

Biomass pyrolysis liquids. Fundamentals, technologies and new strategies.

Líquidos de pirólisis de biomasa. Fundamentos, tecnologías y nuevas estrategias.

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Abstract

Biomass pyrolysis liquids are promising for the production of valuable chemicals, fuels and energy from renewable resources. Fast pyrolysis technologies are selected for maximizing the yield to liquid products, being characterized by short residence times for solids and vapors, very high heating rates and operating temperatures typically in the range of 450-550 °C. The applications for these liquids at a commercial scale still present some challenges that need to be solved. Nonetheless, there are already successful cases of fast pyrolysis technologies at full scale, yielding chemicals or producing energy via combustion of the liquid. New strategies can be proposed for developing integration of processes and valorization of byproducts and residual streams in the fast pyrolysis process. Following this approach, different biorefinery schemes have already been proposed aiming at producing different biobased products with higher added value apart from bioenergy.

Resumen

Los líquidos de pirólisis de biomasa son productos prometedores obtenidos a partir de recursos renovables que pueden ser utilizados para la producción de compuestos químicos valiosos, combustibles y energía. De cara a maximizar el rendimiento a productos líquidos, las tecnologías de pirólisis más adecuadas son aquellas basadas en la pirólisis rápida ("fast pyrolysis"). Estas tecnologías se caracterizan por unos tiempos de residencia cortos tanto de los sólidos como de los gases y vapores, muy altas velocidades de calentamiento y temperaturas de operación en el intervalo entre 450 y 550 °C. Las aplicaciones a escala comercial para estos líquidos todavía presentan algunos retos que precisan ser solventados. No obstante, existen ya casos exitosos de desarrollos de tecnologías de pirólisis rápida a escala industrial, en los que se obtienen bien productos químicos o energía mediante combustión del líquido de pirólisis. En este contexto, se pueden proponer estrategias novedosas de cara a la integración de procesos y la valorización de subproductos y corrientes residuales. Siguiendo esta concepción, existen actualmente distintos esquemas de biorrefinería que tienen como objetivo la producción de toda una serie de bioproductos con alto valor añadido junto con la tradicional producción de bioenergía.

1. Introduction.

Biomass is a renewable resource that has been used by humanity ever since the dawn of ages. Evidences of

biomass transformation dating back to circa a million years ago have been found. Until the XIX century, the massive technology for biomass transformation was direct combustion, mainly for energy production in the form of heat. However, proofs of the ancient conscious utilization of byproducts such as ashes and charcoal derived from these transformations have also been found, e.g., in the form of prehistoric paintings in caves and caverns as old as 40,000 years of age.

The progress in science and the research, development, and innovation carried out by many researchers and scientists led to the apparition of new concepts and technologies for transforming biomass and other non-renewable resources such as coal into a variety of chemicals, commodities, heat and electric power. Among these alternatives, thermochemical processes played an important role. Thermochemical processes can be defined as those processes that imply the transformation of raw materials into different products involving a series of different chemical reactions that take place at temperatures well above ambient temperature. The operating temperature can be very different, depending on the thermochemical process considered, and can range between 200 and 1600 °C.

The thermochemical processing of biomass presents several advantages over alternatives, namely biological or physicochemical processes, derived from the fact that chemical reactions take place at a much faster rate, thus benefitting from the kinetic dependence of the reaction rates with temperature. This implies that thermochemical processes typically have much larger throughputs than any other processes taken into consideration, enabling the production of much higher amounts of products and commodities in much shorter periods of time.

Thermochemical processes are usually classified in terms of the stoichiometric amount of oxidant species (usually oxygen, but not exclusively) present in the reactor with respect to the stoichiometric amount of oxygen necessary to have the complete combustion of the material to be processed. Hence, three main thermochemical processes are usually distinguished according to that:

- Combustion: Oxygen amounts that can range over 100%.
- Gasification: Processes having typical oxygen amounts typically ranging between 25 and 35%
- Pyrolysis: Process having no oxidant species in the reaction atmosphere.

Table 1 shows a classification of different types of

Table 1. Classification of the different types of pyrolysis.**Tabla 1.** Clasificación de los distintos tipos de pirólisis.

Pyrolysis	Residence time	Heating rate	Pressure (bar)	Maximum Temperature (°C)	Main product
Carbonisation	Hours-days	Very low	1	400	Solid
Conventional	5-30 min	Low	1	600	Gas, liquid and solid
Fast	0.5-5 s	Very high	1	650	Liquid
Flash-liquid	< 1 s	High	1	< 650	Liquid
Flash-gas	< 1 s	High	1	> 650	Gas
Ultrafast	< 0.5 s	Very high	1	1000	Gas
Vacuum	2-30 s	Medium	< 0,1	400	Liquid

pyrolysis according to the operating conditions. As can be seen, depending on the operating conditions, a main product fraction can be obtained. Nevertheless, three different product fractions (gas, solid and liquid) are obtained in any pyrolysis process, though their relative proportions vary depending on the process operating conditions. When pyrolysis liquids are targeted, the development of technologies based on fast pyrolysis is sought in order to maximize the liquid fraction and to obtain a liquid product of high quality. The yield to liquid products can be as high as 75 % (mass fraction with respect to the raw material fed in) [1].

The different product fractions that are obtained present different applications. Thus, the gas fraction is typically destined to the production of energy. The solid fraction may be used in different ways, including its use as fuel for the production of energy via direct combustion or through its commercialization as charcoal, or it may be utilized as raw material for the manufacture of active carbons; it may also be utilized in the metallurgic industry as reducing agent in the steel manufacturing process.

2. Fundamentals of fast pyrolysis for the production of liquid.

Fast pyrolysis technologies present some advantages over other biomass and wastes processing technologies, which can be listed as follows:

- Depending on the technology developed, it is a process that can be carbon neutral in terms of net greenhouse gas emissions (because the CO₂ released comes from a renewable resource, and ultimately it can be considered as CO₂ that was captured by plants during the photosynthesis process).
- Mass and energy densification are achieved when a fast pyrolysis technology is applied to low density raw materials such as biomass and wastes.
- Easy and more cost-competitive storage and transportation of biomass pyrolysis liquids.
- A greater energy efficiency can be achieved in combustion processes, as a result of burning a biomass-derived liquid fuel instead of solid biomass.
- The processing of the raw material and the final use of the products can be decoupled.
- It facilitates the valorisation of delocalised biomass resources in small scale autonomous installations.
- Apart from bioenergy, biomass pyrolysis liquids constitute a valuable source for obtaining valuable chemicals.

- Contrarily to other biomass processing technologies, the products from pyrolysis processes are at a higher energy state than the starting raw material (i.e., pyrolysis products possess a greater enthalpic content than the starting level of enthalpy from the raw material).

- Autothermal process: If the gas and solid fractions obtained in the process are used in-situ for heat generation, the process can be self-sustainable in terms of energy, and no external energy input may be required to run the process. Depending on the process, certain fast pyrolysis technologies may require of additional heat supplies, which can be achieved by burning a minor fraction of the raw material.

As can be seen in Table 1, fast pyrolysis process is characterized by short residence times for solids and vapors (in the order of a few seconds, typically less than 2 s), very high heating rates (between 1000 and 10000 °C/s), and operating temperatures typically in the range of 450-550 °C, even though in certain cases reaction temperatures as high as 650 °C can be selected. However, it must be remarked that along with the major liquid fraction, gas and solid fractions are invariably obtained in a fast pyrolysis process. The solid carbonaceous material originated in the pyrolysis process is known as pyrolysis char.

Short residence times for the solids inside the reactor along with a rapid separation of the pyrolysis char from the vapors generated in the devolatilization process are necessary because the metals from the ash fraction contained in the char can have a certain catalytic activity in cracking reactions of the vapors, yielding less liquid and increasing the gas product fraction.

Another key aspect of fast pyrolysis technologies is related to the condensation system. In order to prevent pyrolysis vapors from further reacting and decomposing into more gaseous compounds, it is crucial to design an adequate condensation system that enables a rapid cooling of the pyrolysis vapors. This can be achieved by different means, generally by quenching the vapors with previously obtained pyrolysis liquids (or fractions of these), although other alternatives such as the use of electrostatic precipitators may also be adopted.

There are also other important aspects directly related to the raw material used in the process that also influence the final quality and properties of the products and the product distribution. First of all, the composition of the feedstock will significantly affect these characteristics. Hence, ultimate and proximate analyses have to be done in order to

determine whether a certain raw material is adequate to be processed via fast pyrolysis. Particularly, it is desirable to count on a feedstock with a high content in volatile compounds and low ash content if the main objective is to maximize the yield to liquid product. Other key factors related to the raw material are: its moisture content (it is essential to have low-moisture feedstocks in order to avoid an excessive water content in the final product, which may result in a diminution of the heating value of the final product and phase separation in the liquid, affecting the product quality), its heating value (the greater, the better) and its oxygen content (which will affect the stability of the liquids).

Biomass pyrolysis liquids receive many names, such as pyrolysis liquids, pyrolysis oils, bio-oil, bio-crude oil (BCO), pyrolytic tar, wood liquids, wood oil, liquid smoke, wood distillates, pyroligneous acid and liquid wood among others. Of all these, bio-oil is the most common term used to refer to biomass pyrolysis liquids, even though it must be borne in mind that bio-oil in no means can be considered as the renewable equivalent to crude oil. Biomass pyrolysis liquids differ significantly from petroleum-based fuels both in physical properties and chemical composition.

Bio-oils are quite viscous liquids at room temperature, with a dark red/brown colour and a smoky odour. Their pH is acid (2.3-2.8) and suffer from ageing when they are stored at mild temperatures. This instability is a consequence of condensation-polymerization reactions originated from the presence of reactive oxygenated species, which may increase the water content along with the viscosity. Regarding their composition, biomass pyrolysis liquids are very complex multi-component mixtures comprised of water and many organic molecules with a wide range of size distributions and chemical nature, derived primarily from depolymerization and fragmentation reactions of three key biomass building blocks: cellulose, hemicellulose and lignin [2]. Their miscibility with water is limited, being soluble in other polar solvents such as methanol. Water addition can be tolerated up to about 35 % (m/m) and can result in phase separation of the pyrolysis liquid.

Other characteristics of bio-oils are their high content in water (typical water contents ranging from 15 to 35 % mass fraction, depending on the moisture content of the raw material and on the process conditions) and the possible presence of solid particles in suspension. The high oxygen content in their composition, about 50 % mass fraction, is another significant characteristic. This oxygen is present in most of the compounds identified in the oils [3]. The high oxygen content results in a low energy density (heating value), which is less than 50 % of that for conventional fuel oils. Besides, bio-oils contain a large amount of chemically dissolved water which lowers their heating value and flame temperature. The presence of oxygen in many bio-oil components is the primary reason for differences in the properties and behaviour seen between hydrocarbon fuels and biomass pyrolysis oils [4].

The chemical composition of bio-oils is complex, comprising mainly water, carboxylic acids, carbohydrates and lignin-derived substances. By water addition, or because an excessive water

content during its production, the bio-oils can be split into two fractions [5]: an insoluble fraction usually cited as pyrolytic lignin, which contains poorly soluble compounds from the decomposition of lignin, and a carbohydrate derived fraction soluble in water. The carbohydrate derived fraction is also a complex mixture consisting of carboxylic acids, aldehydes and ketones, alcohols, sugars, low molecular weight oligomers and some other more complex carbohydrates.

3. Fast pyrolysis technologies for the production of liquid.

Depending on the reactor design, different fast pyrolysis technologies can be found. Among the most common technologies developed for fast pyrolysis the following reactor types can be found: fluidised bed, circulating bed, entrained flow, vacuum pyrolysis reactors and ablative pyrolysis reactors.

Typically, a fast pyrolysis installation comprises the following steps:

- Pretreatment and conditioning of the raw materials. Depending on the feedstock and on the reactor type, drying and particle size conditioning (reduction or enlargement: milling, pelletizing, etc.) may be necessary before feeding the material into the fast pyrolysis reactor.
- Reaction zone. The reactor design is the key factor in order to successfully develop a fast pyrolysis technology.
- Solids removal system. Overflow sections, cyclones, and hot filters are typically included in a fast pyrolysis installation.
- Condensing system for the recovery of liquids.
- Flue gas treatment and conditioning system. Depending on the final use of the product gas, different configurations may be taken into consideration.

Some of these technologies have already reached a level of development at full scale. In 2013, the Finnish company Fortum started operating a full scale fast pyrolysis plant for producing bio-oil, with a nominal capacity of 50,000 tons of bio-oil/year. As of this date, the status of this plant is known to be active. Further details on the state-of-the-art of fast pyrolysis technologies can be found in the literature [6].

4. New strategies in fast pyrolysis technologies.

Biomass pyrolysis liquids have three main target applications to date:

- Direct use as fuels in internal combustion engines and boilers.
- As a raw material for the manufacture of valuable chemicals in different industrial applications.
- Energy generation through their use as drop-in second generation biofuels both in transportation and in stationary applications.

Historically, ever since the first attempts at valorizing biomass residues and wastes via fast pyrolysis for the production of liquid, the first two approaches were the most important. These routes aimed at using bio-oils in a direct way or after conducting few and simple treatments (e.g. fractionation of bio-oil in order to obtain flavors from the carbohydrate-rich phase) so as not to compromise the economic feasibility of the

process. Usually, certain post-treatment steps have to be carried out, particularly in the case of its direct use as fuel, which necessarily implies that bio-oil needs to meet the specifications of the energy generation equipment, such as maximum water, solids and ash contents, pH, heating value, etc.

The fuel applications of bio-oils basically comprise combustion in burners, furnaces, boilers, Diesel and Stirling engines and turbines. The main drawbacks in the case of burners, furnaces and boilers are the lack of constant supply of bio-oil with high quality along with problems of handling and optimization of the burner/boiler design, as a consequence of the poor volatility, high viscosity, coking and corrosiveness of bio-oils. Regarding Diesel engines, high CO emissions, wear and corrosion of certain injection and pump elements and the difficulty in adjusting the injection system are the main problems identified, whereas for turbines high CO and hydrocarbon emissions and fouling of the turbine must be overcome yet. Combustion tests in Stirling engines have been completed, but the performance is not satisfactory in terms of electrical and thermal efficiencies.

Nowadays, there are novel approaches that can be encountered in many biobased industries regarding the utilization and processing of biomass pyrolysis liquids. Particularly, the biorefinery concept is an idea that has gained increasing attention in recent years, though the concept of biomass refinery or biorefinery dates back to as early as 1981 [7]. The idea is to process lignocellulosic residues following an integral approach, converting the resulting products or fractions of them into a variety of fine chemicals or high added value products and raw materials serving as a feedstock for other valuable chemicals and commodities. This concept aims at minimizing the residual streams in a given biobased industry, an approach that has historically been adopted by pulp and paper mills. The biorefinery concept has been proposed as the best solution to convert biomass into fuels and chemicals, maximizing economic and environmental benefits while minimizing pollution [8].

Regarding the applications of bio-oil for producing chemicals, the whole bio-oil constitutes an attractive feedstock for the production of valuable chemicals as a result of the abundance of carbonyl, carboxyl and phenolic groups present in the bio-oil constituents. Some companies have developed industrial processes for the production of chemicals from bio-oil, like Dynamotive Corporation, manufacturer of BioLime, which is an organic calcium compound successfully employed in capturing SO_x emissions from coal combustors. This company also produces bio-oil based slow-release nitrogen fertilizers, with attractive properties such as biodegradability and lower leachability than mineral fertilizers, resulting in less pollution of ground waters. It has also been proposed as an environmentally friendly wood preservative, though efforts still have to be done to improve the retention of bio-oil in wood.

Some biorefinery schemes have already been implemented at different scales in fast pyrolysis technologies. Slurries of solid and liquid products from fast pyrolysis of biomass have been successfully fed into an entrained flow gasifier in the so-called BtL2 process [9], which aims at the production of synthetic

drop-in fuels via Fischer-Tropsch synthesis at a demonstration scale. Cereal straw and other thin-walled biomass with high ash content are the raw materials taken into consideration. The fast pyrolysis step is adopted from a regional point of view in which energy densification is targeted so as to prepare biomass for transportation into a centralized large installation for syngas production, benefitting from the more efficient storage and transportation of bio-oil compared to the biomass feedstocks.

Finally, the abovementioned fast pyrolysis plant owned by Fortum is the most significant example to date of the implementation of a biorefinery scheme at full scale. The bio-oil produced in this fast pyrolysis installation is used in the Joensuu (Finland) combined heat and power plant. A more detailed description of the process can be found elsewhere [6].

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6. References

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