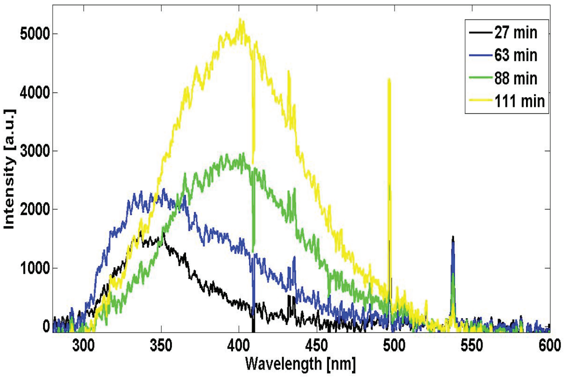

Fig. 12. Evolution of the fluorescence spectra during a gasification process.

Figure 13 shows for early stages of gasification, while heating up the reactor, naphthalene is the main species. Once stationary conditions are achieved and regular feeding takes place, the main PAH species is pyrene.

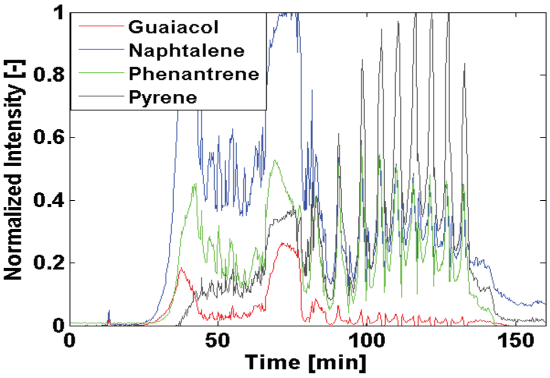

Fig. 13. Temporal evolution of the representative pure species according to the fitting shown in Fig. 12.

Conclusions

A setup for characterization of thermochemical conversion processes in a technical-scale fixed-bed reactor, in particular pyrolysis and gasification is presented. Temperatures, permanent gas composition, and qualitative evaluation of PAH in the volatiles vapours can be characterized on line. Besides, off-line analysis of solid and liquid products can be done to determine, for example, the mass balances or characterize other properties of the products.

By characterizing the temperature evolution at different positions inside the bed it is possible to observe the influence of external conditions (N_2 flow rate) and bed properties (particle size and bed density) on the pyrolysis process. This becomes more significant in the present study in comparison with previous studies found in literature probably due to an increase in the influence of transport phenomena because of the process up-scaling getting closer to real applications. Besides the temperature gradients inside the bed, resulting in different char properties as shown in Section 3.1.2.4, the most significant result found in the temperature characterization is the different behaviour that the temperature evolution (measured at the reference position) shows depending on the external conditions. Higher heating-up rates are observed with lower N_2 flow rates and higher bed densities and particle sizes in the temperature range between around 200 and 400 °C. This could be due to the presence of exothermic secondary reactions. This would be consistent with the products yields presented in Section 3.1.2.1, where higher gas yield and lower liquid yield are observed for lower flow rates.

The qualitative characterization of PAH in the volatiles vapours can be also analysed on line observing the presence of spectra typical of 2 and 3-ring aromatic compounds during primary pyrolysis and afterwards, possibly due to secondary reactions, as it has been already presented in a previous work of this group [15].

The same setup is also applied in updraft gasification with air. In the present study the gasification process using different air to fuel ratios is characterized, observing a more valuable gas product with lower air to fuel ratios. The characterization of PAH has been also performed being possible to monitor on-line the qualitative composition in terms of one- to four-ring aromatic compounds of the volatiles vapours.

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