

Utilization Of Agricultural And Urban Plastic Waste Review: Introduction To Pyrolysis And Hydrocarbon Reformation

KOUMPAKIS DIMITRIOS-ARISTOTELIS.¹ and VLACHOKOSTAS CH*.¹

¹Dept. of Mechanical Engineering, Aristotle University of Thessaloniki, Thessaloniki, Greece

*corresponding author:

e-mail: vlahoco@auth.gr

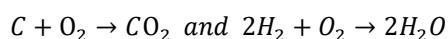
Abstract

Agricultural and urban waste consist of large quantities of biomass and petroleum originated waste. These two categories are rich in hydrocarbons which can be utilized again after their first life cycle. Pyrolysis is a thermochemical process in which solid hydrocarbons decompose in conditions of high temperatures and lack of oxygen (O₂). Normally the chemical elements of carbon (C) and hydrogen (H₂) react by releasing heat called combustion in an environment with oxygen. This paper examines the maintenance of high temperature conditions with oxygen deficiency that keep these chemical elements (C and H₂) distinct until their formation of new chemical compounds of hydrocarbons. These new synthesis have a different number of C and H₂ atoms from the initials, which form fuels in solid, liquid and gas state. It turns out that pyrolysis is the first stage in all the other thermochemicals, as well as combustion and gasification cannot take place. This research presents analyzed parameters that affect the decomposition of hydrocarbons and the composition of new with characteristic suffixes. These new fuels can be utilized into conventional equipment that can produce heat, lighting, mechanical work and electricity.

Keywords: pyrolysis; hydrocarbons; plastic waste; alternative fuels; biomass

1. Introduction

Pyrolysis is one of the basic thermochemical processes, which differ in the percentage presence of oxygen in relation to the stoichiometrically necessary oxygen for the carrying out of the chemical oxidation reactions of hydrocarbons. (Marlair, et al., 1999)



The stoichiometrically necessary oxygen of chemical reactions has an index of $\lambda = 1$

With excess oxygen, combustion takes place in the index of $\lambda > 1$

With a lack of oxygen, gasification takes place in the index of $\lambda < 1$

In the absence of oxygen, pyrolysis takes place in the index of $\lambda = 0$

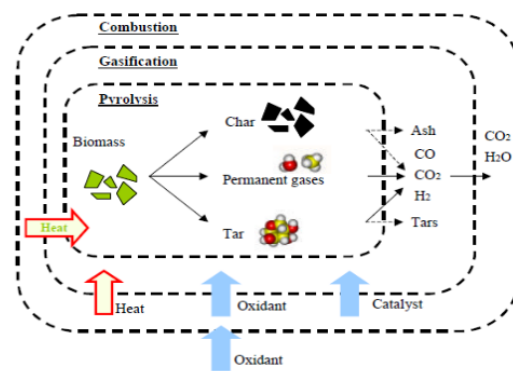


Figure 1. Comparative illustration of the thermal processes of fuel materials (Heyne, et al., April 2013)

2. Pyrolysis principles

2.1. Outcome – products

As far as the reaction of hydrocarbons in oxygen absence the outcomes of the pyrolysis process appear in 3 states.

Gases: Consisting mainly of carbon monoxide and dioxide (CO + CO₂), hydrogen (H₂), methane (CH₄), and others, depending on the characteristics of the organic matter.

Liquids: The fraction is oily with high viscosity and density, it contains alcohols (methanol), carboxylic acids (acetic acid), ketones (acetone) and complex oxygenated hydrocarbons. This fraction can be used as synthetic fuel.

Solids: The solid pyrolysis residue contains pure carbon (C) and possible inert materials that did not participate in the thermochemical pyrolysis process.

In the biomass pyrolysis for example, the matter is heated to atmospheric or even higher pressure and during the increase of temperature, the following sequential processes occur:

- At temperatures below 100°C, volatiles evaporate and thermally sensitive substances decompose.
- At a temperature of 100°C and above, the moisture of the materials evaporates, the hydrated materials trapped in crystalline structures come out at higher temperatures. This process absorbs significant amounts of energy due to the latent enthalpy of the liquid components maintaining the temperature until the completion of the process. Other solid substances, such as fats, waxes and sugars, they melt, break down and separate.
- At temperatures from 100°C to 500°C many organic molecules break down. Specifically at 160 - 180°C the decomposition of most sugars begins. At temperatures of ~ 350°C, cellulose, which is one of the main components of wood, paper and cotton fabrics, decomposes. Lignin, another component of wood, continues to release volatiles up to 500°C. Decomposition products usually include water (H₂O), carbon monoxide and dioxide (CO + CO₂) and some organic compounds. Gases and volatile products extract from the material and some of them condense again. Some volatiles ignite and combust with a visible flame. The non-volatile residues are enriched with carbon forming large molecules, with colors between brown and black. At this point the material is said to be "charred". (Samolada, 1992)
- At 200-300 °C, if oxygen is not excluded, the carbonate residue may begin to burn, with a highly exothermic reaction, often with no or little visible flame. Once the coal starts burning, the temperature rises, turning the residue into a glowing stem, releasing carbon dioxide and carbon monoxide (CO₂ + CO). At this stage, some of the nitrogen (N₂) remaining in the residue can be oxidized to nitrogen oxides such as NO₂ and N₂O₂. The produced Sulfur (S), Chlorine (Cl), Arsenic (As) etc. will be oxidized and volatilized.

The absence of oxygen is a condition for pyrolysis to occur, since it takes place at temperatures higher than the self-ignition of the products produced. (Stefanidis, 2016)

2.2. *Slow-paced pyrolysis (traditional)*

Slow-paced (traditional) pyrolysis is the oldest form of biomass conversion to coal and industrial or domestic-use charcoal. Charcoal was used in industrial processes as a good fuel due to the lack of moisture and its high carbon consistency. This fuel could easily reach higher temperatures required in iron casting industries, steel forging etc. The process requires the wood to be stacked in a pile, be covered with soil, but have the necessary air between the pieces of wood for their initial partial combustion. The pile is covered with soil and is being lit. The materials burn without flame in deficient oxygen for days resulting its carbonization. Then the soil is removed and the product is ready to be packaged and ready to use.

Slow-paced pyrolysis is carried out at a slow - normal heating pace of the material and its main end product is biochar (char). The temperatures that are being developed are low ~400°C and in order not to ignite and burn, the process is continuously monitored on a 24-hour

basis and if necessary, an intervention is made with partial watering or additional burial.

2.3 *Conventional pyrolysis*

The process of conventional pyrolysis takes place in a few minutes. This method has been applied for many years mainly to produce charcoal. In conventional wood pyrolysis, the biomass is heated to 500°C. The produced vapors remain in the place from 5min to 30min, they do not escape quickly as in high-speed pyrolysis. Thus, the components in vapor state continue to react resulting in secondary chemical reactions. When the final product of charcoal is done, these secondary reactions are not desired. By-products such as gases produced during the conventional pyrolysis process are usually used to support the system itself. The raw material can either be kept at a constant temperature or slowly heated.

The conventional method includes the phases of loading a furnace with the biomass material, closing it, removing the finished product (when the container is exposed to the atmospheric air, usually the upper layer catches fire from the hot material and its contact with the atmospheric air). The process can last a few hours classifying it as conventional as well as slow-paced pyrolysis. An initial external energy source is used for the increase of the temperature in the furnace. After the airtight closing of the furnace door, another external energy source (biomass or even gas) is sustaining the temperature of the operation (Roberts & Sankar Bhattacharya, 2017). Starting their decomposition, the hydrocarbons form gases which are biomass vapors. These vapors are removed from the furnace and being fed to the burner to maintain the combustion temperature.

In case the charcoal catches fire when it comes out of the furnace, it is usually extinguished by smooth spraying with water. After the charcoal has cooled in the air, it is ready to be packed and shipped to the market.

2.4 *Fast-paced pyrolysis*

In high-speed pyrolysis, the temperature rise rate of the material is 1000°C/sec, achieving the optimization of bio-oil production. The heating time of the material until the start of its decomposition is short 0.1 - 0.5 sec, resulting the production of ~ 60 - 70% bio-oil, 15 - 25% biochar and 10 - 15% syngas. The produced syngas is fed as fuel to the pyrolysis burner.

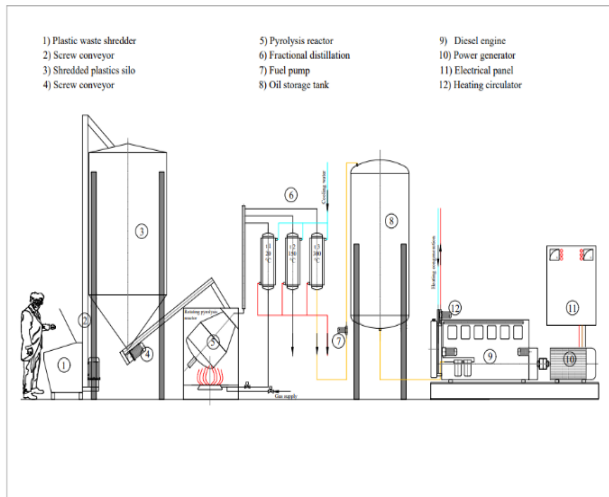


Figure 2. Biofuel and electricity pyrolysis plant

During decomposition of organic substances, the materials are in a gaseous state, just like the materials of crude oil in their refining. The two processes are essentially the same, because oil refining is a type of pyrolysis. The materials from oil refining which are in gas state are being cooled at different temperatures (this is called fractional distillation) resulting the content to be liquefied. The liquefaction temperature of the materials (hydrocarbons) in the gas phase is different for each group of hydrocarbons. By knowing the liquefaction temperatures of hydrocarbon groups, the same matter can be produced from different feedstock, not just crude oil.

Not all waste has the same chemical composition. Tires (from vehicles) and plastics (packaging, etc.) though are made of oil derivatives, as hydrocarbons and have similar chemical components in their structure. Such a targeted pyrolysis is possible to solve a significant part of the environmental problem caused by plastic waste and at the same time produce products such as liquid fuels (gasoline and oil), solid (coal) or metals for recycling. Thus the treatment process (pyrolysis) of plastic waste can be environmentally beneficial and economical at the same time. Pyrolysis may offer a new field of economic activity, with new job opportunities considering the protection of the natural environment, the health of the inhabitants and still the economic benefit for the company.

For example, materials such as hydrocarbons in solid, liquid or gaseous form and steel (the reinforcement of the tire) can be recovered by pyrolysis from the waste of car tires. These materials in relation to the initial fed mass of the pyrolysis are 45% - 55% liquid fuel (petroleum), 10% - 15% steel in the form of wire, 30% -35% pure carbon in the form of powder and 8% - 10% gas fuel. In addition to solving the problem of waste disposal from plastic packaging and car tires, there is also an economic benefit from the liquid and gaseous fuels produced by the management of such waste. Fuels that replace petroleum derivatives.

The energy needed in pyrolysis is partially self-powered. Initially the heating of the raw material is done with fuel from an external source, usually gas (liquefied petroleum gas or natural gas) and by the start of the degradation of the raw materials, the first products extracted are in the gaseous phase, usually methane (CH_4). Gas is fed to the burner to support pyrolysis, reducing the amount of externally supplied gas. Thus, part of the energy for the degradation (pyrolysis) of the raw material comes from the material itself.

From the experiments that have been carried out in high-speed pyrolysis, an improvement in the characteristics of the bio-oil is observed compared to that produced by conventional pyrolysis. At a reaction temperature of $747.15 \text{ }^\circ\text{K}$, 40.93 wt% of the biomass was converted to bio-oil with a GCV energy content of 16.92 MJ/kg and a water content of 28.02 wt%. By reducing the water content, the bio-oil can be used commercially as diesel fuel in engines because all its properties comply to the EN590 standard. (Erdogan, 2020)

Type	Time	Thermal pace	Temperature	Outcome
Slow-paced	Hours-days	Slow	400°C	Solid
Conventional	5 - 30 min	20-100°C/min	500-800°C	Solid, Liquid, Gas
Fast-paced	0,5 - 5 sec	1000°C/sec	900-1050°C	Liquid

Table 1.Types of pyrolysis depending on the time of their process.

3. Conclusion

Summarizing the above, it appears that pyrolysis is a powerful tool for reducing the huge problem of plastic waste in our modern societies and at the same time to produce fuel which can be used with the appropriate equipment for the co-production of electricity and heat energy. It is important to realize that pyrolysis of plastics is not only a waste management method but also a productive procedure.

All plastics have carbon and hydrogen content that can be pyrolyzed with the same principles as biomass. Most of the packaging materials have similar chemical structure which increases the potentials of plastic waste utilization. The raw materials that result of their intended use can be recovered and reconstituted into new fuels in order to begin a new life cycle each, contributing to a more carbon-free energy future design.

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