

BIOMASS PYROLYSIS EXPERIMENTAL INVESTIGATIONS

Adrian BADEA¹, Cora GHEORGHE², Cosmin MĂRCULESCU³, Eduard MINCIUC⁴

Unul dintre cele mai importante procese de conversie termo-chimică a biomasei este piroliza. Aceasta reprezintă degradarea termică a biomasei în absența unui agent oxidant (aer sau oxigen) și conduce la obținerea a trei produși de reacție: gaz, gudron și cocs. În cadrul acestui articol se prezintă rezultatele studiului pirolizei biomasei pentru diferite valori ale temperaturii și ale timpului de desfășurare a procesului, utilizând instalația HTAG (High Temperature Air/Steam Gasification). Experimentele au fost realizate cu scopul de a urmări efectul temperaturii asupra devolatilizării lemnului și efectul timpului de reacție asupra procesului de încălzire a peletelor de lemn. Măsurătorile s-au realizat la trei temperaturi cuprinse între 600°C și 1000°C.

One of the most important processes for the thermal-chemical conversion of the biomass is the pyrolysis. It represents the thermal degradation of the biomass in the absence of oxidizing agent (air or oxygen). Three products result: gas, tar and charcoal. Biomass pyrolysis at different temperatures and residence periods was study in this paper using HTAG grid (High Temperature Air/Steam Gasification). Experiments were performed to investigate both the temperature effect on the wood devolatilisation and residence time effect on the pellet heating stage. Pyrolysis was applied at temperatures in range of 600 to 1000°C.

Keywords: biomass, pyrolysis, mass loss, temperature.

1. Introduction

Biomass is of current interest for replacing coals in energy production. With much more concern to the environmental impact, the use of fossil fuels has been greatly limited. The new goal is the exploitation of renewable energy. These reduce the atmospheric CO₂ level and give low emissions of SO₂, NO_x and heavy metals. Moreover, energy can be recovered from residues and wastes. Biomass, as part of the renewable energy, can achieve zero emission of CO₂ and also can help the sustainable development [1]. Wood, woody and other

¹ Prof., Dept. of Energy Use and Production, University "Politehnica" of Bucharest, Romania

² Assist., Dept. of Energy Use and Production, University "Politehnica" of Bucharest, Romania

³ Lecturer, Dept. of Energy Use and Production, University "Politehnica" of Bucharest, Romania

⁴ Lecturer, Dept. of Energy Use and Production, University "Politehnica" of Bucharest, Romania

forms of biomass represent some of the main renewable solid energy sources available and provide the only source of liquid, gaseous and solid fuels [2].

Thermo-chemical conversion was considered the most promising way for a high efficiency conversion of the biomass, transforming the biomass into solid, liquid and gaseous energy products under thermal conditions. According this, a few type of technology have been developed: pyrolysis, combustion, gasification, liquefaction etc. Pyrolysis is the basic process for the thermo-chemical conversion of the biomass and it is also a first step in the gasification or combustion process [3, 4]. The analysis of the biomass pyrolysis represents a very useful tool for the control and optimization of one efficient thermochemical conversion process of the biomass.

Depending on the operating conditions, the pyrolysis process can be divided into three subclasses: slow pyrolysis, fast pyrolysis and flash pyrolysis. The conventional (slow) pyrolysis is defined as the process that occurs under a slow heating rate. Fast pyrolysis is a thermal decomposition process that occurs at moderate temperatures with a high heat transfer rate to the biomass particles and a short hot vapor residence time in the reaction zone.

The first stage of the biomass decomposition is called pre-pyrolysis. During this stage, many internal transformations – water vaporization, bond breakage, appearance of free radicals, and formation of carbonyl, carboxyl and hyperoxide groups – take place [5]. The second stage of the solid decomposition is represented by the main pyrolysis process. It happens with high rate and conducts to the formation of the pyrolysis products. During the last stage, the char is decomposed at a very slow rate and a solid residual, rich in carbon, forms.

The thermal analysis has been widely used by many researchers in their investigations on the pyrolysis process [6-16]. This analysis represents a method to describe the effects of the process parameters on the feedstock conversion process. Very different experimental conditions have been applied in different types of thermal analysis systems. The studied parameters include reaction temperature, residence time of volatile phase in the reactor, variation of the sample mass, physico-chemical pretreatment of biomass particles, heating rate of the external heating furnace and improvement of the heat and mass transfer ability of the pyrolysis reactor. The often discussed parameters are: the sample mass variation and the temperature. In this study, the biomass behavior was investigated at different temperatures of the pyrolysis process.

2. Experimental rig

The facility developed at KTH (Kungliga Tekniska Högskolan – Royal Institute of Technology – Stockholm, Sweden) and used for experiments is presented in Fig. 1. It is a batch type cylinder reactor and it has more or less 1 m

length. Its combustion chamber has a horizontal position and it is characterised by an inner diameter about 0.1 m.



Fig. 1 HTAG facility

3. Experimental Method

The lay-out of the facility is presented in Fig. 2.

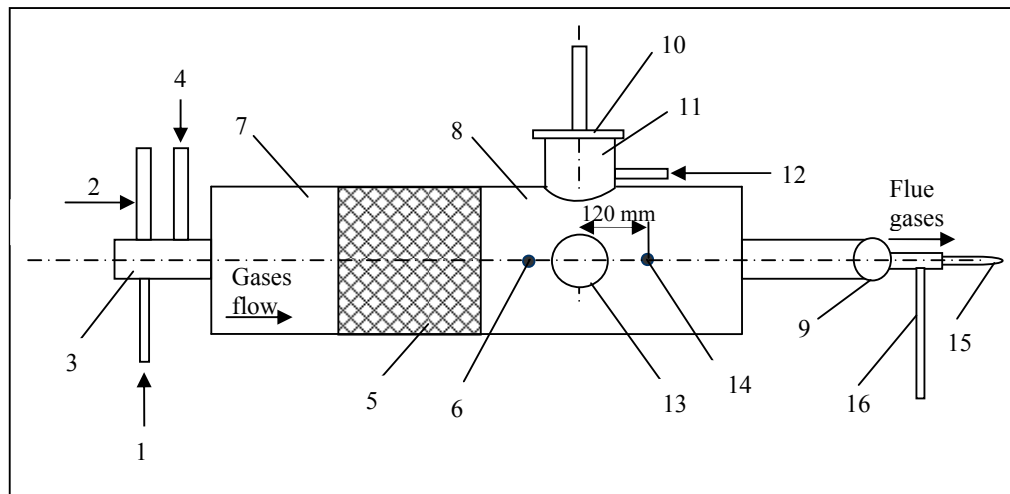


Fig. 2 The lay-out of the batch type HTAG facility

The experimental procedure starts with the heating up of the combustion chamber, when the fuel (natural gas) (1) and the air (2) feed to the gas burner (3). The flow of the gases crosses the first part of the combustion chamber (7), while

they heat the ceramic honeycomb (5) until the desired temperature is reached. The flue gases from the honeycomb cross the second part of the combustion chamber (8) and go to the facility's outlet (9). When the desired temperature was attained, the burner was shut down. After this, the inert flow (4, nitrogen) was introduced in the combustion chamber. The nitrogen is heated by the already hot honeycomb. Its temperature is measured by the thermocouple (6). The flow conditions for the inert gas were adjusted while the sample was inserted through a special flange (10) and kept in the upper position, cooled by nitrogen. When proper flow conditions were obtained, the sample was introduced into a small cooling chamber (11). Here it is continuously cooled by nitrogen (12). After 2 minutes, the sample was introduced in the combustion chamber, when we can see it through a visible glass (13). The temperature is detected by a thermocouple (14). The next stage is the pyrolysis process. The temperature and the composition of the flue gases resulted from the biomass pyrolysis were measured by the thermocouple (15) and the gas analyser probe (16). At the end of the experiment the sample was lifted to the cooling chamber. Here it is cooled for 5 minutes in order to quench the reactions. Then, the sample was removed from the rig.

The experiments were made for different times, which were measured by a stopwatch. During all the experiments, the samples were putted in the peak of one K thermocouple, Alumel (-) and introduced in the cooling or combustion chamber.

Before and after the experiment the weight of the samples mass was determined using an electronic balance. The flows of nitrogen – inert gas or cooling gas – were measured by two BRONKHORST flow meters.

The data were taken by a data acquisition system KEITHLEY Multimeter type 2700 and then there were processed into EXCELINX software.

4. Material

The feedstock used for these investigations was wood pellets, with 10 mm diameter and about 10 – 15 mm long (Fig. 3). The sample's mass varied between 7.1 and 9.6 grams. Proximate analysis of the feedstock was realised in a special laboratory and are given in Table 1. The feeding with wood pellets was carried manually. The sample was putted in the peak of one thermocouple which was introduced in the combustion chamber by a special flange.



Fig. 3 Wood pellets used as feedstock

Table 1

Wood pellets properties

Proximate analysis			Ultimate analysis (dry composition)			
<i>Property</i>	<i>Value</i>	<i>Unit</i>	<i>Component</i>	<i>Symbol</i>	<i>Value</i>	<i>Unit</i>
Diameter	10 – 15	[mm]	Carbon	C	51.0	[%]
Moisture	7.7	[%]	Hydrogen	H	6.3	[%]
Volatile matter	74.7	[%]	Nitrogen	N	0.2	[%]
Ash content	0.7	[%]	Oxygen	O	41.8	[%]
Calorific Value	17.27	[MJ/kg]	Chlorine	Cl	0.02	[%]
Sulphur	0.01	%				

5. Investigation domain

The investigations were carried out on wood pellets, for three temperatures: 600, 800 and 1000°C and for different residence times – range from 15 seconds to 5 minutes, as it is shown in Table 2.

Table 2

Experimental conditions for the experiments with wood pellets:

Temperature [°C]	Residence time [s]
1000	300
	180
	120
	60
	45
	30
	15
800	300
	180
	120
	60
	45
600	300
	180
	120
	60

6. Results and discussion

In the Fig. 4 and Fig. 5 are presented the typical obtained data on the biomass feedstock behaviour.

6.1. Mass loss

The mass loss as function of residence time was studied for wood pellets and for different treatment temperatures.

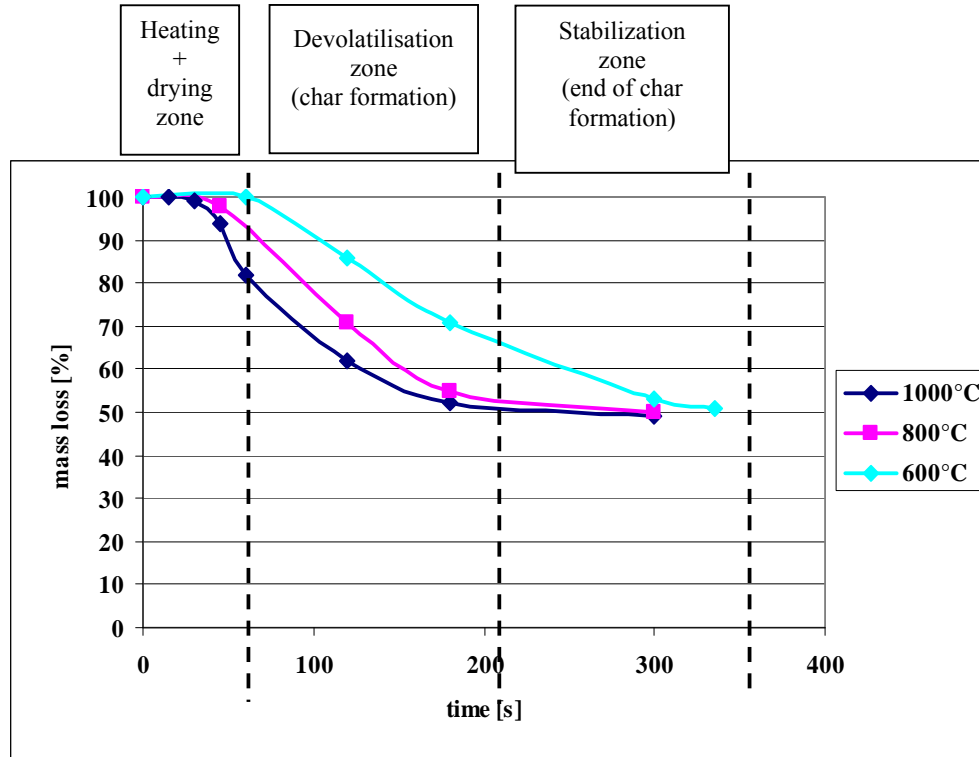


Fig. 4 Mass loss for different treatment temperatures

On the plot, we can observe three steps of the pyrolysis. The first horizontal part of the curve represents the drying process, while the sample is heated up and the vaporisation of the water takes place. If the water content is negligible (hygroscopic humidity approximately zero) the mass loss is insignificant because the sample didn't reach the devolatilisation temperature (approximately 250 – 270°C). After this temperature the curve decreases continuously. That corresponds to devolatilisation stage. The final zone of the curve, horizontal, corresponds to steady state when the char formation is completed. The curves show that the vaporisation of the water accounts over 10% of the total time of pyrolysis, while the devolatilisation represents circa 70% of the total time of the pyrolysis process.

Fig. 4 helps to compare the evolution of the mass loss for all three temperatures of the experiments. We can notice that the time to reach the devolatilisation stage is shorter for high treatment temperature, due to an increased heating rate compared to low temperature conditions. Compared to 1000°C, this stage requires a double period temperature at 600°C. Concerning the

devolatilisation stage, it is also influenced by the process temperature. The curve of the pyrolysis degradation at 600°C presents a smoother slope compared to other two curves.

From those three curves, we can make an important conclusion: the temperature accelerates the kinetic of the mass loss. The curves put in evidence the difference of the residence time for the pyrolysis at low temperature and the pyrolysis at high temperature. Thus, for the temperature of 1000°C, the pyrolysis processes is almost finished after about 200 seconds and for 800°C, the process is finished after 280 seconds.

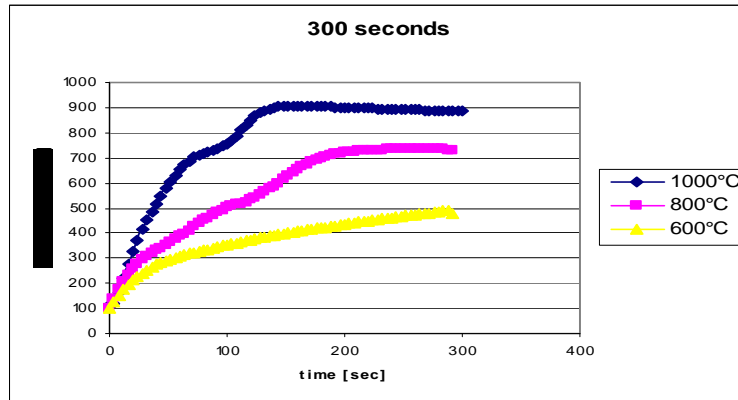
6.2. Temperature of the pellet

We have studied the temperature of the wood pellet for three pyrolysis treatment temperature (600, 800 and 1000 °C) and for different times of the pyrolysis: 300, 120 and 60 seconds.

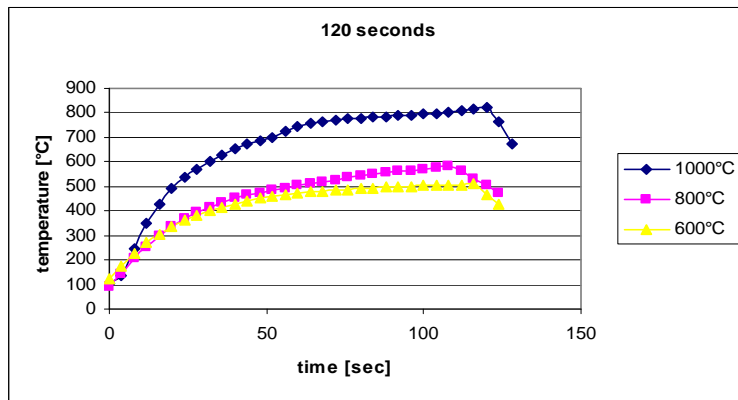
In the Fig. 5 we can see that the pellet temperature depends on the process temperature. Higher is the treatment temperature, the sample temperature increases. It cannot reach the temperature of the treatment, but it tends to reach its value. The temperature of the pellet increases very rapidly for high temperature and slower for low temperatures of the process.

These three graphs show that the pellet temperature depends on the pyrolysis residence time too. For example, for the process temperature of 1000°C, when the pyrolysis residence time is 300 seconds, the maximum of the pellet temperature is almost 900°C. For the same process temperature, in case of a pyrolysis residence time of 120 seconds, the maximum of the pellet temperature is smaller than 800°C and, in case of a time by 60 seconds, the maximum of the pellet temperature not reaches 700°C.

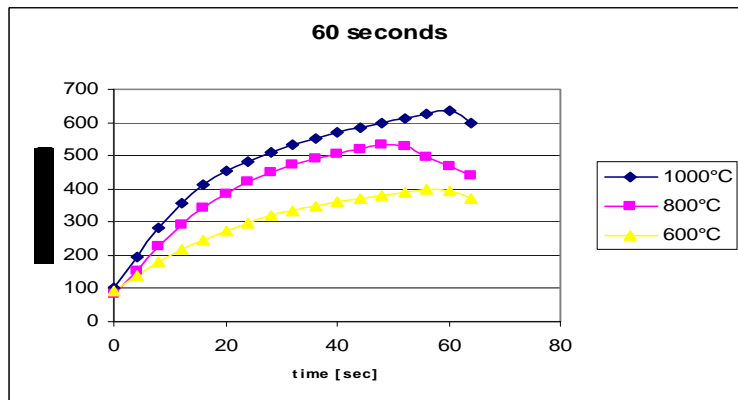
The peak of the pellet's temperature is not stable. It is obtained for a very short period and then the temperature decreases very quickly.



a) Pyrolysis residence time = 300s



b) Pyrolysis residence time = 120s



c) Pyrolysis residence time = 60s

Fig. 5 Evolution of the pellet temperature function of the time for different pyrolysis treatment temperatures

7. Conclusions

Regarding the HTAG experiments for the pyrolysis of the wood pellets it can make the next conclusions:

1. Concerning the mass loss, the treatment temperature has a big influence: the temperature accelerates the kinetic of the mass loss.
2. The vaporisation of the water and the devolatilisation are speed up by the pyrolysis temperature.
3. The curves presented for the mass loss have putted in evidence the difference of the residence time for the slow pyrolysis and fast pyrolysis. Thus, for the temperature of 1000°C, the pyrolysis stages are faster, while for a lower temperature the pyrolysis are slower.
4. Referring on the pellet temperature, it depends a lot on the treatment temperature.
5. The presented experiences allow a more detailed study of the pyrolysis process (the influence of the process parameters on the ignition time, on the volatile content, on the fixed carbon content or on the calorific power of the char and tar resulting form the pyrolysis), that could be one of the future extensions of this analysis.

REFERENCES

- [1] C. Wu, L. Ma, "Modern Utilization Technology of Biomass Energy", Chemistry Industry Press, Beijing, pp. 1-11
- [2] A.V. Bridgwater, D. Meier, d. Radlein, Org. Geochem. 30 (1999) 1479-1493
- [3] Z. Cai, "Thermal Analysis", Higher Education Press, Beijing, pp. 54-66
- [4] J.A. Michael, "Cellulose Pyrolysis Kinetics: The current States of Knowledge", Ind. Eng. Chem. Res., 34, pp. 703-717
- [5] F. Shafizadeh, J. Anal. Appl. Pyrolysis 3 (1982) 283-305
- [6] K. Akita, M. Kase, J. Polym. Sci. Part A-1 5 (1967) 833
- [7] M. Grønli, M.J. Antal, Jr, G. Varhegy, Ind. Eng. Chem. Res. 38 (1999) 2238
- [8] G. Varhegyi, M.J. Antal, Jr, T. Szekey, E. Jakab, Energy Fuels 2 (1988) 267
- [9] G. Varhegyi, M.J. Antal, Jr, T. Szekey, E. Jakab, Energy Fuels 3 (1989) 329
- [10] G. Maschio, A. Lucchesi, C. Koufopoulos, A.V. Bridgwater (Ed.), Advances in Thermochemical Biomass Conversion, Blackie, Glasgow, 1994, p. 746
- [11] M.V. Ramiah, J. Appl. Polym. Sci. 14 (1970) 1323
- [12] K. Raveendran, A. Ganesh, K.C. Khilar, fuel 74 (1995) 1812
- [13] K. Raveendran, A. Ganesh, K.C. Khilar, fuel 75 (1996) 987
- [14] I. Milosavljevic, V. Oja, E.M. Suuberg, Ind. Eng. Chem. Res. 35 (1996) 653
- [15] P.T. Williams, P.A. Horne, Renewable Energy 7 (1996) 233
- [16] P.T. Williams, S. Besler, A.V. Bridgwater (Ed), Advances in Thermochemical Biomass Conversion, Blackie, Glasgow, 1994, p. 771