PYROLYSIS PARAMETERS INFLUENCING THE BIO-CHAR GENERATION FROM WOODEN BIOMASS

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Recent au fost cercetate mai multe tipuri de biomasă, care pot produce energie în vederea înlocuirii combustibililor fosili. Această lucrare prezintă o abordare în vederea optimizării producției de bio-cocs din piroliza prin modificarea parametrilor de proces. Materialul analizat a fost rumegușul de cireș. Experimentele s-au efectuat prin piroliza la temperaturi între 450 ºC şi 800 ºC. Studiul experimental s-a bazat pe influența temeraturii, timpului de staționare şi a ratei de încălzire asupra producției de bio-cocs şi asupra determinării puterii calorifice superioare a cocsului.

Recently much research has been investigated on identifying suitable biomass species, which can provide high-energy outputs, to replace conventional fossil fuels. This paper reports an approach for increasing the yield of bio-char production from pyrolysis with respect to process conditions. The analyzed material was cherry sawdust. The experiments were conducted for pyrolysis temperature between 450ºC and 800ºC. The experimental study focused on the influence of pyrolysis temperature, residence time or heating rate on the bio-char yield and on determination of the HHV of the pyrolysis char.

Keywords: biomass, bio-char, pyrolysis, temperature, heating rate

1. Introduction

Biomass has been recognized as a major world renewable energy source to supplement declining fossil fuel resources [1, 2]. Biomass appears to be an attractive feedstock for three main reasons. First, it is a renewable resource that could be sustainable developed in the future. Second, it appears to have formidably positive environmental properties resulting in no net releases of carbon dioxide and very low sulfur content. Third, it appears to have significant economic potential provided that fossil fuel prices increase in the future [3].

Characterization studies on biomass samples are quite important to express suitability of feedstock for thermochemical conversion. High volatile matter

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content of biomass with low ash and sulfur content is the main criterion for pyrolysis conversion [4].

The biomass energy potential can be recovered either by direct use in combustion systems or by upgrading into a more valuable and usable fuel or gas or higher-value products for the different industries. Investigations have shown that the combustion of biomass is not such economical. So the upgrading by pyrolysis, liquefaction, or gasification becomes more attractive. Biomass pyrolysis has been practiced for centuries in the manufacture of charcoal, but only in the last time the physical and chemical processes during pyrolysis were investigated.

Pyrolysis is formally defined as termochemical decomposition induced in organic materials by heat in the absence of oxygen. This process transforms the organic fraction into gaseous components, small quantities of liquid, and a solid residue (char) containing fixed carbon and ash.

The pyrolysis of wooden biomass has been studied with the final objective of recovering a bio-fuel with medium low calorific power [5, 6 and 7]. The main pyrolysis reaction is

Biomass} $\rightarrow$ bio-char + volatile matter

Depending on the operating conditions, the pyrolysis can be divided into three subclasses: conventional pyrolysis, fast pyrolysis and flash pyrolysis.

The thermal analysis has been widely used by many researchers in their investigations on the pyrolysis process [8-12]. 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. Parameters often discussed are: the sample mass and the temperature. In this study, the biomass behavior was investigated at different temperatures of the pyrolysis process.

The objective of this research was to investigate the effect of a range of the pyrolysis process parameters – temperature, residence time and heating rate – on bio-char production.

2 Experimental

2.1 Material and operating procedure

In the present work a series of chars have been produced by pyrolyzing the cherry sawdust from the furniture industry. The samples of wooden biomass are characterized by a humidity of 8%. The mass of the samples was kept constant: 25 g.

The mass losses tests were realised in a Moufle furnace. It is electrical heated and the temperature is very well controlled. The maximum process temperature is about 1200ºC.

The feeding with biomass was carried manually. For measurements, cylindrical silica crucibles have been used. Every sample of sawdust has been placed in these operating elements without a previous treatment. To maintain a pyrolysis atmosphere, every crucible was covered by a silica hood. Then they were introduced in furnace modifying the operating parameters.

To see the variation of the pyrolysis char yields we have realized a thermo gravimetrical analysis. Using an electronically balance, the devolatilization process was followed by monitoring the weight loss according to temperature and residence time.

The temperature range of the experiments was between 450ºC and 800ºC and conducted at different heating rates.

3 Results and discussions

3.1 Char yields and analysis

3.1.1 Influence of the temperature

The distribution of pyrolysis products is a complex function of the process conditions such as temperature, heating rate, as well as the residence time.

3.1.1.1. Influence of the temperature on the low calorific value of the pyrolysis char

The LHV of the char, that induces its energy quality, depends by the final chemical composition of the char – the volatile and ash content. This property is in conjunction with the temperature of the wooden biomass thermal chemical treatment.

The experimental results have demonstrated an increasing of the LHV concurrently with the increasing of the pyrolysis process temperature. So, it was proved that the pyrolysis at high temperatures can allow obtaining a more energy produce. Figure 1 contains the measured values of the char LHV resulted from the biomass pyrolysis processes realised at different temperatures. The LHV of the char increases from 26829 kJ/kg (pyrolysis at 450°C) to 30982 kJ/kg (pyrolysis at 800°C).

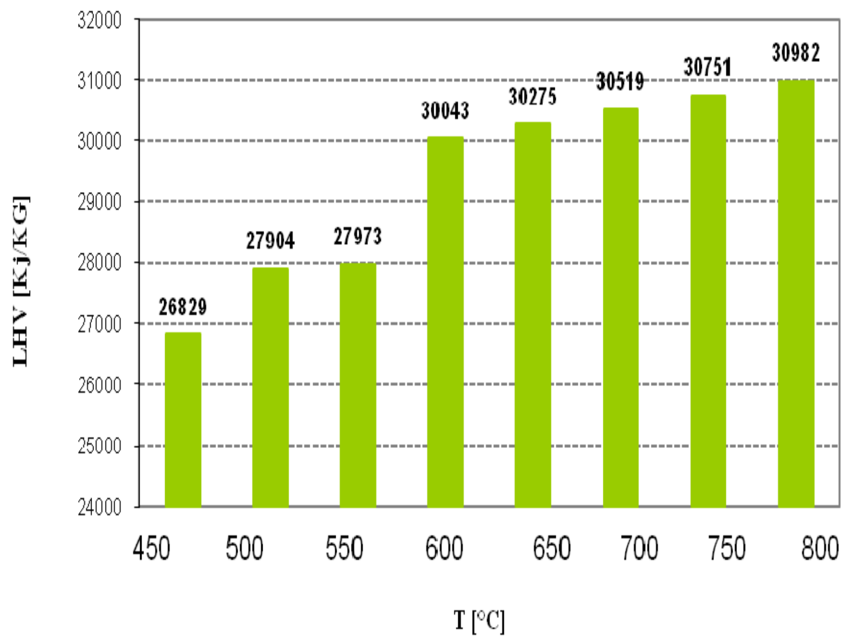

Fig. 1. The LHV of the char resulted from pyrolysis realized at temperatures between T = 450-800°C

3.1.1.2. Influence of the temperature on pyrolysis char composition

Compositions of bio-chars produced from the pyrolysis of cherry sawdust at varied temperatures: 450ºC, 600ºC and 800ºC are shown in figure 2. No matters of heating rate or residence time, the temperature increasing conducts to the increasing of the fixed carbon content existed in the pyrolysis char.

Conforming to French standards (AFNOR, 1984) [13, 14, 15], the char resulted from the pyrolysis realized at 600°C and 800°C belongs to class A. This is characterized by a high quality and can be used in metallurgical, chemical and pharmaceutical industry or food industry. This quality is very fond of fixed carbon content. The experimental results presented in figure 1 show that the fixed carbon mass increases while the process temperature increases. So the increasing of the process temperature from 450°C to 800°C has conducted to the increasing of the fixed carbon content by 1,75%.

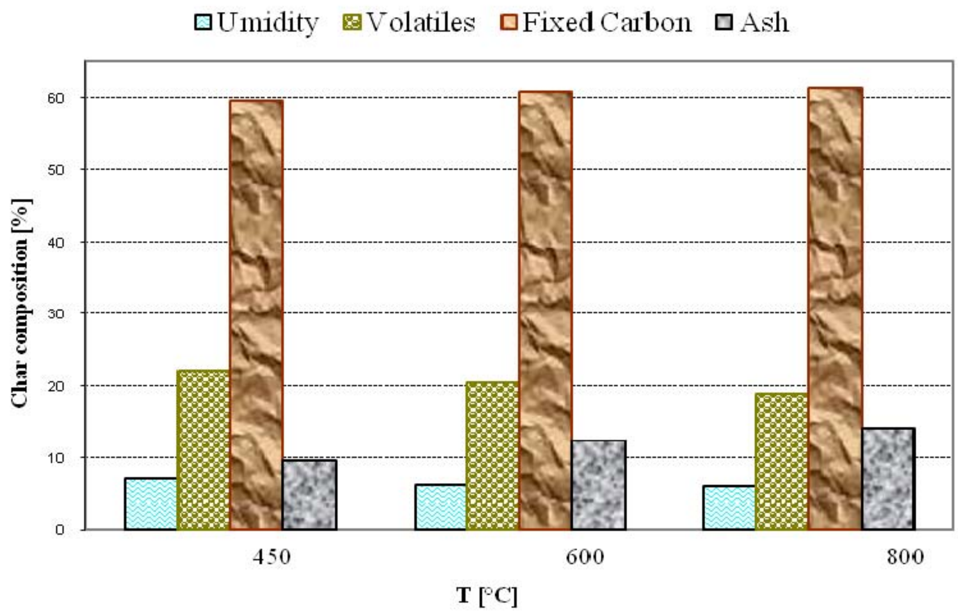

Fig. 2. Volatile matter, fixed carbon and ash content of the solid product resulted from pyrolysis processes of the cherry sawdust

The remaining solid yield for the biomass samples that were heated between 450ºC and 800ºC for a residence time of 5 min is shown in fig. 3. Char yields decreased with increasing of the process temperature from 30.48 wt% at 450ºC to 24.72 wt% at 800ºC at a heating rate of 10 ºC/min.

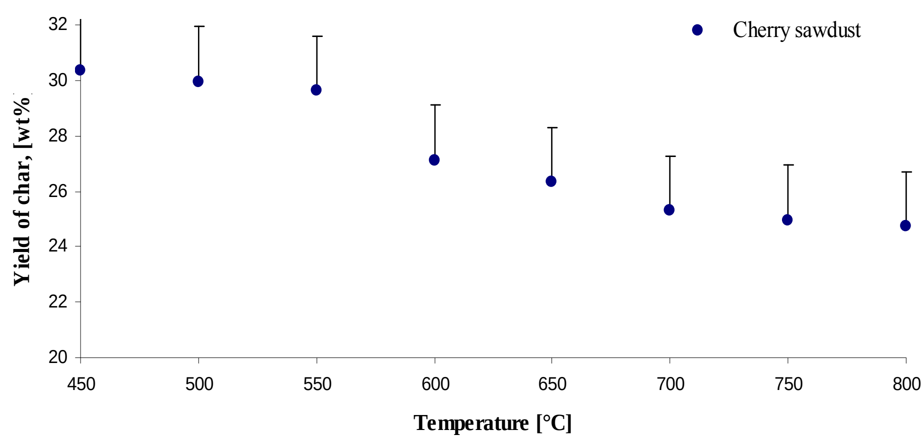

Fig. 3. Plots for the temperature effect on yield of char produced from wooden biomass samples

3.1.2 Influence of the residence time
3.1.2.1 Influence of the residence time on char yield

The char yields reflected by fig. 4 were produced by pyrolysing cherry sawdust at temperatures equal to 450ºC. At this temperature the samples were kept for different residence time: between 5 minutes and 30 minutes. As it can be seen the char yields decreases as the residence time increases. We have obtained the biggest value of char yields in case of the shorter residence time – 30.48% and the smaller value of char for the longer time (30 minutes), equal to 28.71%.

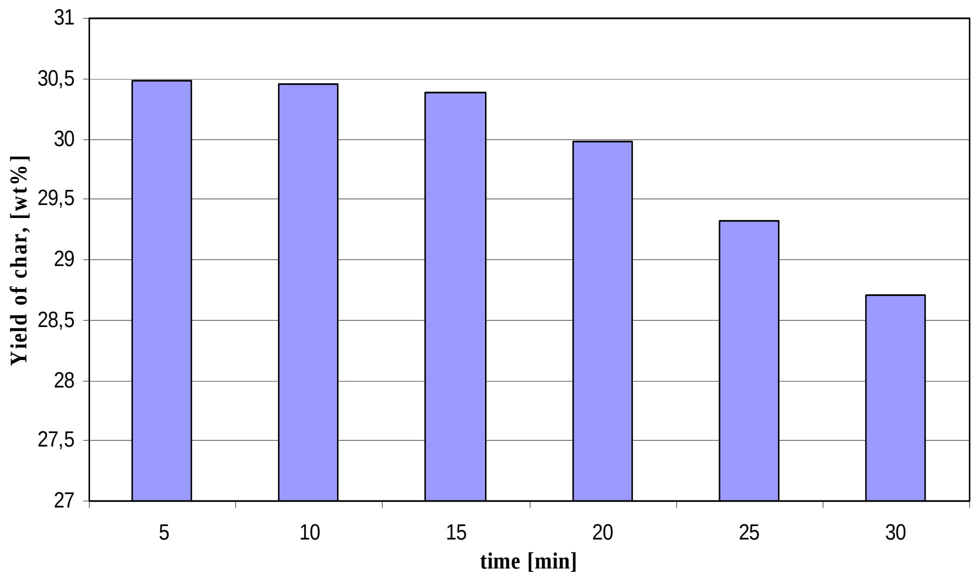

Fig. 4. The pyrolysis char yields versus residence time

3.1.2.2 Influence of the residence time on the low calorific value of the pyrolysis char

The energetic value of the pyrolysis solid product – the char – is represented by the low heating value. This has measured by using a calorimetric bomb IKA C200. The char samples obtained from wooden pyrolysis at 450ºC and 600ºC have been analyzed through this experimental campaign. The values of the LHV of the char resulted from pyrolysis at 450ºC, processes that have been performed for six different residence time, are presented in fig. 5. Comparing these values, it can be observed that the LHV increases once the residence time of the sample increases. For example, the pyrolysis of the cherry wood performed for 5 minutes has generated a char characterised by a LHV equal to 25293 kJ/kg, while the char resulted from the pyrolysis realised for a residence time by 30 minutes has reaches a LHV by 26829 kJ/kg.

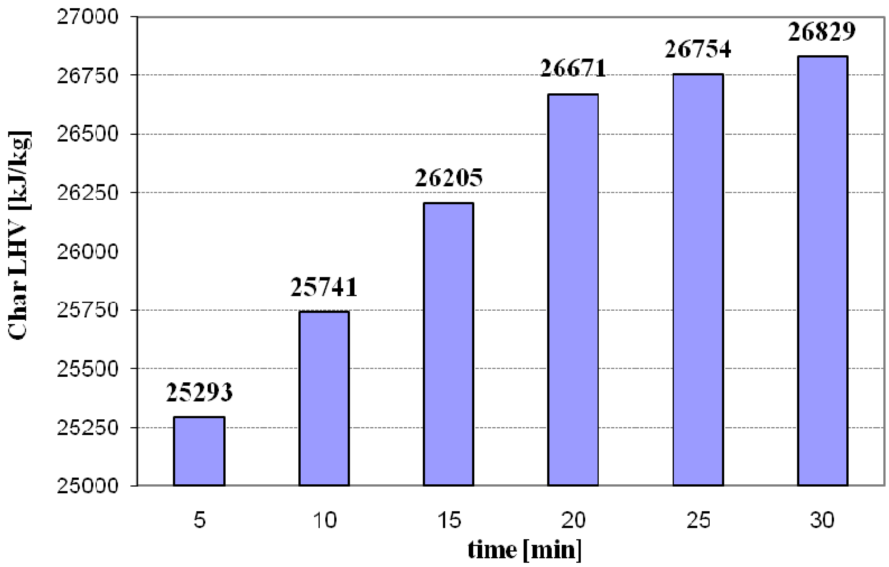

Fig. 5. LHV of the char produced from pyrolysis (T=450ºC) of cherry sawdust function of the residence time

3.1.3 Influence of the heating rate

The heating rate has a big influence on product distribution. A rapid heating rate increases volatile yields and decreases char yield. A rapid heating leads to a fast depolymerization of the solid material to primary volatiles while at a lower heating rate dehydration to more stable anhydrocellulose is limited and very slow [16]. The result is that very small amounts of char are produced in the primary reactions at rapid heating. Our experiments have demonstrated this theory. The char yields for a heating rate of 10 ºC/min were lower than yields achieved at the lower heating rate of 5 ºC/min. The char yield decreased from 39.98 % to 29.98 % as the heating rate was raised from 5 ºC/min to 10 ºC/min.

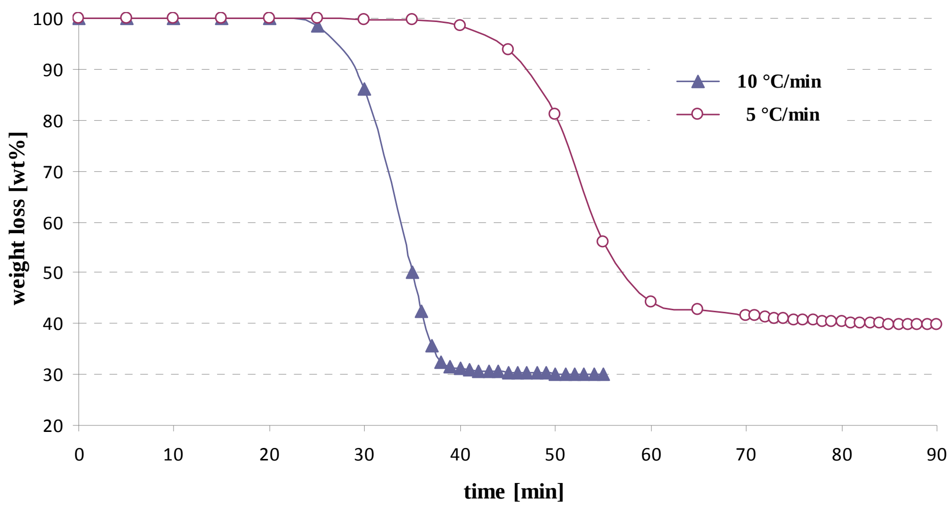

Fig. 6. Influence of the heating rate on char yields

3.2 High heating value of pyrolysis bio-char

Generally the high heating value of char from the biomass pyrolysed increases with the treatment temperature.

A significant linear correlation there is between the pyrolysis temperature and HHV of the char [17]. The equation to calculate relationships between temperature and the char yield is:

$$HHV = 0.0069T + 24.68\ [MJ/kg] \quad (1)$$

For this relation we have use a correlation coefficient equal to 0.9983. The results have proved this linear dependence by the pyrolysis temperature. Thus HHV of char obtained at 450ºC is 27.73 MJ/kg, while the HHV for the char resulted from high pyrolysis temperature (800 ºC) is higher: 30.15 MJ/kg.

4 Conclusions

The aim of this experimental analysis was to watch the influence of the pyrolysis parameters on the bio-char yield and to determine the high heating value of it. For this we have performed analysis for the char from cherry sawdust samples via pyrolysis at different temperatures (between 450ºC and 800ºC) and heating rates (5 ºC/min or 10 ºC/min).

This study showed that the yield of pyrolysis char depends on final pyrolysis temperature, on heating rate and on residence time too.

The char yield decreases as the pyrolysis temperature increases, but the content of the fixed carbon from the pyrolysis char increases. The increasing of the process temperature from 450°C to 800°C has as result the increasing of the fixed carbon content by 1,75%.

The quantities of char resulted from the cherry sawdust pyrolysis have demonstrated that heating rate have an important influence on char yields. Doubling the heating rate of the process results a decreasing by 10% for the char yield.

It is also found that the high heating value of the pyrolysis char is function of process temperature and residence time. The raising of the pyrolysis temperature from 450ºC to 800ºC conducted to a rising of the bio-char HHV of about 2.42 MJ/kg

If the purpose were to maximize the yield of char resulting from biomass pyrolysis, a low temperature and a low heating rate of the process would be chosen.

R E F E R E N C E S

[1] *D. Ozcimen, F. Karaosmanoglu*, Production and characterization of bio-oil and bio-char from rapeseed cake, Renew Energy, **vol. 29**, 2004, pp. 779-787

[2] *M. Jefferson*, Sustainable energy development: performance and prospects. Renew Energy 31 (2006), pp. 571-582

[3] *A. Cadenas, S. Cabezudo*, Biofuels as sustainable technologies: perspectives for less developed countries, Technol Forecast Social Change, **vol. 58**, 1998, pp. 83-103

[4] *A.V. Bridgwater, S.A. Bridge*, A review of biomass pyrolysis and pyrolysis technologies, in: A.V. Bridgwater, G. Grassi (Eds.), Biomass Pyrolysis Liquids Upgrading and Utilization, Elsevier Science, London, 1991, pp. 11–92

[5] A.*V. Bridgwater, D. Meier, D. Radlein*, An overview of fast pyrolysis of biomass, Organic Chemistry, **vol. 30**, 1999, pp. 1479-1493

[6] *G. Maschio, C. Koufopanos, A. Lucchesi*, Pyrolysis, a promising route for biomass utilization, Bio-resources Technologies, **vol. 42**, 1992, pp. 219-231

[7] *T. Barth*, Similarities and differences in hydrous pyrolysis and source rocks, Organic Geochemistry, **30** (1999), pp. 1495-1507

[8] *A.V. Bridgewater, G.V.C. Peacocke*, Fast pyrolysis processes for biomass, Renewable and Sustainable Energy Review, **vol. 4**, 2000, pp. 1–73

[9] *T.R. Bridle*, 2004. Use of pyrolysis to recover energy and nutrients from bio-solids, http://www.wef.org/NR/rdonlyres/7DA581D9-C0D3-4E5C-B127-AC68B7ABA6DD/0/Bridle_Paper.pdf

[10] *A. Demirbas*, 2001a, Biomass to charcoal, liquid, and gaseous products via carbonization process, Energ. Source, **vol. 23**, pp.579–587

[11] *A. Demirbas*, 1997, Calculation of higher heating values of biomass, Fuel, **vol. 76**, 1997, pp.431–434

[12] *A. Demirbas*, 2001b, Carbonization ranking of selected biomass for charcoal, liquid and gaseous products, Energy Conversion and Management, **vol. 42**, 2009, pp. 1229–1238

[13] *Jr. M.J. Antal, M. Gnonli, A.V. Bridgwater,* (Ed.), Fundamental of Charcoal Production in Fast Pyrolysis of Biomass, A Handbook, **vol. 3**, 2005, pp. 149–160
[14] *J.M. Encinar, F.J. Beltran, A. Bernalte, A. Ramiro, J.F. Gonzàlez,* Pyrolysis of two agricultural residues: olive and grape bagasse. Influence of particle size and temperature, Biomass and Bioenergy, **vol. 11**, 1996, pp. 397–409
[15] *W.F. Fassinoua, L. Van de Steene, S. Toure, G. Volle, P. Girard,* Pyrolysis of Pinus pinaster in a two-stage gasifier: Influence of processing parameters and thermal cracking of ta*r*, Fuel Processing Technology, **vol. 90**, 2009, pp. 75-90
[16] *G. Chen, Q. Yu, K. Sjöström,* Reactivity of char from pyrolysis of birch wood. Journal of Analytical and Applied Pyrolysis, **vol. 40–41**, 1997, pp. 491–499.
[17] *A. Demirbaş,* Effect of Temperature on Pyrolysis Products from Biomass, Energy Sources, part A: Recovery, Utilization, and Environmental Effects, **vol. 29:4**, 2007, pp. 329-336.