COMPOSITION OF PRODUCTS OBTAINED VIA FLASH PYROLYSIS OF DIFFERENT LIGNOCELLULOSIC BIOMASS. EFFECT OF PYROLYSIS TEMPERATURE

A. Marcilla[1], A. N. Garcia[1], M.V. Pastor[1], A.J. Sanchez[2] and D.M. Gomez[2]

[1]Chemical Engineering Department, University of Alicante, 03080 Alicante, P. Box 99, Spain
[2] Acciona Infraestructuras. Technological Center I+D+I, Valportillo II, nº 8, 28080 Alcobendas, Madrid, Spain
e-mail[1]: antonio.marcilla@ua.es
email[2]: dianamaria.gomez.lozano@acciona.es

Abstract

Flash pyrolysis experiments were carried out with six different lignocellulosic biomass (almond shell, olive stone, conglomerate wood, eucalyptus leaves, eucalyptus branches and eucalyptus wood) in a fluidized bed reactor. Low temperatures were selected in order to maximize the liquid yields obtained. So, pyrolysis experiments were conducted at 500 and 600 ºC under a nitrogen atmosphere with the aim to study the effect of temperature on the proportion of gas, liquid and solid fraction, which were analyzed to identify and quantify the compounds detected. A total of 29 and 96 chemical species were positively identified and quantified in the gas and liquid phase respectively. Note the large number of phenolic compounds detected in the liquid phase as well as compounds that only were part of eucalyptus biomass (eucalyptol, calarene, alloaromadendrene, etc.). Respect to the gas phase, CO_2 and CO were the major compounds, the sum of these increasing with temperature as solid and liquid fractions decreased, in a more or less pronounced way, depending on the material being pyrolyzed.

Keywords: *flash pyrolysis, almond shell, olive stone, conglomerate wood, eucalyptus*

1. Introduction

Renewable energy is of growing importance in satisfying environmental concerns over fossil fuel usage. Wood and other forms of biomass including energy crops and agricultural and forestry wastes are some of the main renewable energy resources available. These can provide the only source of renewable liquid, gaseous and solid fuels [1]. In this way, thermochemical methods such as pyrolysis are the most appropriate to provide a liquid fuel that can substitute for fuel oil in any static heating or electricity generation application.

The overall objective of this work was to study the use of biomass pyrolysis as a means of characterization of the samples and to obtain molecules of interest, especially those from the lignin fraction (mainly phenolic compounds) from the liquid phase.

2. Materials and Methods

Six lignocellulosic biomass samples, almond shell (AS), olive stone (OS), conglomerate wood (CW), eucalyptus leaves (EL), eucalyptus branches (EB) and eucalyptus wood (EW) were studied. Almond shell and olive stone were supplied by region manufacturers, conglomerate wood by the carpentry of the University of Alicante and eucalyptus biomass were supplied by Acciona Infraestructuras. The samples were dried before performing the experiments.

Flash pyrolysis experiments were carried out in a fluidized bed reactor which consisted of a 71 x 5.2 cm cylindrical stainless steal reactor surrounded by a refractory furnace with a controller to select the temperature of pyrolysis. Moreover, it had a side exit to the volatile compounds generated during pyrolysis. Furthermore, the furnace and the reactor could be rotated on its horizontal axis to facilitate removal of solids inside at the end of the experiment. As a feeding system was used a hopper where about 2 g of sample was loaded. Experiments were carried out at low temperatures (500 and 600 ºC).

In this case, the fluidized bed was silica sand with a particle size between 70-210 μm. The particle size of the sample selected was between 710-1000 μm in order to facilitate, after the experiment, the separation of the residue from the sand by sieving. The gas used to carry out and drag the gaseous products generated was nitrogen, which flow was controlled through a previously calibrated rotameter.

Condensable volatiles generated in the pyrolysis process were collected through a series of glass traps submerged in ice-water bath, filled with stainless steel Dixon rings. This liquid fraction was extracted with ethanol and analysed by gas chromatography/mass spectroscopy. Non-condensed volatile products were collected in Tedlar bags of 5 and 25 liters for further analysis in TCD and

FID chromatographs. Finally, the solid fraction was obtained after sand bed sieving and weighting.
Response factors of some patterns were determined to quantify obtained compounds in gas and liquid fractions.

3. Results and Discussion

The percentages of gas and liquid fractions obtained in each pyrolysis experiment carried out are shown in Table 1. The gas percentage increases with temperature, in more or less extent as a function of the biomass, as can be seen in Table 1.

Table 1. Gases and Liquids yields (% wt)

Biomass	T (ºC)	Gases (% wt)	Liquids (% wt)
OS	500	20.4	37.2
	600	23.7	28.8
AS	500	21.8	34.5
	600	29.9	40.6
CW	500	13.1	30.2
	600	24.4	39.4
EL	500	15.3	39.1
	600	31.8	21.8
EB	500	19.7	37.0
	600	34.4	35.7
EW	500	18.6	39.4
	600	26.7	30.2

In the gas fraction, CO_2 and CO were the compounds with higher yield obtained, summing up between 12 and 31% as a function of temperature and biomass. Almond shell and eucalyptus branches were the biomasses which produced higher yield of these compounds while conglomerate wood was the biomass which produced a lower amount of them. Other compounds detected in this fraction were light hydrocarbons such as methane, ethane, propane, n-butane, pentane, n-hexane, n-heptane, toluene etc, being methane the major compound after CO_2 and CO. The sum of all of these hydrocarbons obtained was in the range 0.6 and 3.5 %.

About the liquid fraction, a large number of compounds were identified and quantified. As an example, Table 2 shows the major yields obtained from the olive stone. As can be seen in this Table, the major compound detected was Acetic Acid. In addition to this, most of the compounds decreased their yield with temperature. However, compounds as Maltol, Pyrocatechol, 3-Methoxycatechol and Levoglucosan increased their yield when temperature increased. Note that this behavior was different as a function of the biomass under study.

Moreover, it is worth mentioning the different compounds detected in eucalyptus biomass, such as Allo-ocimene, Aromadendrene, Gurjunene, Calarene, Selinene, etc., being the most notable Eucalyptol which higher yield obtained was around 1% from leaves of eucalyptus.

Table 2. Major compounds detected in liquid fraction of olive stone

Compound	OS	
	500 ºC	600 ºC
Acetic Acid	7.8	5.1
Furfural	1.1	0.68
Furfuryl alcohol	0.17	0.12
Phenol	0.21	0.18
3-Metilhidantoin	0.50	0.20
Corilon	0.30	0.22
Guaiacol	0.58	0.26
Maltol	0.037	0.063
Pyrocatechol	0.35	0.52
3-Methoxycatechol	0.14	0.20
p-Ethylguaicol	0.062	0.036
Siringol	0.56	0.15
Levoglucosan	0.22	0.44
Methoxyeugenol	0.063	0.012
Coniferyl alcohol	0.12	0.048
Others phenolic derivatives	2.6	1.6
Other compounds	4.1	2.9

4. Conclusions

The experiments carried out at 500-600 ºC lead to the following conclusions:

- The percentage of hydrocarbons on the gas fraction obtained was in the range 0.6-3.5 %. The calorific value of this fraction was around 2000 kcal/kg
- Respect to the liquid fraction, the major compound obtained was acetic acid (1.2-7.8%). The percentage of phenolic compounds were in the range 0.5-6.7%, and other compounds (such as aldehydes, ketones and other acids) in the range 0.8-5.8 %.

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