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INFLUENCE OF TEMPERATURE AND HEATING RATE ON BIOMASS PYROLYSIS IN A FIXED-BED REACTOR

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ABSTRACT. Biomass is one of the renewable energy resources with near zero CO_2 emissions; consequently much research has been investigated in order to replace conventional fossil fuels with biomass in energy conversion sector. Pyrolysis is a thermo-chemical conversion for the production of char, oil and gas products and it is also the initial step for other important thermo-chemical conversion processes like combustion and gasification. This paper focuses on the effects of operating parameters (pyrolysis temperature and heating rate) on pyrolysis product distribution. Therefore 178 experiments were conducted in a lab scale fixed-bed reactor at different temperatures and heating rates for differnet types of biomasses. The experiments were carried out for several types of biomass: spruce wood (SPW), corn stalks (CST), wheat straw (WST) and sawdust (SWD), meaning 58 experiments.

Keywords: *Pyrolysis, Biomass, Heating rate, Pyrolysis Temperature, Pyrolysis Yield, Thermo-chemical conversion*

INTRODUCTION

Biomass is a renewable energy source, formed from living or recently living species. The most important biomass fuel is wood, but the trees are too valuable to be burned, instead residues from woodworking industries as sawdust, could be a very valuable feedstock. Other biomass fuels are the agricultural residues such as: wheat straw, corn stalks, husks from rice, coconuts etc. Fossil fuels (e.g. oil, coal, lignite) are also derived from plant or animal species only that they have been formed during millions of years. Biomass is one of the renewable energy resources with near zero CO_2 emissions and low ash and sulphur contents. Biomass is formed absorbing CO_2 from the atmosphere, hence when is burned is not contributing to the overall carbon dioxide emissions. For this reason is considered to have nearly

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a zero carbon footprint. The primary products from biomass processing are: liquid, gaseous and solid, further derive the major categories of products: electricity, heat, chemicals and transportation fuels. For easier handling biomass has to be converted into liquid or gaseous products, either by biochemical or thermochemical processes [1-3].

Thermochemical processes include: gasification, combustion, hydrogenation, liquefaction and pyrolysis [4-6]:

- *Gasification* is the conversion of solid fuels (coal, biomass, coke, oil, tar, pitch) with air, oxygen and steam or a mixture of this gases at a high temperature (above 800°C) into a gaseous product containing mainly CO and H_2 (called syngas) which can be used either to produce electricity or as a raw material for the synthesis of chemicals or liquid fuels.
- *Combustion* or burning is a chain of exothermic chemical reactions between a fuel and an oxidant agent (air or oxygen) in order to produce heat which can be then converted via mechanical power into electricity. Any type of biomass can be burned only if the biomass moisture is less than 50%.
- *Hydrogenation* represents a chemical process involving reactions between a compound and hydrogen in the presence of a catalyst, which is particularly used for methane production by hydro-gasification, after the syngas is formed, the carbon monoxide reacts with hydrogen to produce methane.
- *Liquefaction* is the thermochemical conversion of a fuel into a liquid product, at low temperature and high pressure, using a catalyst. When the fuel used in liquefaction is biomass the process is called Biomass to Liquid (BtL)
- *Pyrolysis* is a thermochemical decomposition of solid fuels (e.g. biomass, fossil fuels) for the production of chemicals, heat or power, in the absence of oxygen. Pyrolysis is the initial step in all the other thermal conversions technologies, such as combustion and gasification. The process takes place at relatively low temperatures (500 - 800°C), compared with 900 - 1500°C in gasification. [2,7-9]

Depending on the heating rate, the pyrolysis process can be slow or fast, carried out in the absence of a medium. Pyrolysis can take place in the presence of a medium: H_2 – hydropyrolysis or H_2O – hydrous pyrolysis. When char production is desired, slow pyrolysis (carbonization or conventional) is used, but when the desired products are gas or liquids, fast pyrolysis (flash or ultra-rapid) is used. The main difference between slow and fast pyrolysis is the residence time of vapor in pyrolysis zone: for slow pyrolysis is in order of minutes, whereas for fast pyrolysis is in order of seconds or milliseconds. Table 1 summarizes the main characteristics of the main categories of pyrolysis [2, 8, 10].

Table 1. Characterization of main pyrolysis technologies

Pyrolysis Technology	Residence Time	Heating Rate	Final Temperature (°C)	Products
Carbonization	Days	Very low	400	Charcoal
Conventional	5-30 min	Low	600	Oil, gas, char
Fast	0.5-5 s	Very high	650	Bio-oil
Flash-liquid	<1 s	High	< 650	Bio-oil
Flash-gas	<1 s	High	< 650	Chemicals, gas
Ultra-rapid	< 0.5 s	Very high	1000	Chemicals, gas
Vacuum	2-30 s	Medium	400	Bio-oil
Hydropyrolysis	< 10 s	High	< 500	Bio-oil
Methano-pyrolysis	< 10 s	High	> 700	Chemicals

The main categories of pyrolysis products are: gas, liquid and solid, the quantity depends on the process parameters: temperature, heating rate and pressure. The gas product from pyrolysis (CO, CO_2, H_2O, C_2H_2, C_2H_6, C_2H_4 etc.) is a fuel gas with a Lower Heating Value (LHV) in the range of 11 – 20 MJ/Nm^3. The liquid yield is also known as tar or bio-oil, with a LHV in the range of 13 – 18 MJ/kg. The crude pyrolysis liquid is a black tarry fluid, with viscosity as heavy oil and it contains up to 20% water. The solid yield of pyrolysis is char and it contains about 85% carbon. The char LHV is approximately 32 MJ/kg, much more than the LHV corresponding to liquid or gas products [2, 8, 11].

RESULTS AND DISCUSSION

This paper investigates pyrolysis process for four types of biomass: spruce wood (SPW), corn stalks (CST), wheat straw (WST) and sawdust (SWD) at different temperatures and different heating rates. The main characteristics of the solid fuel are [1, 12]:

- Proximate analysis provides general informations about the fuel type and its quality. This analysis gives the amount of volatile matter, fixed carbon, moisture and ash.

- Ultimate analysis gives the elemental composition in term of percentages of carbon, hydrogen, nitrogen, sulphur, oxygen and other elements (e.g. chlorine).

- Calorific value also known as heating value, which can be Lower Heating Value (LHV) or Higher Heating Value (HHV). The heating value represents the amount of energy produced by burning a unit quantity of fuel (e.g. 1 kg).

Table 2 presents the characteristics of the four investigated sorts of biomass.

Table 2. Biomass characteristics

Parameter	SPW	CST	WST	SWD
Proximate analysis(% wt. dry)				
Fixed carbon	7.64	14.93	18.67	14.01
Volatile matter (dry)	91.55	80.90	73.17	85.65
Ash	0.81	4.16	8.16	0.33
Ultimate analysis (% wt dry)				
Carbon	45.97	46.31	45.57	50.65
Hydrogen	6.03	6.11	5.57	6.11
Nitrogen	0.18	1.07	0.63	0.23
Oxygen	46.64	42.24	39.94	42.57
Sulphur	0.37	0.11	0.13	0.11
Ash	0.81	4.16	8.16	0.33
Calorific value(MJ/kg dry)				
HHV - Gross	17.875	18.559	17.939	19.711
LHV – Net	16.560	17.225	16.724	18.378

On account of the complex mechanisms taking place during the thermochemical decomposition of biomass, pyrolysis is influenced by several parameters depending on feedstock properties and process conditions. The biomass was burned at different temperatures and different heating rates into a lab scale fixed-bed reactor to produce char, gas and oil.

Pyrolysis product composition is described above [13, 14]:

- Char contains mainly elemental carbon (~85%) and also hydrogen, oxygen and inorganic species;

- Pyrolysis gas, besides CO, CO_2 and CH_4, which are the mainly components, contains also propane, propylene, hydrogen, butane, butenes, ethane etc.;

- Bio-oil obtained through pyrolysis contains both organic (e.g. alcohols, acids, phenols, ketones, esters) and inorganic species (e.g. Fe, Si, Ca, Na, K, Al, Mg, Cr, Ni).

Pyrolysis reaction is an endothermic reaction which it can be represented as follows:

$$C_nH_mO_p \xrightarrow{Heat} \sum_{liquid} C_xH_yO_z + \sum_{gas} C_aH_bO_c + C\ (char) + H_2O$$

The relative yields of pyrolysis products can be modified by changing the heating rate, the final temperature or the residence time in the reactor.

Effect of pyrolysis temperature

Pyrolysis temperature is the maximum temperature which is achieved during pyrolysis. The composition and the product yield are affected by pyrolysis temperature. Figure 1 presents the effect of temperature on product distribution of pyrolysis of four selected biomasses at temperatures between 250ºC and 700ºC in a fixed-bed reactor.

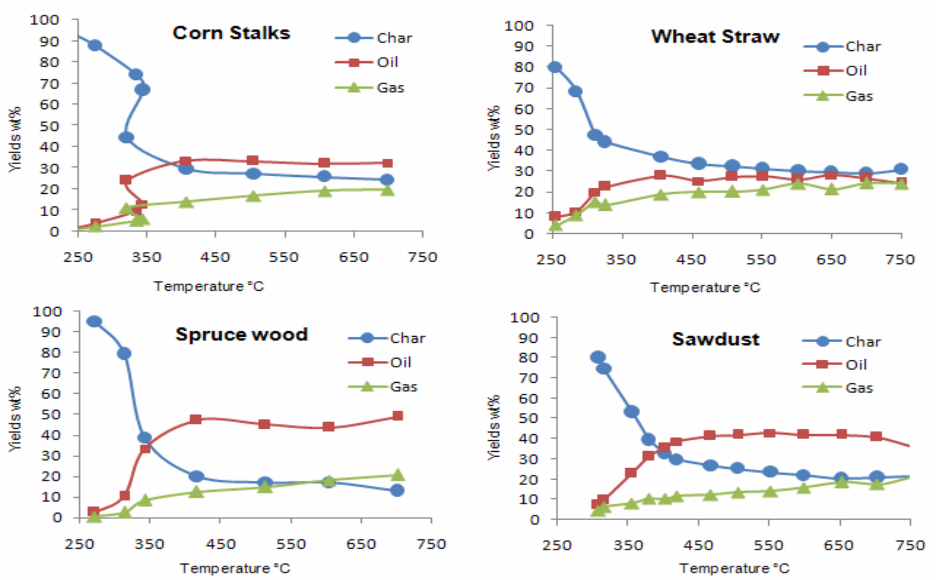

Figure 1. Temperature influence on product distribution

The results show that the amount of char significantly decreases with increasing pyrolysis temperature. This behavior could be due to greater primary decomposition of the sample at higher temperatures. Meanwhile, as expected, the oil and gas yields increases with the same temperature rising. This could be due to secondary cracking of the pyrolysis liquid, at higher temperature, into gaseous product.

Effect of heating rate

An important influence on the composition and yield of the pyrolysis product has the heating rate of biomass particles. In order to investigate the influence of heating rate on the product yields of selected biomasses, the experiments were conducted at different heating rates and keeping pyrolysis temperature constant. Figure 2 presents the effect of heating rate (5–83 C/min) on product distribution of pyrolysis of four selected biomasses at a constant temperature in a fixed-bed reactor.

As shown in Figure 2 the heating rate has a big influence on product distribution. The oil yield is found to increase when heating rate is increased, whereas the solid yield and the gas yield decrease when rising the heating rate. If char production or gas production are desired, is recommended to use a slow heating rate of maximum 20 C/min, whiles if oil production is desired instead, is recommended to use a higher heating rate, around 60 – 80C/min.

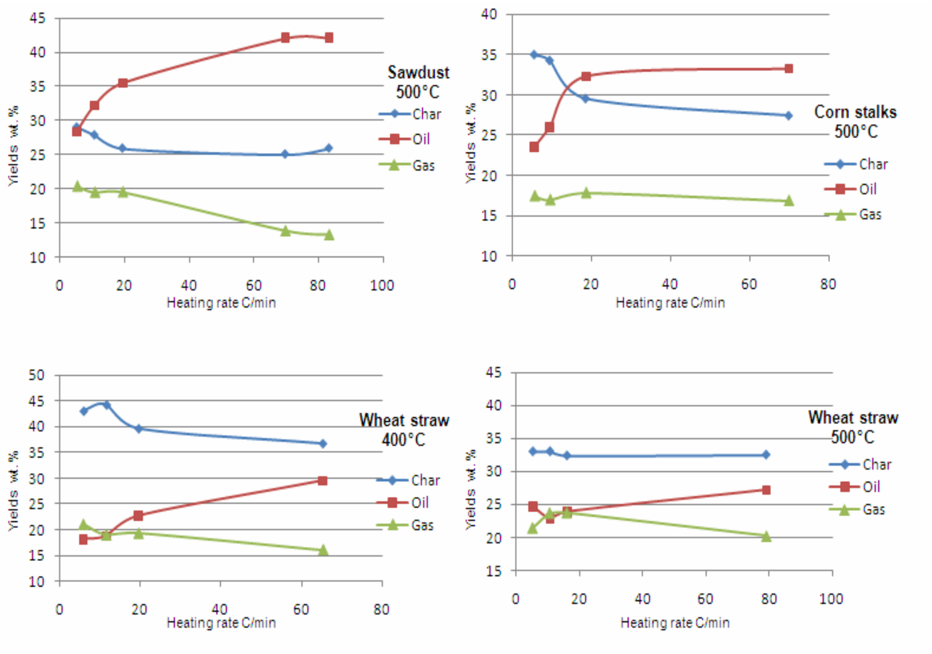

Figure 2. Heating rate influence on product distribution

CONCLUSIONS

The aim of this experimental analysis was to evaluate the effect of temperature and heating rate on pyrolysis process under various conditions. Four different biomasses were pyrolyzed in a lab scale fixed-bed reactor at different temperatures and heating rates. The results show that char yield significantly decreases with increasing pyrolysis temperature, whereas the oil and gas yields increases with the same temperature rising. When the heating rate is increased the solid yield ad the gas yield decrease and the char yield decreases. The paper shows that the operating parameters can be adjusted in order to fulfill the demand of the final product. Therefore to maximize gas production is recommended to use a slow heating rate and high final temperature. If char production is desired instead, is recommended to use a slow heating rate and a low temperature. Whereas to maximize oil production both the temperature and heating rate are required to have higher values.

EXPERIMENTAL SECTION

The aim of this study is to determine the influence of temperature and heating rate on pyrolysis product distribution, consequently 178 experiments were made. A series of biomasses have been pyrolyzed: spruce wood (SPW), corn stalks (CST), wheat straw (WST) and sawdust (SWD), meaning 58 experiments for this study. The biomass samples are characterized by a humidity of 12%. The experiments were conducted in a lab scale fixed-bed reactor at temperatures between 250ºC and 700ºC at different heating rates. The reactor feeding with biomass was carried manually. This reactor ensures a very good repeatability and an almost complete recovery of pyrolysis products. Product composition was determined by: proximate analysis (char), ultimate analysis (char, oil) and gas chromatography (gas).

Figure 3 presents a schematic diagram of lab scale pyrolysis system.

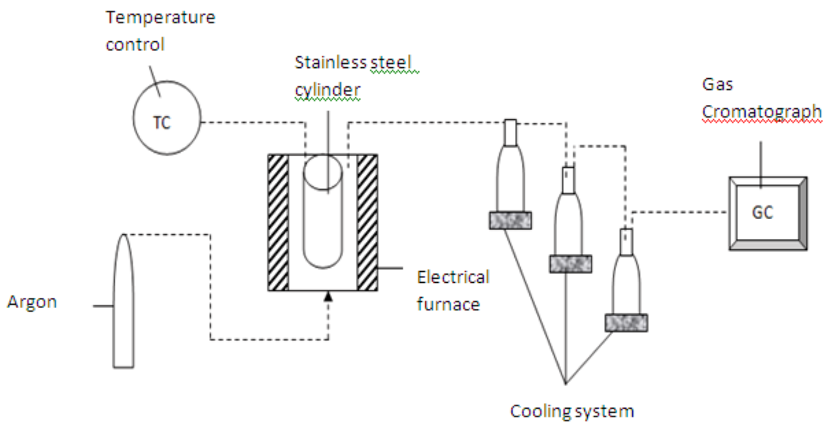

Figure 3. Schematic diagram of lab scale pyrolysis system

The pyrolysis reaction takes place into a stainless steel cylindrical container, where the biomass is introduced manually (between 0.6 – 0.7 Kg/s). The container is introduced in a small electrical furnace of which temperature is controlled by a temperature controller. The reaction takes place under inert atmosphere using Argon. The biomass is introduced in the reactor and it is heated with a heating rate between 5 – 80 C/min until the final pyrolysis temperature is reached. The volatile compounds which are formed during the pyrolysis are sent to a condensation system which is formed of three bottles on an ice bath. The gas fraction composition, mainly hydrogen, carbon monoxide, methane, and carbon dioxide, were analyzed using a gas chromatography. The solid residue remaining in the basket and the liquid fraction were weighed after the system cooled down.

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