

UTILIZATION OF MANURE FROM POULTRY FARMS USING THE PYROLYTIC PROCESS

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Abstract: *The development of a sustainable environmental strategy regarding waste management procedures in poultry farms is a major goal for all European Union countries.*

The European Union strategy aims to reduce the amount of waste generated in production processes sent to landfills, to valorize them to obtain compost and thermal energy.

The main benefits of implementing the strategy are both increasing the efficiency of activities and profitability of the field, reducing the impact on the environment, reducing costs and obstacles to recycling, and reducing pollution caused by waste, especially greenhouse gas emissions.

Within the ADER 25.3.1. Technology for valorization of poultry manure by obtaining biofertilizers rich in phosphorus, the project partners proposed to develop technology and create equipment for the processing by pyrolysis of waste from poultry farms, resulting from the activity of production farms, reproductive farms, incubation stations (animal manure: barnyard manure/chicken litter, animal tissue waste: bird carcasses, incubation waste: clear eggs, dead embryos resulting from the mirage operation, eggshells, non-viable embryos, down, non-conforming chicks resulting from hatching, technological: non-conforming eggs for the incubation operation, coming from production farms or from the incubation station, chimney cleaning sludge). Among the waste mentioned above, animal manure, with the highest contribution to technological processes in the poultry farm sectors, is best suited for energy recovery, as biomass for the production of thermal or electrical energy through the gasification process, or for obtaining solid or liquid biofuels through the pyrolysis process.

Keywords: *Pyrolysis, animal manure, biochar*

1. Introduction

Biomass is considered to be both a renewable source of energy and carbon dioxide neutralization, through the process of photosynthesis. Due to its high moisture content and sometimes low energy density, biomass is in many cases an economically unfeasible source for use as a feedstock in energy systems.

Using conversion processes such as pyrolysis, biomass can be converted into solid or liquid biofuels with up to five times the energy density [1] [2].

Currently, biomass represents an important percentage (7% of the world's primary energy consumption, according to [3] [4].

The other two major sources of unconventional energy (with higher usage shares than biomass) are nuclear energy and hydropower [5].

In other words, wind and solar energy currently account for less than 1% of global energy demand [6].

In the current context, biomass is one of the most interesting and promising resources in the category of renewable energy resources, with intensively studied energy recovery technologies. [7].

Biomass has a real potential to increase energy security in regions without abundant fossil fuel reserves, to provide alternatives to the need for liquid fuels and to reduce net carbon emissions into the atmosphere per unit of energy delivered [8].

The conversion of biomass into energy can be achieved through several pathways, which involve different processes dependent on temperature, pressure, process conditions and microorganisms. The main methods of energy recovery of biomass are: combustion; biological (biochemical) conversion; thermochemical conversion.

2. Conceptual presentation of the method and critical analysis of the main pyrolysis processes, technologies and products

Pyrolysis is a thermal decomposition process of organic matter, carried out in an inert atmosphere or in the partial absence of oxygen. There are two major differences between the pyrolysis process and the combustion process, in terms of the type of thermal process and the products of the process. First, combustion is an exothermic process that generates heat, while pyrolysis is an endothermic process that requires heat to activate the process. Second, the products of the combustion process are CO₂, water and ash, and the products of the pyrolysis process are biofuels or products for chemical recovery [9].

The name of the word comes from the Greek language and is made up of two parts: "pyro" which means fire and "lysis", which means total disintegration. Pyrolysis technology has been used since ancient times, 5500 years ago in southern and eastern Europe. The first applications were for the production of charcoal.

The Egyptians used a technique to obtain tar, necessary for boats [10], [11].

In the 18th century, the process of pyrolysis of coal was used to obtain coke (which was used in the metallurgical industry as a substitute for charcoal). In the early 1800s, the technology of coal pyrolysis was invented and applied to obtain synthesis gas, used for street lighting in London, New York and other major cities in the world [9].

Recently, due to the trends of depletion of raw material resources for petroleum products and the increase in their price, industrial-scale technologies have been developed for the conversion of unutilized waste, through pyrolysis or other processes. Pyrolysis technology is a viable alternative for the energy crisis but also for reducing pollution, being considered one of the most efficient technologies for the treatment and disposal of various wastes.

The fuels obtained from the pyrolysis process have a high energy density, have the advantage of being easy to transport and store, being a viable alternative fuel for turbines, industrial combustion applications, power plants or engines. The conversion of biomass through the industrial pyrolysis process is a technology that is in the attention of many research specialists because it can provide an alternative for energy needs and for environmental protection.

Pyrolysis is one of the most important methods of biomass conversion. Through this process, biomass is subjected to a thermal treatment of 300-1000°C, in the absence of oxygen, producing three fuels with energy value: coal, oil and synthetic gas. Pyrolysis is the first stage encountered in thermal conversion processes, where it is followed by combustion and gasification [9].

Biomass pyrolysis is a complex process, due to the diversity, heterogeneity and thermal equilibrium for certain components. Biomass has cellulose as its main component, the decomposition of this component being the most studied in the specialized literature, being the easiest mechanism to understand [12].

Table 1 presents the stoichiometry of cellulose in pyrolysis reactions [13], [14]. Pyrolysis technology can be classified according to the conditions provided in the process, both for slow pyrolysis and for fast pyrolysis.

The **slow pyrolysis** process is carried out at low heating rates and low temperatures, with a vaporization time of 5-10 minutes [15].

Volatile organic components undergo decomposition reactions, forming coal as the main component, along with gas and bio-oil in small percentages [16]. The slow pyrolysis process does not require special conditions for processing the raw material (drying, sorting, shredding), the energy flow transmitted is lower than in the case of fast pyrolysis; the duration of the process is long, between tens of minutes and several hours.

Table 1: Stoichiometry of cellulose

Stoichiometry	Temperature (°C)	Enthalpy (kJ)
$C_6H_{10}O_5 \rightarrow 5CO + 5H_2 + C$	300	180
	1000	209
$C_6H_{10}O_5 \rightarrow 5CO + CH_4 + 3H_2$	300	105
	1000	120
$C_6H_{10}O_5 \rightarrow 4CO + CH_4 + C + 2H_2 + H_2O$	300	-26
	1000	-16
$C_6H_{10}O_5 \rightarrow 3CO + CO_2 + 2CH_4 + H_2$	300	-142
	1000	-140
$C_6H_{10}O_5 \rightarrow 3CO + CH_4 + 2C + H_2 + H_2O$	300	-158
	1000	-152
$C_6H_{10}O_5 \rightarrow 2CO + CO_2 + CH_4 + C + H_2O$	300	-274
	1000	-276

Figure 1 shows the block diagram of a slow pyrolysis plant, with the main integrated components for obtaining coal, oil and synthetic gas.

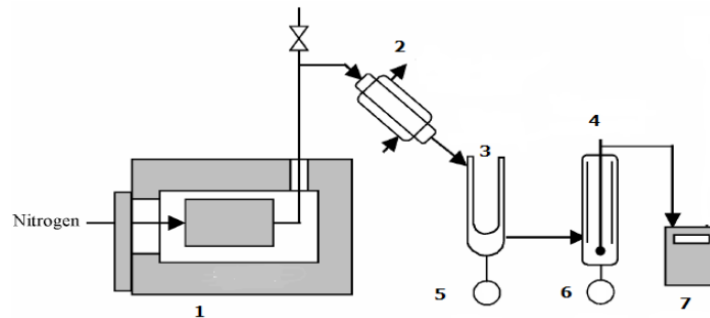


Fig. 1. Block scheme of a slow pyrolysis plant

1. Pyrolysis reactor; 2. Water-cooled condenser; 3. Secondary condenser, for additional cooling of non-condensable gases (down to -70 °C) and oil recovery; 4. Non-condensable gas filtration device; 5. Pyrolysis oil collection container; 6. Secondary pyrolysis oil collection container; 7. Gas collection device.

The **fast pyrolysis** process takes place at high heating rates of up to 200°C/min, largely favoring the production of bio-oil in proportions of 60-75%. The resulting coal and gas are in proportions of 15-25% [17].

Fast pyrolysis is characterized by a short vaporization time and a rapid cooling of the gases to favor the production of a high percentage of bio-oil. In integrated industrial fast pyrolysis systems, to meet the process conditions, the most used types of reactors are fluidized bed ones.

The necessary conditions for obtaining fast pyrolysis are:

- high heating rates accompanied by rapid heat transfer for biomass particles;
- crushing of the biomass raw material into particles with an equivalent diameter of less than 3 mm, since biomass has a low thermal conductivity;
- ensuring a vaporization time shorter than 2 seconds, to limit side reactions;
- temperature control around 500°C, to maximize the percentage of bio-oil;
- rapid cooling of pyrolysis vapors, to obtain bio-oil and rapid collection of pyrolysis char, to minimize vapor cracking;
- drying the biomass to a moisture content of less than 10% [18].

An improved variant of fast pyrolysis is ultra-fast pyrolysis, which requires very high heating rates, over 1000 °C/s and a vaporization time shorter than 1 second. The main disadvantage of this process is the catalytic effect of coal, due to which the pyrolysis oil becomes viscous and contains solid residues [19]. Figure 2 shows a fast pyrolysis plant, with the main integrated components for obtaining coal, oil and synthetic gas.

The biomass is subjected to a series of physicochemical transformations by means of the components described above, being converted into the three biofuels as a result of the technological circuit. The biomass is brought into the plant by an automatic feeding system, which introduces it into a fluidized bed reactor. Fluidization is maintained with the help of inert gas preheated to the process temperature. Primary coal is formed inside the reactor, which is carried into the main collection container. The volatile substances formed inside the reactor together with the inert gas pass through a heated cyclone (to prevent condensation), where due to the high speeds, the matter will collide several times with its walls, causing the separation of fine coal particles, which will be collected in the secondary container. The volatile matter will continue the circuit to the condenser, where a large part of the gases will condense, generating the pyrolysis oil, stored in a container located below the condenser. The non-condensed gases will continue the circuit through two purification filters, thus being prepared as synthesis gases. The gases can be transported by means of a blower to a burner that completes the heat required for the pyrolysis system, or they can be stored.

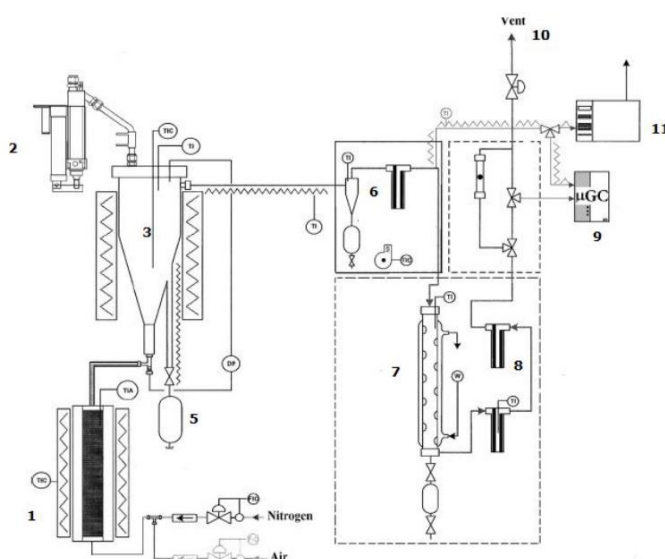


Fig. 2. Scheme of a fast pyrolysis plant [20]

1. Inert gas preheater; 2. Automatic biomass feeding system; 3. Pyrolysis reactor heated by an electrical or thermal source; 4. Secondary pyrolysis coal collection container; 5. Primary pyrolysis coal collection container; 6. Cyclone and filter for recovering fine coal particles in the heated medium; 7. Secondary condenser, for cooling non-condensable gases and recovering pyrolysis oil; 8. Filters for purifying non-condensable gases; 9. Non-condensable gas analysis station; 10. Blower for transporting gases to bottling or reuse in the thermal source of heat generation.

Depending on the parameters of temperature, heating rate and vaporization resistance, pyrolysis was differentiated into different technologies, according to Table 2, [21].

Table 2: Pyrolysis technologies, depending on the process parameters [15]

Technology	Heating speed	Vapor resistance	Temperature [°C]	Main product
Carbonization	Very slow	Days	400	Coal
Conventional	Slow	300-1800 s	600	Oil, gas, coal
Fast	Very fast	0.5-5 s	650	Bio oil, gas
Ultra-fast	Very fast	<1 s	1000	Chemicals and gas
Vacuum	Medium	2-30 s	400	Bio oil
Hydro-pyrolysis	Fast	<10 s	<500	Bio oil
Methanol-pyrolysis	Fast	<10 s	>700	Chemicals

The table shows that depending on the pyrolysis technologies applied, **the three pyrolysis products** are obtained in different percentages: coal, bio-oil and synthetic gas.

Pyrolysis coal (bio-coal) is a solid product obtained from the degradation of lignin and hemicellulose during the pyrolysis process. The physicochemical properties of pyrolysis coal are dependent on a series of factors that must be analyzed: the type of reactor, the species and properties of the biomass, particle size, kinetics, heating rate, inert gas flow rate, etc. Pyrolysis coal has a high content of fixed carbon, combined with volatile matter, moisture, hydrogen and other constituents. The aromatic structure of pyrolysis coal consists of elements such as H, S, O, N and P, which are found in different proportions, depending on the species of pyrolyzed biomass. Comparing the results of the two types of pyrolysis processes - slow and fast - a higher quality is observed for the coal obtained by fast pyrolysis. Specialized studies have shown that for different temperature conditions, varying percentages of coal were obtained, at high temperatures the percentage of coal being minimal, approximately 8-10% [22].

Pyrolysis coal (biochar) can be used directly in industrial systems for the generation of heat and electricity, being a fuel with a higher thermal power and a low sulfur and nitrogen content, being the carbon-rich product obtained from biomass, such as wood, manure or vegetable residues, heated in a closed container, through the so-called thermal decomposition of organic material, with limited oxygen (O₂) supply and at relatively low temperatures (<700°C).

Biochar is an organic product rich in C, valuable for agriculture, which by incorporation improves soil fertility, sequesters carbon (C) from its gaseous compounds, ensures the filtration of water percolated into the groundwater.

The role of biochar is also highlighted by Barrow C.J., [23]: biochar attracts attention as a means of carbon capture and as a potentially valuable input for agriculture to improve soil fertility, aid sustainable production and reduce contamination of streams and groundwater.

Pyrolysis oil is an attractive product of the pyrolysis process, as it is an easy to transport, store and upgrade fuel. The highest percentage of pyrolysis oil is obtained under conditions of rapid vaporization in less than 1 second, at a reaction temperature of approximately 775 K [24].

Pyrolysis oil is viscous, corrosive and unstable, consisting of a mixture of approximately 300-400 components [25]. The viscosity of biofuel and biocrude varies greatly depending on the liquefaction conditions. The increase in viscosity can be attributed to the continuous polymerization and oxidative coupling reactions in biocrude during storage. Due to a high oxygen and water content, the calorific value is 16-19 MJ/kg, almost half that of petroleum with 40-45 MJ/kg. In order to be able to use it as a fuel, it is necessary to improve the qualities of the oil by methods such as solvent fractionation or catalytic cracking. The high water content (15-30%) generates ignition problems, a low flame and a low density of the liquid. The water content can be removed by conventional methods such as distillation [24].

The third product of the pyrolysis process, **the synthesis gas**, has as main components H₂ and CO in combination with CO₂, N₂, H₂O, alkanes and [26].

A high syngas content is obtained at higher temperatures, where tar decomposition takes place and implicitly a reduction in the percentage of coal and oil. The highest percentage of synthesis gas (76.64%) from the pyrolysis process can be obtained in plasma reactors using radio frequencies [15], [26].

The use of synthesis gas as a fuel has the advantage of producing low amounts of hydrocarbons and carbon monoxide. On the other hand, the main components of synthesis gas produce an intense combustion flame and high temperatures in engines.

2.1 Conceptual presentation of the main types of slow pyrolysis reactors

The main types of reactors designed and implemented in pyrolysis systems are diversified, depending on the specific process conditions characteristic of the respective technologies. Applications differ due to the variety of raw materials, the number of resources, the desired energy requirement, the required capacity or the desired end products to be obtained.

Pyrolysis reactors have been designed to meet specific process conditions, in order to optimize and increase the percentage of biofuel desired to be obtained. Taking into account the considerations listed above, several types of reactors can be distinguished.

Fixed bed reactors have traditionally been used to produce coal. Slow heat transfer results in low amounts of liquid following the pyrolysis process. Their technology is simple and has proven to be reliable for materials that exhibit dimensional uniformity. A disadvantage of the fixed bed reactor is given by the fact that due to the vertical movement of the solid material, the produced gas retains the components of the tar, requiring its cracking by means of other cyclone-type devices. Another disadvantage is tar deposits inside it, a fact that requires complex maintenance after use, in order not to reduce the efficiency of the system.

Thermal modules with CHAB concept

The first type of energy module with which biochar was produced was the TLUD type micro-gasification process.

In principle, the up-draft gasification process is not a biochar producer and as a result, most current installations use variants of the down-draft process.

Installations that produce both heat and biochar are divided into two categories:

- with a controlled gasification process from which biochar can also be obtained;
- with two processes in parallel: TLUD type gasification that produces thermal energy and biochar and a second subsystem, put in series in which the thermal energy produced before is used for the pyrolysis of another quantity of biomass, which produces combustible gases burned in the following those from gasification, thermal energy that can be used in thermal applications.

Installations with a controlled gasification process from which biochar can also be obtained

An example is the DRAGON type installation produced by CHIP ENERGY (USA), which can gasify a variety of biomass, produce hot water or hot air and biochar in proportion of 15-20%. Figure 3 shows the functional scheme, and Figure 4 shows the system mounted in a transportable container.

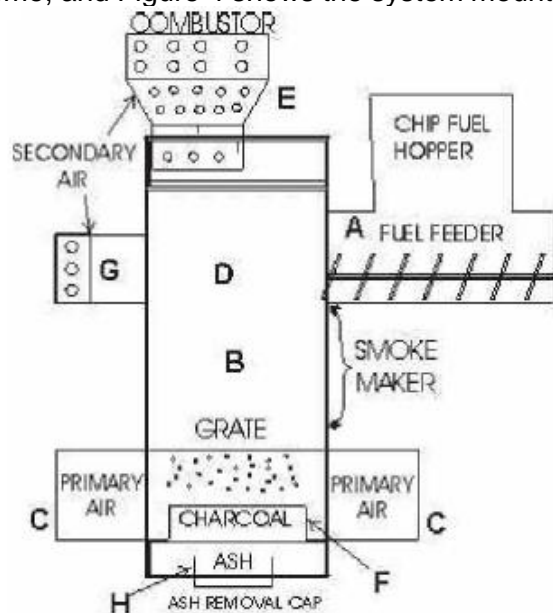


Fig. 3. DRAGON type installation functional scheme from CIP ENERGY

A. Conveyor feed hopper B. Biomass layer C. Gasification air inlet D. Generator gas collection area E. Combustion air inlet F. Biochar area G. Combustion regulation air inlet H. Ash tray

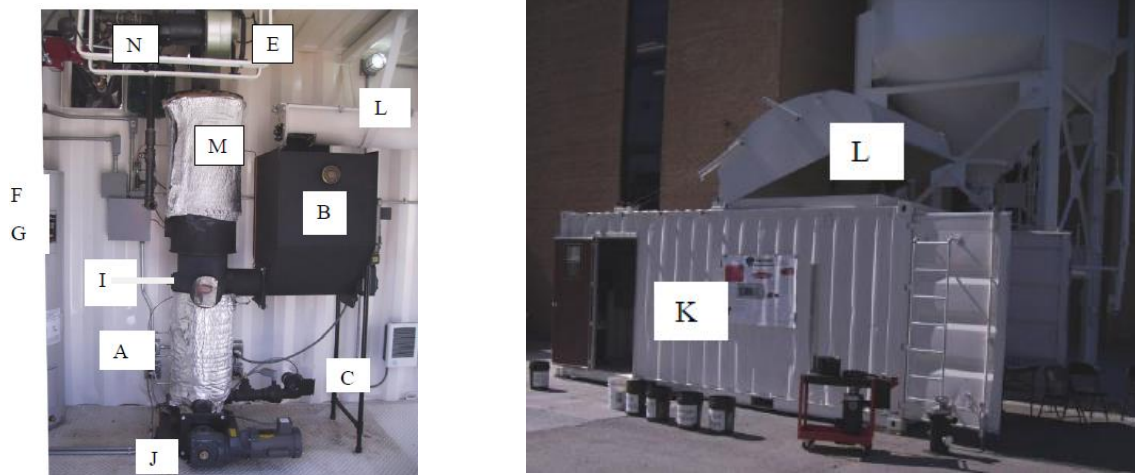


Fig. 4. DRAGON type installation from CIP ENERGY

A. 60 kWt gas generator B. Biomass feed hopper C. Primary air fan D. Secondary air fan E. Draft fan F. Automatic control system G. Operator monitor J. Biochar conveyor K. Container L. External biomass hopper M. Flach type steam boiler N. Hot water pump and pipes

Installations with gasification and pyrolysis processes

In order to analyze in more detail the processes that occur in this type of installations, the block scheme presented in figure 5 will be analyzed; this is the block diagram of the general structure of the thermal energy and biochar production facilities in a combined regime: gasification + pyrolysis. Biomass and air enter the system and thermal energy comes out that can be used for heating and biochar processes. The system has as component entities: the gasification reactor, the gas burner and the anaerobic pyrolysis reactor.

Fuel gases and biochar come out of the gasification reactor. The gasification gases are sent to the burner where they mix with the pyrolysis gases leaving the pyrolysis reactor. Combustion is maintained with strongly swirling combustion air and hot flue gases are produced that transfer part of their thermal energy to the pyrolysis reactor for the needs of the endothermic process, and most of it leaves the system in the form of thermal energy usable in processes of heating.

In the pyrolysis reactor, under anaerobic conditions, a pyrolysis process takes place resulting in an average of 25% biochar and 75% pyrolysis gases that are burned in the burner.

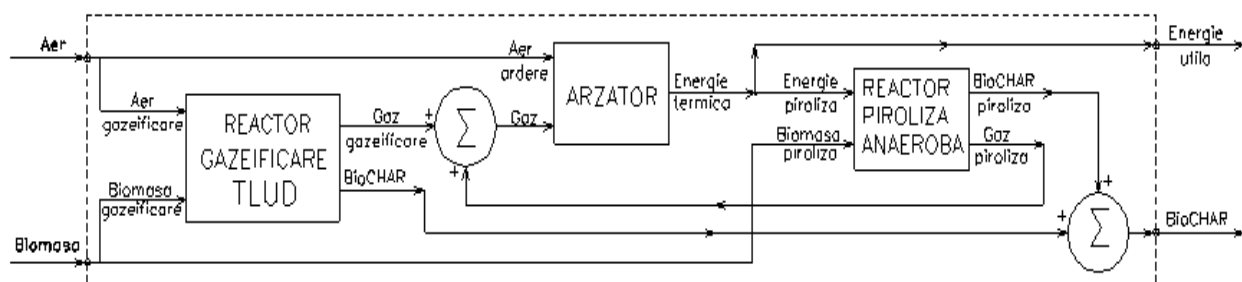


Fig. 5. Block scheme for combined energy and biochar production

A first achievement in the application of this structure is the ANILA thermal device designed by Professor RV Ravikumar, from the University of Mysore in India. The device is part of the structure with parallel reactors that produces thermal energy and biochar at household level. Figure 6 shows the functional scheme and figure 7 the operating phases of the ANILA reactor.

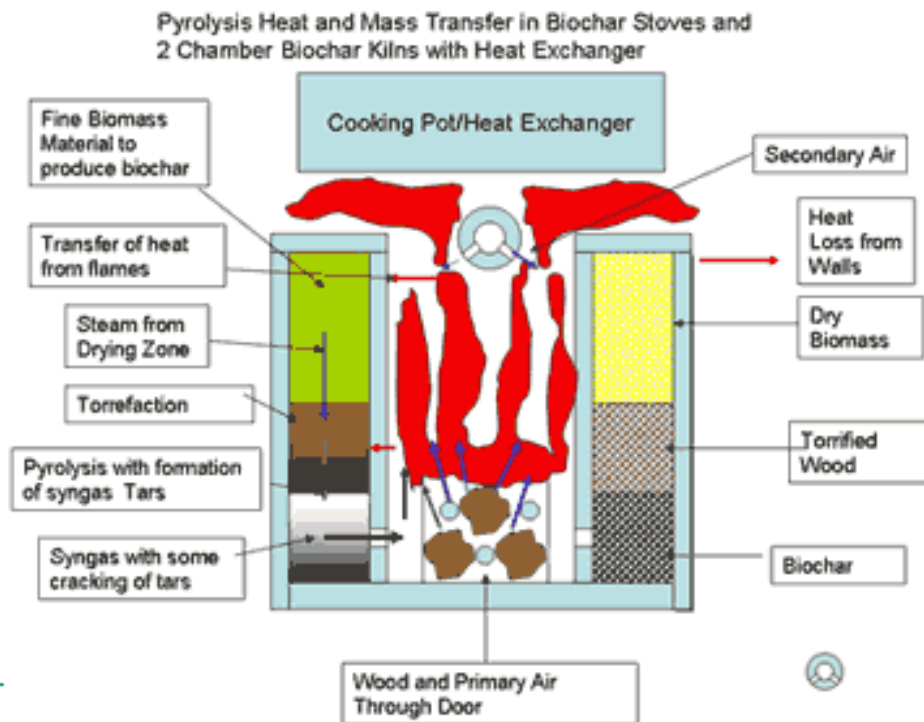


Fig. 6. Functional scheme of the ANILA type reactor

The ANILA device is a structure with two concentric reactors, in which biochar is produced, which does not enter into another combustion process. The inner reactor, intended for the micro-gasification process of the TLUD type, is filled with chopped biomass, from which, through gasification, generator gas is produced, which, through combustion, produces the heat necessary to maintain the pyrolysis of the biomass in the outer reactor.

The outer reactor, in which an anaerobic environment is maintained, is filled with biomass that will be carbonized. The wall of the inner reactor is very hot, it transmits heat to the biomass in the outer reactor which enters the anaerobic pyrolysis process. The pyrolysis gases produced pass through holes into the inner reactor, where they are completely burned in the combustion chamber, producing useful thermal energy.

It is a batch-type process with reactors mounted in parallel, which reduces the height of the installation and makes it easy to handle.

In order to obtain a quality biochar, however, it is necessary to increase the pyrolysis temperature above 500 °C, by insulating the outer wall of the pyrolysis reactor.

Another variant is the structure with reactors mounted in series, fig.8. A first demonstration achievement is the system made by Jolly Roger (2012).

It consists of a TLUD gas generator with a reactor volume of 200 l at the bottom, on which is mounted a pyrolysis reactor with a volume of 120 l heated by the combustion gases and which through the perforated bottom transfers the pyrolysis gases to the burner, contributing to the heat transfer to the pyrolysis reactor.

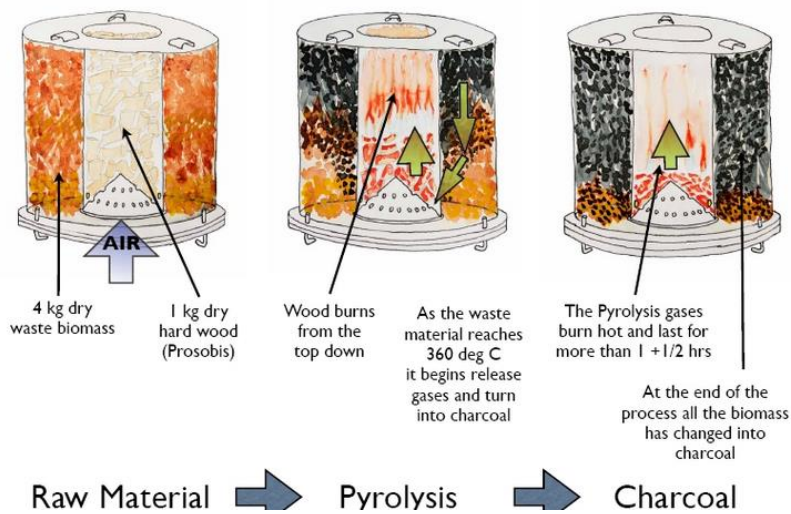


Fig. 7. Operating phases of the ANILA type system



Fig. 8. Artisanal biochar and heat production system made by Jolly Roger

Since the artisanal system was found to produce quality biochar at a low production cost, the structure and process were taken over by the company BioCharWorks (NY, USA) which designed, tested, produces and markets the systems in the family - A BIO-ENERGY CONVERTER: HYBRID 250, fig.11 - mobile system mounted on a semi-trailer and HYBRID 500, fig. 12- stationary installation.



Fig. 9. Heat and biochar production plant type HYBRID 250



Fig. 10. Heat and biochar production plant type HYBRID 500

The pyrolysis process offers a competitive alternative for the valorization of numerous sources of renewable energy, but also for the treatment and energy valorization of municipal, industrial waste, and those originating from agricultural or medical technological processes.

The pyrolysis process is considered the most environmentally friendly thermochemical process compared to combustion and incineration processes, as it has low emissions.

The pyrolysis equipment, symbolized EP, fig. 11, was designed and partially realized during the stage 2 of the ADER 25.3.1 project. Technology for capitalizing poultry droppings by obtaining biofertilizers rich in phosphorus, and its main purpose is to carry out the pyrolysis process of poultry droppings, but also of other types of materials (vegetable residues, in order to obtain biofertilizers with a high phosphorus content).

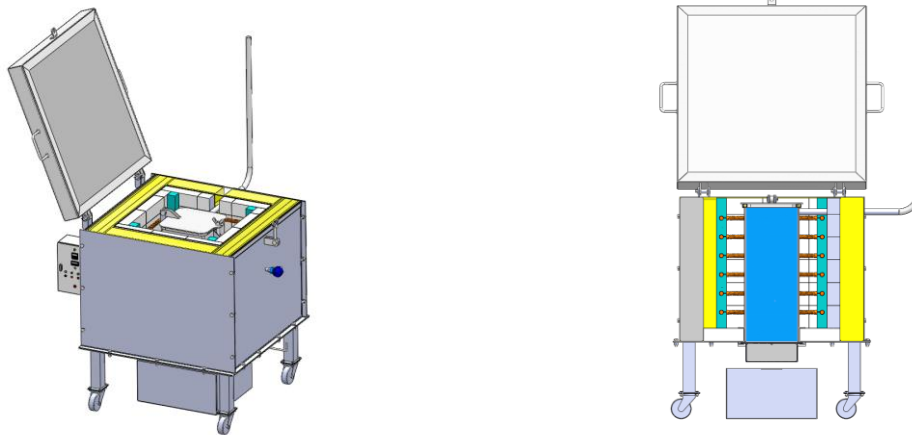


Fig. 11. Poultry waste pyrolysis equipment

The equipment for obtaining phosphorus-rich biofertilizers from poultry droppings is powered by a photovoltaic panel system and has an exhaust air purification system equipped with a pre-filter and an activated carbon filter. This system has the role of eliminating odors and possible harmful gases generated in the premises where the pyrolyzer is located.

The equipment is composed of the following subassemblies: reactor EP 1.0, combustion chamber EP 2.0, external casing EP 3.0, assembled target EP 4.0, heating system EP 5.0, collection box EP 6.0, insulation EP 7, EP 8, EP 9, control panel 10.0, air purification system 11.0.

3. Conclusions

1. Currently, biomass represents approximately 7% of the world's primary energy consumption, thus being a significant source in the global energy mix.
2. Due to their dominant weight in the technological processes of poultry farms, waste of poultry origin is suitable for processing by pyrolysis, a method that allows obtaining biofertilizers rich in phosphorus.
3. Biomass conversion through the pyrolysis process is a technology of major research interest, offering an alternative solution for both energy requirements and environmental protection; the products generated by pyrolysis have a high energy density, constituting a viable alternative for fuels.
4. Depending on the parameters of temperature, heating rate and vaporization resistance, the pyrolysis process can be adapted in different technologies to obtain, in variable percentages, the three main products of the process: coal, bio-oil and synthetic gas.
5. The physicochemical properties of char resulting from pyrolysis are influenced by numerous factors, including the type of reactor used, biomass species and characteristics, particle sizes, kinetics, heating rate, and inert gas flow.
6. Pyrolysis coal, also known as biochar, is a solid product obtained by the degradation of lignin and hemicellulose in the pyrolysis process.
7. In addition to its direct use in industrial systems for heat and electricity generation – having a superior calorific value and low sulfur and nitrogen content – pyrolysis coal (biochar) is a carbon-rich organic product. It has multiple agricultural applications, where, by incorporation into the soil, it contributes to the improvement of soil fertility, the sequestration of carbon from gaseous compounds, and ensures the filtration of percolated water to the water table.
8. The main types of equipment used to produce biochar by slow pyrolysis of biomass include: thermal modules based on the CHAB concept, controlled gasification process plants (which can also generate biochar), and fixed bed reactors.

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