

Role of the particle size on the yield of hazelnut shell pyrolysis products

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Abstract

The yield and composition of pyrolysis products depend on the characteristics of feed stock and process operating parameters. This study focuses on the effect that biomass particle size has especially on the conversion of biomass into gas of pyrolysis. Pyrolysis experiments of piedmont hazelnut shell were performed in a lab-scale reactor system and via TGA analysis at a temperature range from room temperature to 800 °C using four different heating rates (6, 12, 20, 30 °C/min). The particle size studied were 0.5 cm and 100 µm. The results indicated that the gas yield decreases as the particle size decreases, while increasing as the heating rate decreases. The variation of the particle size had a significant effect on the water content of the tar, obtaining a higher water content with the smaller particles sizes. The maximum yield of bio-oil obtained was 62.1 wt% using a heating rate of 30 °C/min with the particle size of 100 µm.

Furthermore, the small particles sizes have reduced slightly the char yield, which is the product with the highest energy content and because of that, the energy content at the same heating rate was higher in case of hazelnut shell particles size of 0.5 cm. The maximum chemical energy yield reached was 94% for the pyrolysis with particle size of 0.5 cm using a heating rate of 30 °C/min.

Keywords: biomass, hazelnut shell, pyrolysis, particles size effect, TGA analysis.

1. Introduction

Climate change is one of the most significant threats facing the world today. One way to reduce emissions would be to switch from fossil fuels to alternative sources of energy such as biomass [1–3]. Biomass is fuel that is developed from organic materials, then it provides a clean, renewable and sustainable energy source that may dramatically improve the environment, economy, and energy security [4–7]. Biomass energy generates much less air emissions than fossil fuels, reduces the amount of waste sent to landfills, and reduces dependence on foreign oil. Biomass energy also generates thousands of jobs and helps revitalize rural communities [6]. Biomass includes products, byproducts, residues and waste from agriculture, forestry and related industries such as straw, husk, cobs, stalks, leaves, bark, fruits, cutting vines, as well as the non-fossilized and biodegradable organic fractions of industrial and municipal solid wastes [4–6]. Biomass particularly contains cellulose, hemicelluloses, lignin, extractives and minerals [8, 9]. The inorganic material content ends up in the pyrolysis ash [4, 10].

There are several ways to convert biomass into useful products depending on the biomass characteristics and the requirement of the final product and its applications. Pyrolysis is one of the most widely used methods to convert residual biomass into valuable fuels [11]. It is a thermochemical conversion process in which the organic matrix undergoes direct thermal decomposition in the absence of oxygen resulting in liquid bio-oil or tar (high molecular hydrocarbons and water), solid biochar, and non-condensable gas products (mainly CO, CO₂, H₂, CH₄, C₂H₂, C₂H₄, C₂H₆) [11–14]. Water is one of the most abundant compounds in pyrolysis oil, it lowers the viscosity and the heating value of the oil [15].

Many serial and parallel reactions take place during the pyrolysis of the biomass. These include dehydration, depolymerisation, isomerization, aromatisation, decarboxylation, and charring [14, 16]. The pyrolysis process can be described in three main stages: (I) initial evaporation of free moisture, (II) primary decomposition followed by (III) secondary reactions (oil cracking and repolymerisation). These stages are intermingled, with a possibility to observe their transitional behavior through thermal analysis [14].

During transient heating of the particle, temperature increases locally, leading first to the humidity evaporation (drying stage) and then to the progressive release of pyrolytic volatiles (primary pyrolysis stage). The primary volatiles are produced from the thermal scission of chemical bonds in the individual constituents of biomass (cellulose, hemicellulose, lignin and extractives), and comprise permanent gas species (e.g. CO₂, CO, CH₄) and

condensable species at ambient conditions (tar). Although each of the biomass constituents decompose at faster rates in different temperature ranges, the overall primary pyrolysis stage is complete at relatively low temperatures (<500 °C), yielding the char. The produced char also contains a significant part of the mineral matter originally present in the parent fuel. Nevertheless, if the fuel is converted at higher temperatures some of the primary volatiles released inside the particle can further participate in a variety of secondary reactions to form secondary products. Serial and parallel reactions can take place, occurring either heterogeneously or homogeneously, as for example cracking, reforming, dehydration, condensation, polymerization, oxidation and gasification reactions [14, 16, 17].

Several factors affect the process of pyrolysis of the biomass, yields and properties of products. These include the type, chemical composition and initial moisture content of the biomass, as well as biomass pretreatment (physical, chemical, and biological), reaction atmosphere, pyrolysis temperature, heating rate (HR) and residence time of the vapour [14, 18].

Shen et al. postulated that destruction of the wood particle structure by milling could be a reason for higher oil yields for smaller particles [19]. Salehi et al. pyrolyzed three fractions of milled wood particles, <0.59, 0.59–1, and 1–1.4 mm, in a fluidized bed operated at 500 °C and noticed that the oil yield decreased rapidly from 62 to 52 wt % as the sawdust dimensions increased from <0.59 to 0.59–1 mm. They observed that larger sawdust sizes, decrease the oil yield [20]. On the other hand, Haas et al. performed real-time microscope analysis of poplar wood undergoing pyrolysis. The biomass was heated with 150 °C/min to 500 °C. It was clearly observed that liquid droplets exist inside the decomposing wood structures and that some of the droplets were trapped inside the particle. This is a clear indication on limitations for newly formed liquid (partly depolymerized biomass) to leave the particle. Vapors created inside the biomass particles find their way out mainly via channels inside the biomass structure. When these compounds do not leave the hot biomass particle fast enough, they will cross-link and eventually form char [21]. Westerhof et al. studied the effect of particle geometry and microstructure on the fast pyrolysis of beech wood in a fluidized bed reactor operated at 500 °C. They explain that for milled particles, the pyrolysis oil and water insolubles yields decrease rapidly as the particle size increases. The char yield increases drastically when the particle size is increased, while a less sharp increase in water and gas yield is observed. This is underpinned by the lower yield of high boiling point molecules like the water insolubles for the larger milled particles and an increasing yield of water, a component that is known to be formed as a side product of cross-linking and polycondensation reactions [15]. However, in other experiments at 400–600 °C [19], changes in the yield of water due to tar cracking over char surfaces were found to be of little significance. Other behavior noted by Westerhof et al. in their experimental study is that lower gas yield for the smallest particles is maybe due to gas is not only a product from vapor phase cracking but also a side product of cross-linking and polycondensation reactions inside the particles. For smaller particles, cross-linking reactions are reduced indicating a decrease in production of char and water [15].

Particularly, small biomass particles have low mass transport resistance to the vapors, which are then released quite quickly before secondary cracking, resulting in a higher yield of liquid product. The size, shape, and physical structure of biomass affects the pyrolytic product. Di Blasi et al. has conducted a study about the effect that produce the size reduction on the pyrolysis of hazelnut shell. They have shown that once the particle structure is destroyed by milling for example, the global exothermicity of the pyrolytic conversion process is almost eliminated, as a consequence of the reduction in the intraparticle residence time of volatile products and the activity of secondary reactions [22]. Hazelnuts have in fact exhibited an exothermic effect during pyrolysis much more sustained than any other wood-cellulose biomass due to secondary intraparticle reactions of organic vapors produced by primary degradation [22]. This is due to the particular nonporous structure of hazelnut shells, which causes the trap of primary vapors and favors secondary reactions. In other lignocellulosic materials, these marked variations in the particle size variation are not apparent because they have a much more porous and interconnected structure, typical of wood. This micropore network does not cause trapping of organic vapors as in the case of hazelnut shells [15]. The compact and nonporous structure of hazelnut shells causes almost instantaneous release of the entire volatile matter contained within it due to the exothermic effect generated and its local temperature rise. In the thickness of the shell the mass transport resistance of the vapor phase and the gas phase is very high and the conversion process is controlled by the mass transfer [23].

Larger particles, on the other hand, present more mass transport resistance to the escape of the primary tar [24]. So, there is high residence time that leads to secondary reactions take place which contributed to the formation of char and a loss in tar yield [21]. Larger particles sizes are economically more convenient but also contribute to

creating a non-isothermal reactor environment. Since the costs associated with biomass grinding increase with decreasing particle size, there is need to identify the optimal particle size for desired application [15].

Moreover as mentioned before, the pyrolysis temperature significantly influences the distribution and properties of products [25–27]. Most studies report that higher pyrolysis temperatures favor the production of gas [25]. Generally, the bio-oil yields reach their peak concentrations at temperatures between 400 and 550 °C, and then decline after proceeding with heating. At temperatures higher than 600 °C, the bio-oils and char products are converted into gas due to the dominant secondary cracking reactions [26, 28]. Char formation is minimized as the reaction temperature rises, while low heating ramp (high residence time) and high maximum reaction temperatures are favorable for pyrolysis gas production. Conversely, very slow heating rates coupled with low maximum temperatures in the reactor, lower than 500 °C, maximize char yield due to the repolymerization reactions [16, 29].

To date, thermogravimetric analysis (TGA) is considered as a powerful technique for pyrolysis behaviors characterization and kinetic study. In a TGA experiment, the pyrolysis behaviors (mass loss and mass loss rate) can be measured as functions of temperature and time in an inert atmosphere [7, 30, 31].

In our previous study, by-products from agro-food industries in Piedmont were pyrolyzed without any prior treatment (drying or grinding) to evaluate the possibility of using them to limit costs for the companies. The results shown the hazelnut shells as the most suitable biomass with the higher chemical energy yields [13].

The objective of this study was to investigate the effect that biomass particle size has on products yield of hazelnut pyrolysis, especially on gas production yield, at different heating rates. This research tries to expand the understanding of the pyrolysis of the hazelnut shells from the piedmont (Italy). Hazelnut shell with particles size of 100 µm and 0.5 cm were explored. Pyrolysis experiments were performed in a lab scale reactor and by TGA analysis. A maximum reactor temperature of 800 °C and four different heating rates (6, 12, 20, 30 °C/min) were used.

2. Materials and Methods

2.1. Biomass samples

Samples consisted of hazelnut shells generated during the processing of hazelnuts from the same batch used before [13]. HS with particle sizes of 100 µm and 0.5 cm were used. For the sake of simplicity, in this study the hazelnut shell with “original dimensions” (0.5 cm) and the Hazelnut Shell Milled (100 µm) are referred as HS and HSM, respectively. HS particles were subjected to a milling process for 30 minutes to produce average sizes of 100 µm.

Table 1 Chemical composition, proximate and ultimate analysis of the HS [13].

Analysis	Hazelnut Shells (Feedstock)
Ultimate analysis (dry, wt.%)	
C (%)	55.1
H (%)	6.3
N (%)	1.6
O (by difference) (%)	37
Proximate analysis (wt.%)	
Moisture (% p/p)	5.3
Volatile matter	77.1
Fixed carbon	21.1
Ash (%)	1.8
Composition of lignocellulosic material (wt.%)	
Cellulose	30.5
Hemicellulose	25.9
Lignin	35.1
HHV (MJ/Kg)	18.8

PH	5.3
Average size	0.5 cm & 100 μ m

The chemical composition, proximate and ultimate analysis, reported in Table 1, were performed according to the ASTM standards (E871, D1102-84) by using a programmable ash oven. The higher heating value (HHV) of the biomass and pyrolysis products were measured with a bomb calorimeter.

2.2. Thermogravimetric analysis

The thermogravimetric analysis (TGA) of hazelnut shell was carried out in a Mettler Toledo TGA/SDTA 851e system. The weight loss was recorded in the temperature range of 25°C-800°C. 50 mg of sample (HS and HSM) was heated up to 850 °C under an argon constant gas flow (50 ml/min) using four different heating rates (HR1: 6, HR2: 12 and HR4: 30 °C/min) in order to determine the effects of heating rate. All experiments were repeated twice to confirm the repeatability of the experiments and the authenticity of the generated data.

2.3. Pyrolysis experimental Setup

The pyrolysis experiments were conducted in a lab-scale batch reactor unit as illustrated in [13]. It comprises a cylindrical fixed-bed reactor, a furnace, a liquid product collection system (condenser) and a gas meter.

The cylindrical pyrolysis reactor was made of AISI 310 austenitic stainless steel and it has an internal diameter of 26.64 mm, a height of 139 mm and a wall thickness of 6.76 mm. The reactor was placed inside of an electrical oven. The sample was heated from room temperature to 800 °C using different heating rates. The temperature ramps were managed by a temperature PID controller. The reactor is connected to the condenser through a 6 mm diameter tube.

The condenser is made entirely of AISI 316 stainless steel and it operates in countercurrent to optimize heat exchange and to promote pyrolysis vapors condensation. It has an internal diameter of 23 mm and length of 146 mm. Heat exchange is carried out between the pyrolysis vapors coming from the reactor and passing through the inner tube of the condenser, and the coolant which is a mixture of 50% distilled water and 50% Paraflu®. The coolant passes into the condenser jacket, in countercurrent to pyrolysis vapors, at an operating temperature of 6 °C.

A safety valve is connected to the cylindrical reactor to limit the reactor pressure to 2 bar in case the tube connected to the condenser is obstructed. Two thermocouples were placed inside the reactor. One was in contact with the biomass and the other one, was in the middle of the reactor to control the oven temperature. Moreover, at the output of the condenser there is a thermocouple to control the output gas temperature, in order to monitor the correct functioning of the condenser and always ensure that the vapors are condensed. Temperatures in the bed, in the reactor and at the exit of the condenser were continuously monitored. Excellent stability and reproducibility of these temperatures were achieved.

2.4. Pyrolysis experiments

Each experiment was initiated by flowing nitrogen 100 ml/min for 30 minutes to remove the air within the system. In each test, 3 g of sample was heated from room temperature to 800 °C and an operating pressure close to the atmospheric pressure. Heating rates of 6, 12, 20, 30 °C/min were studied.

The condensable matter (tar) was quenched as the pyrolysis vapors pass through to the condenser. The non-condensable pyrolysis gases passed through a quartz-wool silica gel filter and subsequently through the gas meter where the volume and the flow rate are recorded. Then, the gas product was collected in a gas-sampler and analyzed using a micro gas chromatograph (SRA Micro GC equipped with a thermal conductivity detector (TCD)). More details about the equipment can be found in our previous publication [13].

After each test, in order to calculate the yields of pyrolysis products, a mass balances were performed through quantification of all the inputs and outputs. After each run, the liquid and solid phases were recovered for off-line analysis.

The char was recovered from the bottom of the reactor and was weighed by an analytical balance. The weight of the gases was calculated by measuring the total volume and the percentages of their constituents.

The yield of tar (including water) was determined by the weight difference of the condenser before and after the experiment. The condenser was then washed using a mixture of isopropanol and hexane (1:1). The tar was

collected in a beaker and the water in the collected solution was removed by anhydrous sodium sulfate; then, the remained solution was dried at 60 °C to remove the solvent, and the residue liquid oil was weighed and stored in a glass sample bottle for further analysis.

$$Y_{tar} = Y_{bio-oil} + Y_{H_2O} \quad (\text{Eq. 1})$$

The value obtained from the equation (Eq. 1) was compared to the difference on the basis of the mass balance of the fed biomass and the gas and char obtained.

The sum of char, tar and gas products was reported in the range of 94-98% over the fed biomass. The rest 6-2% could be some condensed matter evaporated during the tar step recovery. For the correct result analysis and comparison, the value of tar yield used was the one calculated by the difference between the inlet biomass and the gas and char.

3. Results and discussion

The effect of the particle reduction of hazelnuts shell on pyrolysis products at different heating rates has been investigated. The pyrolysis results obtained with HS and HSM were compared and analyzed. The effects of changes in the properties of the samples are observed in relation to the temperature field, the weight loss curves (TGA), the yields, energy content and composition of products.

Firstly, the influence of the pyrolysis temperature on the yield of the gaseous product was analyzed and the value for the experiments was optimized with the aim of increasing the yield of the produced gas. The results of the gas yield from the pyrolysis of HS from room temperature to 750 °C and 800 °C, using different heating rates (HR1, HR2, HR3 and HR4) are shown in Figure 1.

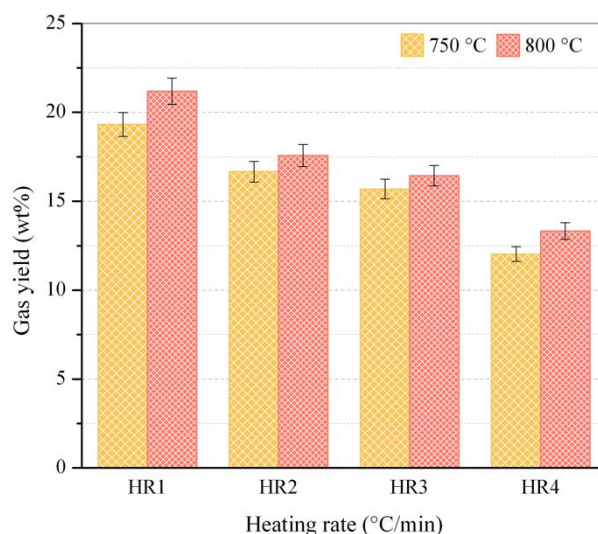


Figure 1. Gas yield (wt%) from the pyrolysis of HS with two maximum pyrolysis temperatures, 750 °C and 800 °C using different heating rates.

The figure highlights increase in gas yield when the maximum pyrolysis temperature increases. The increase in gas performance is probably due to an increase in the rate of devolatilization and thermal degradation within the pyrolysis, which is in line with the literature [6, 25]. Since the results obtained of gaseous product percentages, at the same rate of heating, were always higher in the case of setpoint at 800 °C, this value was selected as the maximum pyrolysis temperature for the following pyrolysis tests.

3.1. Thermogravimetric analysis results

Thermal behavior of the hazelnut shell was studied by TGA in the temperature range of 25–850°C. The TG/DTG curves obtained in an argon environment at a heating rate of 16, 12 and 30 °C/min of HS and HSM are compared in Figure 2. The recorded weight loss history was normalized for the initial weight, and its rate was calculated (Figure 2 (left)).

The thermal decomposition actively took place below 500 °C. The DTG curves (Figure 2 (right)) show that the pyrolysis process of HS and HSM be further divided into three stages. Both samples, HS and HSM present similar decomposition behaviors. In the first stage, the drying process takes place at temperatures below 130 °C and results in low mass loss. It is believed to be attributed to the evaporation of physically adsorbed water and light volatiles [24, 30, 32]. The devolatilization or pyrolytic cracking take place in the second stage, and it covers a wide temperature range from 130 to 500 °C during which a large proportion of weight of the sample lost with two significant mass-loss peaks (shown in derivative thermogravimetry (DTG) curve); but these two distinct peaks are more notable for the HSM than for the HS. This stage consists of two exothermic simultaneous processes where the main components, hemicelluloses, cellulose and lignin are decomposed and a high amount of volatile matter formation occur [31–34]. The first peak was mainly attributed to the degradation of the hemicellulose. The thermal stability of the hemicellulose is lower than cellulose, because hemicellulose is a mixture of various polymerized monosaccharides with lower degree of polymerization [31]. Instead, the second peak, a contiguous and/or simultaneous degradation process is mainly due to the composition of cellulose, because cellulose is a high-molecular compound and part of cellulose has crystalline structure made of ordered microfibrils that resulted in thermal degradation more difficulty than hemicellulose [31, 35]. And these results are in according with the results obtained from the single degradation TGA of xylan (representing hemicellulose) and cellulose reported by Ma et al. [31].

Then, the third stage was a slow degradation stage, which evidences the last endothermic decomposition of the lignin at temperatures above 500 °C [31, 33]. It has been shown that, the degradation of the lignin occurs in a wide temperature range (100–800 °C), which results in a high char yield [30]. After 700 °C only a slight change in weight loss has observed.

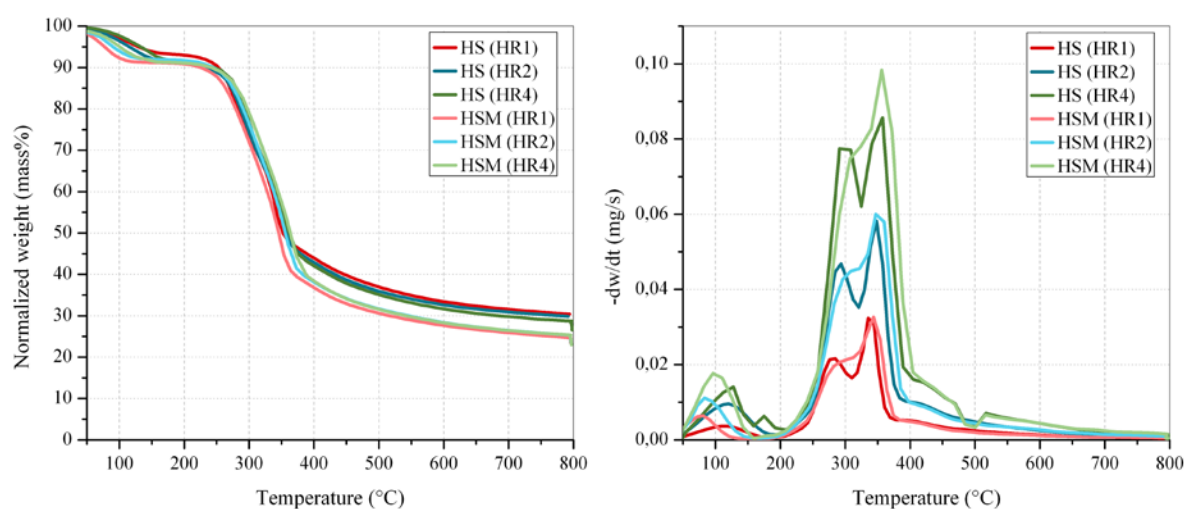


Fig. 2 TG (left) and DTG (right) results of the HS and HSM at different HR

There are some notable differences between the two particle sizes mainly below 400 °C. In the first stage, HSM weight loss faster than HS. On the other hands, the second stage, the two significant peaks of mass loss are sharper for HS than for HSM. The reason could be the low mass transport resistance to the vapors due to the destruction of the particle structure by milling, allowing a high and faster decomposition.

The heating rate not only affect the temperature at which the highest weight loss rate reached, but also affect the maximum value of weight loss rate. The maximum value of weight loss rate increases with increasing heating rate as shown in Figure 2. It can be seen from the graph that increase in heating rates only shifts the peak temperature to higher value without changing thermal profile of decomposition. This could be due to the decrease in heat transfer efficiency at higher heating rates. It is reported in literature that at lower heating rates, heating of biomass particles occurs more gradually and leads a better heat transfer to the inner parts of biomass. Moreover, that the maximum rate of decomposition increase with an increase in heating rate because of increase in thermal energy present [33, 36, 37].

3.2. Pyrolysis experiments results

The effect of the particle reduction of hazelnuts shell on pyrolysis products at different heating rates and a maximum reactor temperature of 800 °C has been also investigated in a lab-scale batch reactor. Figure 3 shows the pyrolysis products yields of HS (left side) and HSM (right side) using different heating rates. In general, fast heating rates lead to higher yields of tar and lower yields of char [16]. For example, the increase of heating rate from 6 (HR1) to 12 (HR4) °C/min was observed to result in higher yields of tar by about 15.2 and % 9.9 (wt %) for HS and HSM, respectively. That can be explained due to higher heating rates i.e., shorter residence time favors tar production due to the quick removal of organic vapors from reactors which minimizes the secondary reactions, in other words, it favor bond scission reactions to form tar fragments while the lower heating rates favor the recombination of tar fragments on the biomass matrix (secondary reaction, charring reactions) [14, 16, 29]. Moreover, it also observed that the gas yield also decreases even when the heating rate increases.

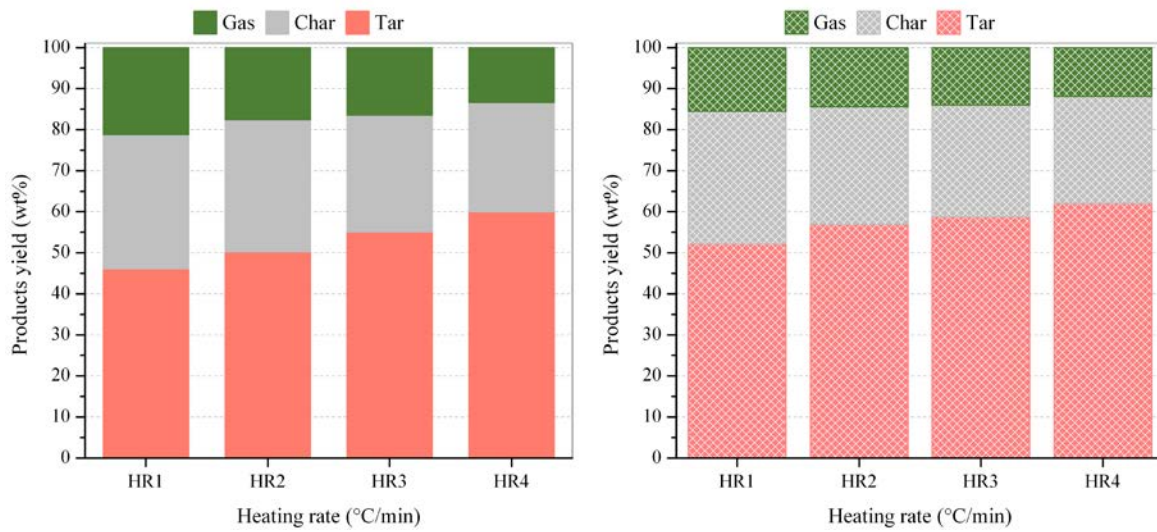


Fig. 3 Gas, char and tar yields of HS (left) and HSM (right) at different heating rates.

However, product distribution was also found dependent on the particle size of the biomass, which, in turns, is inversely proportional to heating rate. In fact, lower yields of liquids were measured when pyrolyzing larger fuel particles (HS), as a result of the particle size effect on the secondary reactions of volatiles [14]. Larger particles, present more mass transport resistance to the escape of the primary tar [24]. So, there is high residence time that leads to secondary reactions take place which contributed to the formation of (secondary) char and a loss in tar yield [21].

On the other hand, HSM (Figure 3 (right)) shows higher yield of tar than HS at the same heating rate because the smaller particles have low mass transport resistance to the vapors, which are then released quite quickly before secondary cracking [15]. This can be explained because the particle structure is destroyed by milling, then the mass transport resistance of the vapor phase and the gas phase is low, reducing the intraparticle residence time of volatile products and the activity of secondary reactions [22].

In addition, the figure also shows that the HSM produces a slight lower gas yield than HS, and this is because the gas is not only a product of the vapor phase cracking but also a secondary product of cross-linking and polycondensation reactions within the particles [15].

Figure 4 shows the oil and water yields of HS (left side) and HSM (right side) at different heating rates. Particle size variation had a significant effect on the water content of the bio-oil, with very high-water content at lowest particle size. The water content ranges from 11% to 15 % and from 16% to 21% for the HS and HSM samples, respectively, but the ratio between water and oil does not change much as the ramp increases. In general, increasing the heating rate, slightly increases the water content. Further, as discussed before, the heat transfer rate in HSM particles is high which may result in localized high temperatures causing secondary fractionation reactions. This could be the reason why higher water content was observed at the lowest particle size.

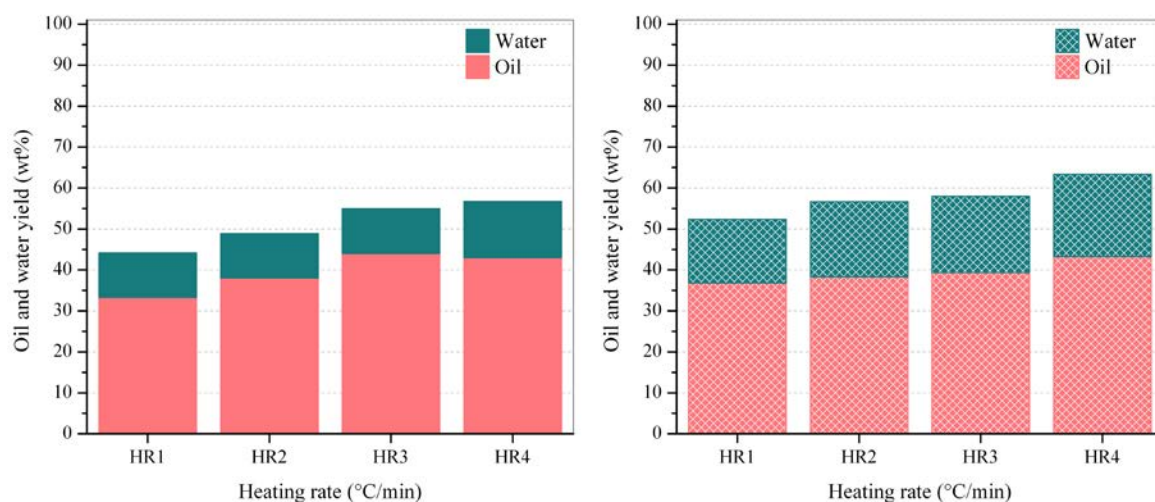


Fig. 4 Oil and water yields of HS (left) and HSM (right) at different heating rates.

Figure 5 shows variations in the gas production from HS and HSM pyrolysis at 6, 12, 20 and 30 °C/min, HR1, HR2, HR3 and HR4, respectively. These results can be compared with the ones obtained from the TGA experiments for a better interpretation.

The thermal profile degradation here can be also interpreted as the resultant of multiple, parallel and simultaneous reactions, related to three distinct stages. The drying process for temperatures lower than 130 °C; the pyrolytic cracking from 130 to 450°C/500 °C, stage where the lignocellulosic components are degraded reaching a maximum of evolved gaseous products; and the latest stage in which takes place the lignin degradation, at temperatures higher than 450°C/500 °C.

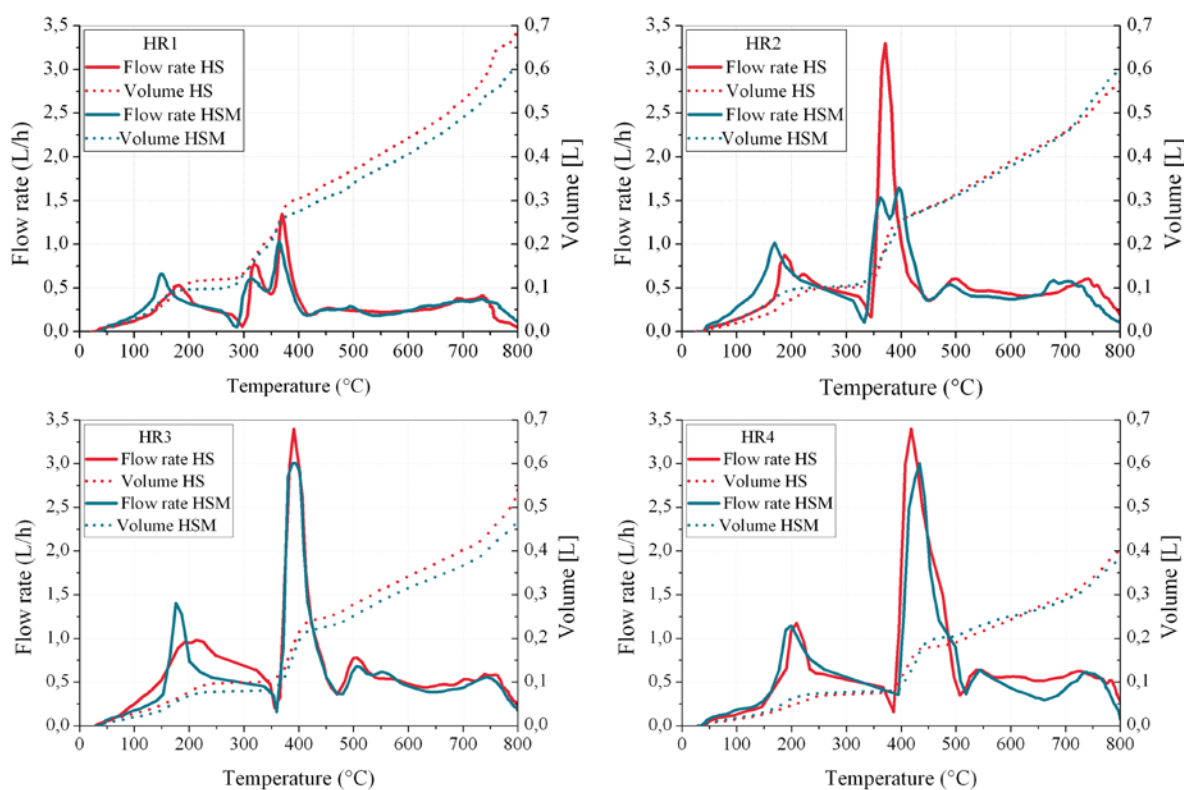


Fig. 5 Gas production from the pyrolysis of HS and HSM at HRs of 6, 12, 20 and 30 °C/min.

In the first stage, the evaporated water goes out from the reactor and is then condensed in the condenser to form part of the pyrolysis liquid. The volume of gas shown in this first stage is mainly the remaining nitrogen inside

the reactor used to ensure an inert atmosphere before starting the experiments. The same behavior was observed in the blank tests (without biomass) which is not shown here due to space limitations.

On the other hands, Figure 5 shows also that increase in heating rates only shifts the peak temperature to higher value without changing thermal profile of decomposition as also observed in Figure 2. TGA was performed under a continued argon flowing to guarantee an inert environment, which means that the presence of argon cools also the biomass shifting the temperature peaks. Lower heating rates of biomass particles occurs more gradually and leads a better heat transfer to the inner parts of biomass. Here again, it is observed that (Figure 5), the maximum rate of decomposition increase with an increase in heating rate as shown also in Figure 2 [33].

The gas composition from HS and HSM pyrolysis is illustrated in Figure 6. Small molecular gaseous components (e.g., CH₄, CO₂, H₂, CO, C₂, C₃ and C₄) were easily identified via a micro-gas chromatograph. CH₄ came primarily from the decomposition of methoxy, methyl, and methylene groups under elevated temperatures. CO₂ was formed via the decarboxylation reaction and the breakage of carbonyl groups. The breakage of ether bonds and C=O bonds likely formed CO. There are no large differences in the gas composition from HS and HSM, but the pyrolysis of HS favors the H₂ formation.

It is interesting to note that the percentages of gas C₂ and C₃, ranging from HR1 to HR4, progressively increase, witnessing a thermal degradation of the lower long chain organic vapors. C₄ compounds, however, are always absent from gas analysis.

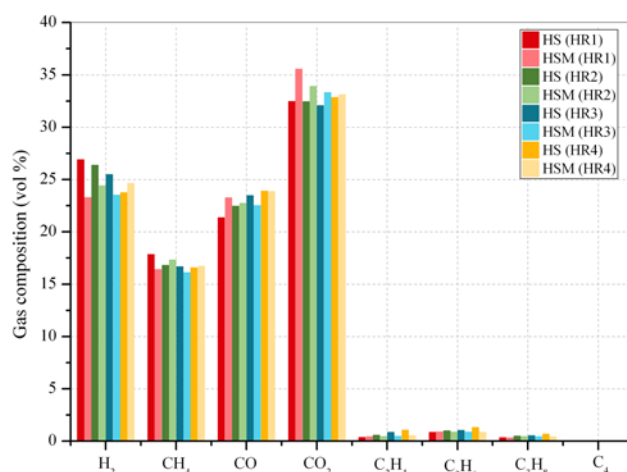


Fig. 6 Gas composition from the pyrolysis of HS and HSM.

Chemical energy yield

Energy stored as chemical compounds in pyrolysis products has been evaluated with reference to original biomasses. The chemical energy yield is the ratio between the HHV of the products and the HHV value of the original biomass. This parameter is therefore an indication of the efficiency in converting chemical energy from one form (biomass) to another one (pyrolysis products), while neglecting the thermal energy the latter has at the outlet (whose possible integration in the process has not been taken into account) [13].

The HHV values of the pyrolysis products from HS are similar to those from HSM. The char from HS range from 30 to 31 MJ/kg, instead from the HSM the values are between 28-31 MJ/kg. The HHV of the tar are in between of 13-15 MJ/kg, and the HVV for the gas are 12-15 MJ/kg,

Table 2 HHV values of the char, tar and gas from the HS and HSM pyrolysis.

		HS	HSM
Char [MJ/kg]	R1	31,38	28,33
	R2	30,30	31,13
	R3	30,29	30,34
	R4	30,24	28,99

Tar [MJ/kg]	R1	15,02	14,49
	R2	14,14	14,65
	R3	13,84	14,34
	R4	14,41	14,21
Gas [MJ/kg]	R1	12,61	12,23
	R2	13,41	12,60
	R3	13,30	12,18
	R4	15,11	12,64

Figure 7 shows the energetic chemical yield of the biomasses pyrolyzed under HR1 – HR4 conditions. Pyrolysis of HS has produced higher energetic chemical yield than HSM at the same heating rate. This could be because larger particles sizes (HS) produced higher amount of char (with C% >97%) than HSM (with C% >96%), and as shown in the Table 2, char is the product with higher HHV. The higher chemical energy yield obtained was 94% for the HS using a heating rate of 30°C/min (HR4).

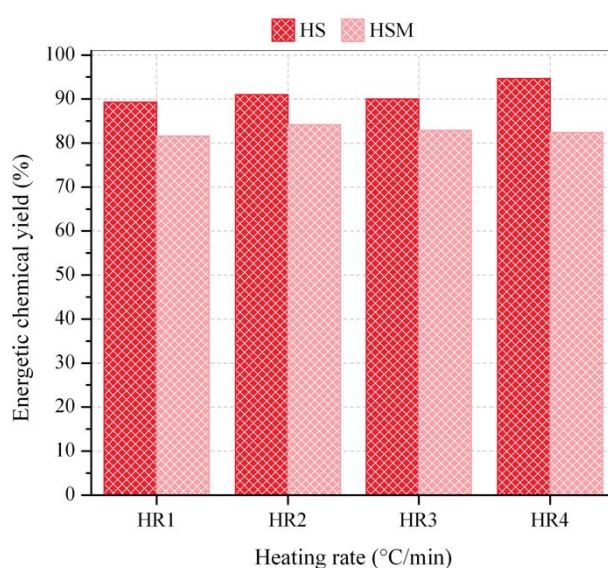


Fig. 7 Energetic chemical yield of the biomasses pyrolyzed under HR1 and HR2 conditions.

From the point of view of the energy content and gas yield, the particle reduction is not economically convenient. The energy content and gas yield decrease as the particles sizes decreases. In our case, using the lab-scale reactor described before, that allows only “conventional pyrolysis”, this pretreatment increases the costs associated but not improve the results for the desired application. The particles sizes and other factors as maximum temperature and heating rate can be optimized for the desired application in order to reduce the costs of waste/by-products valorization.

4. Conclusion

The effect of particle size on the pyrolysis of hazelnut shell was studied in a batch reactor and TGA experiments. The products were analyzed for quality and energy content and the yields were quantified.

In general, the TGA and pyrolysis experiments (lab-scale reactor) showed that the increase the heating rates only shifts the peak temperature to higher value without changing thermal profile of decomposition; and this is due to the decrease in heat transfer efficiency to the inner part of the biomass particles at higher heating rates.

By manipulation of the particle size of biomass in pyrolysis reactions, it is possible to have some influence on the products yield, especially on the bio-oil produced from pyrolysis reactions. The effect of particle size was more pronounced for tar yields from HSM than from HS with a maximum yield of 62.1%. Gas yields decreased as the particle size increased as lower particle size biomass were more thoroughly broken down. Moreover, the

energetic chemical yield was higher for the pyrolysis with HS (100µm). The micro-GC results show that the gas composition did not change significantly with the change in particle size or by changing the heating rates. Particle size variation had a significant effect on the water content of the bio-oil, with very high-water content at lowest particle size. These manipulations will be useful in optimizing the pyrolysis process for larger or commercial grade pyrolysis gas/tar/char production, especially when used together with temperature optimization and upgrading techniques to reduce cost, simplifying processing, and create high value products with high energy content.

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