



RESEARCHES REGARDING WASTE PROCESSING OF CELLULOSIC MATERIALS BY PYROLYSIS PROCESS

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ABSTRACT

In this paper were performed laboratory experiments regarding processing by pyrolysis process of urban waste components (wood, paper, textiles). The authors designed and developed an experimental equipment and were applied several technological parameters such as temperature and plant maintenance time. The analysis of physical and chemical properties of obtained products found that pyrolysis process can be an effective alternative treatment of urban waste to reduce their quantity and to increase environmental protection.

KEYWORDS: urban waste, physical and chemical properties

1. Introduction

The waste amount at global level is currently increasing. This is due, firstly, to the global population growth and the urbanization increasing process and secondly, to the high rate of industrialization. These contribute to increasing quantity and diversification of solid waste, not only in developed countries but also in developing countries. Waste concentration is much higher in cities than in rural areas, because of the urban population tendency to consume more than the rural one. Therefore, currently, there is more acute the problem of waste reduction, recycling and recovering a part of the waste, or by destruction, using different methods of those who cannot be recovered.[1]

Recycling and recovering of urban waste at global level is aiming, firstly, to an advanced processing (and therefore decrease the amount) and, secondly, to reduce pollution and environmental protection. Products obtained from these processes can be used in other industries.

The largest amount of urban waste is organic (biomass): wood products, plastics, paper, cardboard, textiles, food waste, rubber, leather, etc.. The main substances contained in municipal solid waste are: cellulosic substances, albuminoidal and protein, fat, minerals, etc.

There are different methods of waste processing: biological, mechanical, thermal, etc. Among the most commonly used heating methods are drying, incineration, pyrolysis and co-incineration.

Pyrolysis is a thermal process occurring in the absence of oxygen and consists of successive decomposition of the main constituents (cellulose, lignin, hemicellulose), which have different thermal stability. The process of breaking and rearranging of the bonds in polymers (constituents) that form the biomass, leading to a large number of products, grouped into three fractions:

- *solid fractions* (coal) is the solid residue formed mostly of carbon;

- *liquid fraction* (bio-oil, tar, steam): a mixture of compounds, volatile pyrolysis temperature, which then condenses at ambient temperature. They are high molecular weight components;

- *gas fraction*: CO, CO₂, H₂, hydrocarbons. They are low molecular weight components. Considering that biomass has as basic component the cellulose, we state that the pyrolysis (thermal decomposition) is governed by the following scheme (Figure 1) [2].

In terms of energy, pyrolysis reactions are endothermic and have multiple effects:

- removal and transformation (neutralization) of waste and other waste type, take into account the environmental conditions;

- reducing of treated waste in volume and weight;
- obtaining liquid and gaseous fuels.

The composition and quality of products obtained from pyrolysis depend on the processed waste quality, but also on the equipment operating and service conditions. With appropriate equipments, some products can be separated and recovered completely as fuel or raw material for chemical industry.

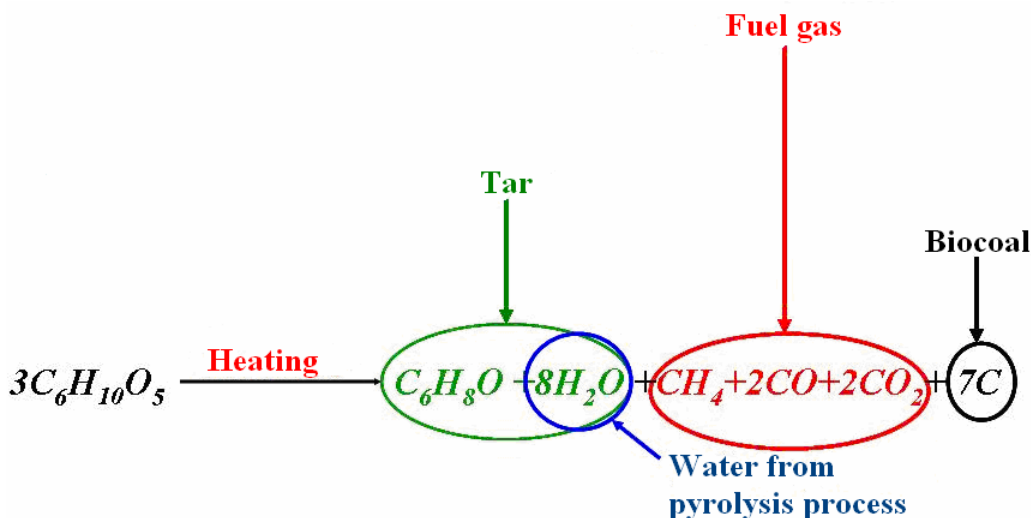


Fig. 1. Cellulose pyrolysis.

Pyrolysis can be applied in several ways, depending on working conditions: [3]

- low temperature pyrolysis (400 ... 600 ° C) and medium temperature (600 ... 1000 ° C);
- high temperature pyrolysis (2000 ° C);
- pyrolysis in molten metal bath salts or;
- vacuum pyrolysis.

- Lignin [C₉ H₁₀ .3 (OCH 3) 0.9 to 1.7] n about. 20 ... 30% (characteristic for wood – it is found in bole, leafage and bark)

- Organic substances: polysaccharide, pentozans, hexozans, resins, tannins, dyes, waxes, alkaloids.

2. Materials used and experimental procedure

To achieve the laboratory experiments, were used household waste as wood flour, paper packaging (cardboard) and yarns [4]. All these materials have approximately the same composition:

- Cellulose (C₆H₁₀O₅) x, proportion of 40 ... 50%;
- Similar hemicellulose xylan (C₅H₈O₄) m, proportion of 15 ... 25%;

To carrying out the pyrolysis process in optimal conditions, fine particles materials are necessary. It has been selected wood flour and cardboard was cut into very fine strips, while for textile were chosen cotton waste.

The experiments were conducted in the University "Dunarea de Jos" of Galati, Faculty of Metallurgy, Materials Science and Environment and Faculty of Chemistry laboratories.

It has been established a technology to carry out the pyrolysis process, based on the following steps (Fig. 2).

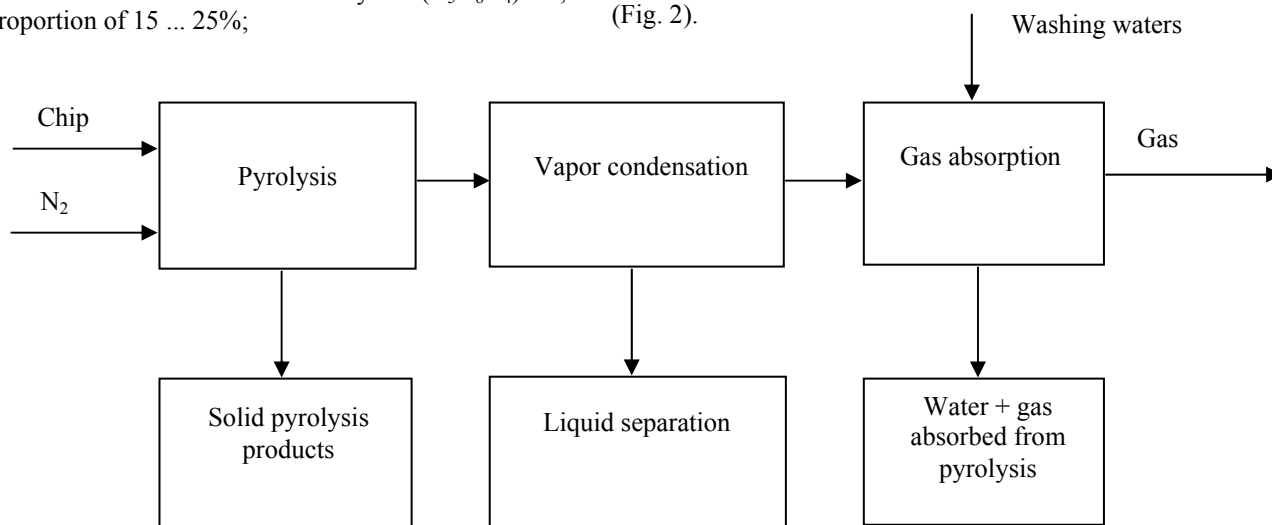


Fig.2. Pyrolysis process technology diagram for wood waste.

It was designed an equipment consisting of an Automatica electric furnace with silit bar heaters in which an air-tight enclosure with protective atmosphere was entered.

For a complete removal of resulting gas, it was introduced nitrogen, circulating throughout the deployment process at a pressure of 1.2×10^5 Pa.

For gas capture, two vessels for washing plastic (PET) were used and introduced in distilled water and were connected to the pyrolysis chamber. Resulting gas were dissolved in water and the liquid can be analyzed. The third plastic container was left empty, to capture the last amount of gas insoluble in water (Fig.3).



Fig.3. Pyrolysis equipment.

Pyrolysis process was carried out according to the following steps:

- *sample preparation.* Waste samples were dried in the oven, placed in two metal tanks and were weighed on an electronic balance, then placed inside the enclosure work.

- *pyrolysis process.* We have chosen several temperatures: 600°C , 400°C , 300°C , 200°C . Maintenance times: 4 hours, 1 hour, $\frac{1}{2}$ hours. Nitrogen continuously circulated through the equipment.

- *process ending.* The equipment stops by furnace cooling after the established time and nitrogen

flows through to fully capture any resulting gas;

- *sampling and laboratory analysis.*

Final, pyrolysis products are presented as three fractions:

- solid fractions of small particles (wires) of coal with original waste size and shape (Fig. 4);
- liquid fraction, collected in a silicone rubber coil, connected to the first gas capture container;
- gas fraction, dissolved in distilled water containers. We used this method to determine the physical properties of resulted gases.



Fig. 4. Solid fraction resulting from pyrolysis process:
a – from wood flour, b – from paper.

3. Experimental results

In the process of pyrolysis were analyzed the resulting three fractions as follows: *Solid fraction*. The obtained coal sample was weighed and compared

to initial sample in terms of mass, after its chemical composition was analyzed.

In Tables 1, 2, 3 are presented the main parameters of the process and mass samples, initial and final mass loss after thermal processing.

Applied thermal regime and mass loss of analyzed samples

Table 1. Wood Flour

Sample	Thermal regime		Solid mass fraction (g)		Weight loss (ΔG)	
	Temperature ($^{\circ}C$)	Time (hours)	initial G_0	final G_1	(g)	%
B ₁	600	4	20	5.30	14.70	73.5
B ₂	600	1	20	6.40	13.60	68.0
B ₃	400	1	20	6.59	13.41	67.07
B ₄	300	1	20	8.10	11.90	59.5
B ₅	200	1/2	20	8.70	11.30	56.5

Table 2. Paper waste

Sample	Regime		Solid mass fraction (g)		Weight loss (ΔG)	
	Temperature ($^{\circ}C$)	Time (hours)	initial G_0	final G_1	(g)	(%)
H ₁	300	1	20	6.90	13.10	65.50
H ₂	300	1/2	20	7.49	12.51	62.55
H ₃	200	1	20	9.23	10.77	53.85
H ₄	200	1/2	20	11.17	8.83	44.15

Table 3. Textile waste

Sample	Thermal regime		Solid mass fraction(g)		Weight loss (ΔG)	
	Temperature ($^{\circ}C$)	Time (hours)	initial G_0	final G_1	(g)	%
T ₁	600	1	20	3.95	16.05	80.25
T ₂	400	1	20	7.49	12.51	62.55
T ₃	300	1	20	9.07	10.93	54.65

ΔG mass loss is determined by the relationship: $\Delta G = G_0 - G_1$

The diagrams in Figure 5 show the variation of mass

loss depending on process parameters and sample's material.

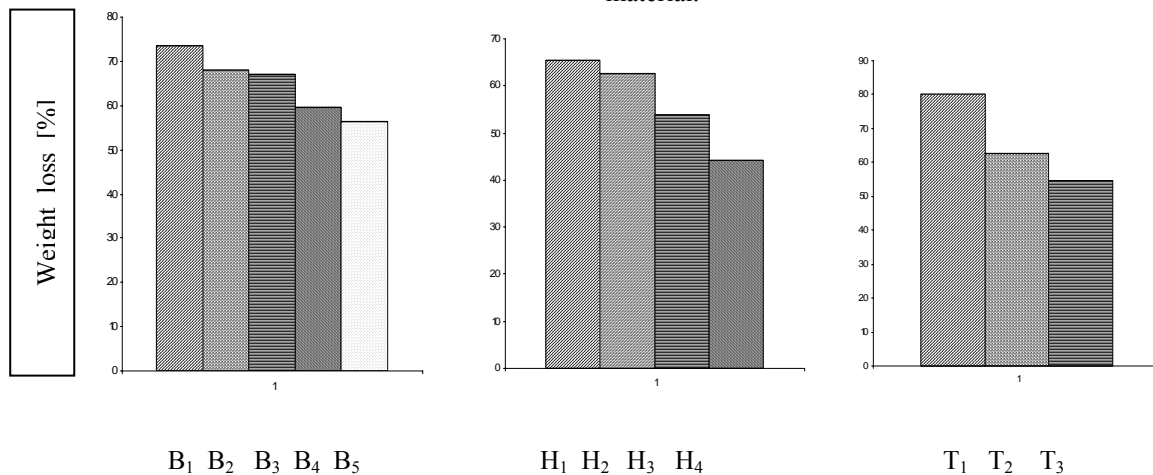


Fig.5. Mass loss resulting from pyrolysis: a) wood flour, b) board, c) textile.



Mass loss increases with increasing temperature and working time, also is quite important even at low temperatures (200 ... 300^oC). On an LECO equipment was analyzed the result coal of pyrolysis of wood and cardboard waste. The carbon percentage shows the process efficiency and solid fraction recovery

possibilities (Table 4). Carbon content is high, so the thermal decomposition is advanced even at low temperatures.

For identification of other elements present in the solid fraction was used XRF spectrometer. The results are presented in Table 5.

Table 4. Carbon and sulphur content of analyzed samples

Material	Sample	Thermal regime		Carbon (%)	Sulphur (%)
		Temperature (°C)	Time (hours)		
Wood flour	B ₄	300	1	73.24	0.30
Wood flour	B ₅	200	1/2	71.90	0.32
Wood flour	B ₆ *	300	1	70.95	0.34
Cardboard	H ₁	300	1	57.33	0.18
Cardboard	H ₂	300	1/2	56.89	0.17
Cardboard	H ₃	200	1	53.44	0.18

*B₆ sample was obtained by pyrolysis of wood waste in the absence of nitrogen.

Table 5. The content of the main elements present in pyrolysis material

Sample	Zn	Fe	Mn	Cr	Ca	K
H ₁ (Cardboard)	31.61	353.93	41.91	386.01	15728.2	28552.15
B ₄ (Wood flour)	26.29	321.09	39.62	335.07	15310.34	27698.71
T ₃ (Textile)	442.91	362.89	-	396.46	12162.84	3033.41

The analyzed samples were subjected to the same working regime (temp = 300^o C, time = 1 hour). Liquid fraction resulted is a strong smelling tar, dark brown color and consistency of oil. Because small amount were obtained, could not achieve a complete material analysis. The resulting gas from pyrolysis was dissolved in distilled water to determine the

physicochemical properties of the resulting liquid, using a multifunctional analyzer with Consort C862. For each sample were determined pH, electrical potential (V), conductivity (λ), resistivity (ρ) and total dissolved salts (TDS).

The results are presented in Table 6.

Table 6. Physical properties of dissolved gases

Parameter	Measurement units	Sample code		
		Wood flour (B ₄)	Cardboard (H ₁)	Textile (T ₃)
pH	upH	3.74	4.44	3.67
V	eV	164	116	185
λ	$\mu\text{S}/\text{cm}$	62.5	24.9	141
ρ	$\text{k}\Omega\cdot\text{cm}^{-1}$	15.99	47.5	7.09
TDS	mg/L	37.1	11.2	83.6

All liquid samples analyzed have low acidic pH. The sample's acidity is given by the content of organic acids and carbon dioxide, retained as a result of distilled water barbotage of the gas resulting from the pyrolysis process.

Liquid samples have variable conductivity, the highest values occurring in those from the textile waste. The total content of dissolved salts recorded higher values throughout the textile waste.

Gas fraction. For gas analysis was conducted a wood waste pyrolysis at a temperature of 300^o C for one hour.

Gases were captured in two plastic containers, without using distilled water. It was used a combustion gas analyzer MSI type. The results are shown in Table 7.

The pyrolysis conditions applied resulted in a high content of NO and CO.



Table 7. Gas fraction composition of wood waste pyrolysis

Container	O ₂ (% vol)	SO ₂ (ppm)	NO (ppm)	CO (ppm)	CO ₂ (% vol)
1	10.8	281	509.5	853.6	9.8
2	19.4	35	412.3	543.8	1.5

4. Conclusions

The experimental research led to the following observations:

- the organic decomposition by pyrolysis process was carried out in a simple equipment with low energy consumption;
- the low temperature and time process;
- the small amount of solid fractions after pyrolysis and working conditions;
- the resulted coal is called "biological coal" and it has a high mineral content, useful as fertilizer in agriculture;
- the captured gases contain a high percentage of NO and CO. In an industrial gas plant, the resulted gas can be used as fuel in the pyrolysis process, thereby eliminating carbon monoxide;
- the possibility of energy recovery products;
- the possibility of a wide variety of organic waste;
- low environmental impact.

From observations during experimental research it can be concluded that in an urban area, depending on waste storage and processing possibilities, pyrolysis may be preferred to other waste treatment processes due to the advantages it presents:

- waste consumption;
- use of charcoal as a solid material for wastewater treatment, including those resulting from the pyrolysis.

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