

# **FAST PYROLYSIS OF SPRUCE WOOD AND WHEAT STRAW IN A FLUIDIZED BED REACTOR**

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## **Abstract**

Fast pyrolysis is a thermochemical conversion process that has gained increased attention over the last decade, since it offers an effective way to produce valuable bio-oil as a green alternative to crude oil in the production of liquid fuels, platform chemicals and materials. A clear understanding of how the feedstock composition impacts on the distribution and quality of pyrolysis products is important for both the optimization of the process and the design of bio-oil upgrading strategies. To address this knowledge gap, the conversion of two different types of biomass (i.e., spruce wood and wheat straw) into bio-oil has been experimentally investigated and the obtained results are described in the present work. In more detail, the pyrolysis experiments were performed in a bench scale fluidized bed reactor at 500 °C and at atmospheric pressure, using a feed particle size smaller than 1 mm and a gas residence time of about 1 s, which allowed to achieve relatively high yields of the liquid product for the two investigated feedstocks (72% for spruce wood and 44% for wheat straw). Results highlight that the biomass composition significantly affects the distribution and the composition of pyrolysis products.

## **Introduction**

The problems associated with the use of fossil fuels demand a transition to renewable sources for energy and chemicals and hence, a replacement of traditional refineries with biorefineries, which are self-sustainable and are not harmful towards the environment. An optimal renewable energy source is biomass [1]. In particular, lignocellulosic biomass is especially suitable as raw feedstock since it is abundant and largely available at low-cost [2]. Biomass can be processed through different processes (thermal, biological and mechanical or physical ones) into heat, power, chemicals and fuels. Among the different thermochemical processes, pyrolysis plays an important role. Pyrolysis is a thermal decomposition that takes

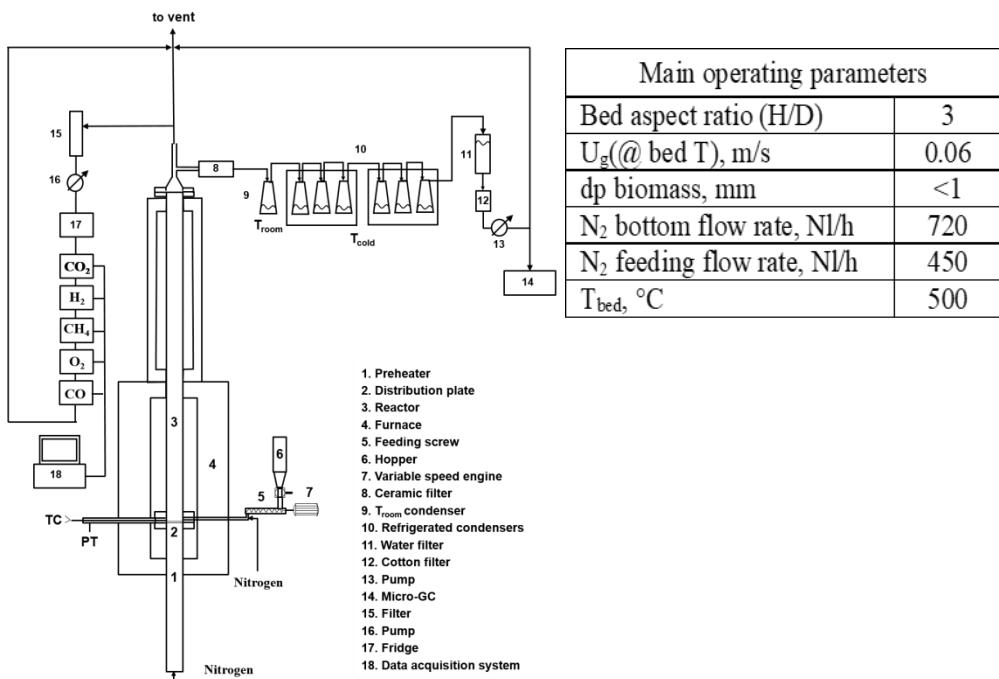
place in the absence of oxygen (inert atmosphere) at moderately high temperatures, and with relatively short residence times of vapours. The pyrolysis products consist of a solid fraction (bio-char), composed of fixed carbon and ash, a non-condensable gaseous fraction (bio-gas), mainly made-up by CO, CO<sub>2</sub>, H<sub>2</sub> and CH<sub>4</sub>, and a liquid product obtained by condensation of vapours (bio-oil), composed of higher hydrocarbons (C>5). Generally, fast pyrolysis is employed to maximize the liquid product yield, while slow pyrolysis is employed to maximize the solid product yield. The essential features of a fast pyrolysis process for producing liquids are: very high heating rates and very high heat transfer rates; biomass dimension typically less than 3 mm, to ensure a fast reaction; short hot vapour residence times (less than 2s), to minimise secondary reactions; rapid removal of product char, to minimise cracking of vapours; rapid cooling of the pyrolysis vapours to give the bio-oil product. The heart of a fast pyrolysis process is the reactor. In this work, a fluidized bed is used to realize continuous pyrolysis tests. The experimental conditions (temperature and residence time) have been chosen to maximize the production of bio-oil containing a spectrum of marketable products following a biorefinery approach [3].

## Experimental

Fast pyrolysis tests were performed on two different biomass feedstocks, i.e., spruce wood (SW) and wheat straw (WS), using a bench scale fluidized bed reactor.

The schematic representation of the experimental apparatus is shown in Figure 1. The pyrolysis reactor consists of stainless steel (AISI 310) fluidization column having an inner diameter (ID) of 41 mm and a height of 1000 mm. A gas distributor consisting of a series of stainless steel nets separates the gas inlet chamber or windbox (41 mm ID and 600 mm height), which also acts as a preheater, from the fluidization column above it. A ceramic filter located downstream of the reactor allows for the collection of the elutriated char. The reactor is equipped with an under-bed biomass feeding system, which uses a combination of mechanical and pneumatic conveying and is connected to the fluidization column by a stainless steel cylindrical pipe (ID of 4 mm). Two nitrogen streams enter the reactor, the first one (720NL/h) injected through the windbox, which acts as a fluidization agent, and the second one (450NL/h) as a conveying gas through the feeding system. The gas flow leaving the reactor is split in three substreams. The first one is sent to a set of on-line ABB gas analyzers to continuously monitor the concentration of O<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub> e H<sub>2</sub>. It is worth noting that the integration of the collected gas profiles allows calculating the amount of each gas evolved during the test. The second substream passes through a chilled impinger train to condense the vapour to liquid pyrolysis oils, whereas the remaining part is sent to vent. In more details, the condensation train consists of 7 flasks connected together. The first flask is at room temperature, while the other 6

are refrigerated at a temperature of - 12°C, using a frozen supersaturated solution of water and sodium chloride. The flasks are weighted before and after the test to evaluate the amount of produced bio-oils. The gas leaving the condensation unit is then analyzed using a micro-GC (Agilent 3000 A) allowing to determine the concentration of light hydrocarbons ( $C_1-C_5$ ) in addition to that of CO,  $CO_2$ ,  $CH_4$ ,  $H_2$ . A data acquisition system and a control unit are used to process signals from the pressure transducer, the thermocouples and the on-line gas analyzers.



**Figure 1.** Experimental apparatus and main operating conditions

Quartz sand in the size range of 0.3–0.4mm is used as a bed material with an initial bed inventory of 0.18 kg. During the experimental runs, the biomass was fed to the reactor with a mass flow of about 90 g/min, a moisture content of about 7-8 % and a particle size smaller than 1 mm. The reactor was operated at 500°C by adopting a gas residence time of 1s.

The reaction temperature was chosen on the basis of the results of thermogravimetric measurements (not shown here for the sake of brevity) performed by using a Simultaneous Thermal Analyzer (PerkinElmer STA 6000). More specifically, the optimal temperature required for the complete devolatilization of each of the investigated feedstocks was determined by reproducing in TG runs the operating conditions adopted in the bench scale pyrolysis tests (i.e., high heating rate 30°C/min under nitrogen flow and same

particle size). A fluidization velocity of 0.7m/s was adopted to ensure a high char elutriation rate and, hence, to minimize the catalytic effect of char on vapour cracking as well as secondary reactions.

The characterization of the collected bio-oils was performed by means of an Agilent 7890A GC equipped with a mass spectrometer 5975C-VLMSD. The elutriated fine particles, collected into the ceramic filter, were weighted and characterized as concerns their size distribution using a laser light scattering particle size analyzer (Malvern Instruments Mastersizer 2000). Proximate and ultimate analysis of the fuels and of the elutriated fine particles, were also carried out by means of LECO CHN 628, LECO CS144 and LECO TGA701, while the higher heating value was determined with PARR 6200 isoperibol oxygen bomb calorimeter. The main properties of the investigated biomasses are summarized in Table 1.

**Table 1.** Main properties of spruce wood and wheat straw.

	Spruce Wood	Wheat Straw		Spruce Wood	Wheat Straw
<i>Proximate analysis, %<sub>wt, ar</sub></i>			<i>Ultimate analysis, %<sub>wt, ar</sub></i>		
Moisture	8.0	6.9	C	50.2	39.4
Volatile matter	74.2	63.2	H	6.1	4.8
Fixed carbon	17.4	13.4	N	0.1	0.5
Ash	0.4	16.3	S	0.1	-
<i>Heating value, MJ/kg<sub>fuel, ar</sub></i>			O (by diff.)	42.7	32.0
HHV (measured)	18240	14695			

## Results and Discussion

The reaction temperature was set at 500°C since the TG measurements highlighted that the devolatilization of both the biomasses is already complete at 450°C. In addition, moderate temperature levels (< 600 °C) allow to minimize the secondary cracking of volatiles as well as the undesired gasification reactions between pyrolysis gases and char [4,5].

Table 2 shows the distribution of pyrolysis products (bio-gas, bio-oil and bio-char) arising from the tests performed on SW and WS samples. In particular, the yields shown are calculated as the ratio between the quantity of species produced during the entire test duration and the total amount of as received supplied feedstock.

It is worth noting that the yield of char takes into account both the amount of elutriated fine particles and the carbon accumulated in the bed.

Table 2 also shows the error associated with the mass balance closure.

**Table 2.** Products yields from fast pyrolysis experiments performed at 500 °C.

	Bio-gas (%)	Bio-oil (%)	Bio-char (%)	Total (%)	Error (%)
Spruce wood	8.7	72.0	5.8 (17.4*)	86.5 (98.1*)	14.0
Wheat straw	22.5	44.0	8.5 (29.7*)	75.0 (96.2*)	3.8

\* theoretical from proximate analysis

The quite high bio-oil yield (72.0 %) from spruce wood sample (74.2 % volatile matter) points out that the volatile compounds evolved during the performed fast pyrolysis test were collected efficiently, whereas the low yield in bio-char suggests that a small fraction of elutriate solids has been most likely lost during the tests.

On the other hand, a lower bio-oil yield (44.0 %) was obtained by the fast pyrolysis of wheat straw sample (63.2 % volatile matter), which can be ascribed to its high ash content (16.3 %) compared to SW (0.4 %). WS ashes are, in fact, particularly rich in K<sup>+</sup> and Ca<sup>2+</sup> [6], which are known to catalyse cracking and dehydration reactions, respectively [7]. The high yield in bio-gas (22.5 %) from WS fast pyrolysis is consistent with the abovementioned catalytic effect of inorganic elements in ash on bio-oil cracking.

The GC-MS qualitative analysis (not shown for sake of brevity) performed on the collected bio-oils during WS and SP fast pyrolysis, show that both of them contain a wide variety of oxygenated organic compounds including phenols, alcohols, aldehydes and ketones and they are almost all within the gasoline fraction (C<sub>4</sub>-C<sub>11</sub>). In more details, Furfural, Furanone, Guaiacol, p-Cresol, Creosol, Eugenol, Vanillin, Trans-Isoeugenol and Homovanillic acid, which are compounds typically found in bio-oils [8], have been detected in both WS and SW bio-oils, whereas Levoglucosan has been identified only in bio-oils from spruce wood sample. This is consistent with the findings by Lin et al. [7] that alkali metals (Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup>) all catalyse the Levoglucosan decomposition. It is also worth noting that, nitrogen compounds, both heterocyclic and amino, have only been detected in the oils from WS most likely due to its higher content in nitrogen compared to SW (cf. Table 1).

Table 3 shows the average concentrations (dry basis) of the gaseous species as obtained by both the on-line gas analyzers and the off-line measurement by micro-GC in a balance of N<sub>2</sub>. The very low values recorded for the gas concentration are due to the high dilution by nitrogen, which was used as a fluidization gas during the tests.

**Table 3.** Average concentration of the product gas.

Species	On-line gas composition (ppm)		Micro-GC gas composition (ppm)	
	Spruce Wood	Wheat Straw	Spruce Wood	Wheat Straw
CH <sub>4</sub>	630	800	478	402
H <sub>2</sub>	132	400	81	443
CO <sub>2</sub>	2659	5500	1921	4500

CO	-	3100	-	1800
C <sub>4</sub> H <sub>10</sub>			72	6
C <sub>2</sub> H <sub>4</sub>			97	48

Results show that data obtained by the two analysis systems are in good agreement. According to the catalytic effect of the ashes discussed above, a higher amount of H<sub>2</sub> and CO<sub>2</sub> was detected in the WS bio-gas, whereas a higher concentration of C<sub>4</sub>H<sub>10</sub> and C<sub>2</sub>H<sub>4</sub> was observed in SW bio-gas.

## Conclusions

In the present work, bio-oils were produced from two different kinds of biomass (SW: spruce wood and WS: wheat straw) via fast pyrolysis experiments (about 1s residence time) performed at 500 °C and atmospheric pressure in a fluidized bed reactor. Results highlight that the biomass composition significantly affects the distribution and the composition of pyrolysis products. In particular, while a high oil yield was obtained by SW fast pyrolysis (72%), the higher ash content in WS (particularly rich in K<sup>+</sup>, well-known to catalyse vapours cracking reactions) led to a lower amount of recovered oils and higher yields in bio-char and bio-gas. In both cases bio-oils were found to contain a wide variety of oxygenated organic compounds due to the high oxygen content of both WS and SW samples. Findings of the present work suggest that pretreatments, such as washing/leaching and torrefaction, which act changing the biomass composition by reducing, respectively, its content in ash and oxygen may offer a suitable strategy to improve the biomass composition for bio-oils production and, hence, deserve further investigations.

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