Notes on Pyrolysis and Gasification

Pyrolysis (or thermal cracking) is a chemical decomposition process generated by the intervention of thermal energy. One of the first reactions developed by alchemists is remembered, although today it maintains its relevance in many important applications, especially in the petrochemical industry. Even in nature pyrolytic processes take place: the formation of oil from the decomposition of organic material is an impressive example. From an energy point of view, pyrolysis is a completely endothermic process; carried out in the absence of air and then in a reducing environment, it intervenes on organic matter and decomposes it by distillation. The particular operating conditions in effect make the organic macromolecules thermodynamically unstable which then decompose, according to the reaction mechanisms still little known, into shorter molecules and elemental carbon. Its application to the elimination of waste originated only in recent times (70s) with the adaptation of specific technologies already experimented with other materials. The first developments, related to purely economic reasons, are in the U.S.A.
Pyrolysis carries out the modification of the rejection by intervening with the breakdown of complex molecules that form rubber, plastic, starches, cellulosic compounds and other organic components, which are transformed into structurally simpler molecules, obtaining:

a solid residue of variable composition formed by carbonaceous material (char), residue of the organic component, mixed with metals and other inert materials present in the starting MSW. The carbonaceous part is used as fuel, or alternatively as an adsorbent material (the pyrolysis process favors the formation of a certain porosity). The separation of the carbon component is associated with the possibility of easy recovery of the fractions of interesting products, such as glass and metals.

a non-condensable gas phase consisting essentially of hydrogen, light hydrocarbons (CH4, C2H4, C2H6, ...), carbon monoxide and carbon dioxide. Being characterized by a moderate heating value, it is generally reused in the process as an energy support.

a condensable product that consists of two different phases, which tend to separate in an aqueous solution of low molecular weight organic species (mainly aliphatic and / or aromatic hydrocarbons, acids, alcohols, aldehydes, ketones, ...), and in a completely organic phase composed of oxygenated molecules with high molecular weight. The latter is called tar or bio-oil and is made up of tars, oils, naphthalenes.

In the condensed phase, the product hardly presents employment opportunities. The high percentage of oxygenated compounds present in bio-oil, causes values of acidity, viscosity and instability that make it difficult to use as fuel. Its use is carried out only by means of a partial elimination of oxygen (much complicated hydrogenation processes).

Instead, the residual aqueous phase, which is a solution consisting of 80 ÷ 90% water (as a result of moisture supply and produced by pyrolysis itself), with numerous organic species dissolved and produced by distillation, is characterized by high values COD (chemical oxygen demand) and BOD (biochemical oxygen demand); its eventual disposition can be a major problem.

The decomposition of organic materials begins at 180 ÷ 200 ° C, with the development of acetic acid and formic acid, in addition to methanol. Temperatures below imply only physical phenomena (drying, plastic softeners). At 260 ÷ 280 ° C exothermic reactions are ignited that lead to the formation of tars and an increase in the temperature of the materials, up to 400 ÷ 450 ° C. The emission of gaseous products begins with the formation of carbon dioxide, monoxide carbon, hydrocarbons, and finally hydrogen.

The amounts by weight and the composition of the different fractions obtained depend on:

- type of material to be treated, its distribution and humidity
- the content and composition of the ashes
- the average size of the loaded material
- the temperature reached by the material
- the residence time in the reactor
- the amount of air that can come into contact with the waste during decomposition
- the rate of heating and the type of reactor.

The main variables that regulate pyrolysis are, as for all chemical processes, temperature, residence time and pressure. Depending on the choice of the parameters of the procedures, there are three different pyrolysis technologies, which lead to a different distribution between the components produced:

Conventional pyrolysis: operates in a relatively low temperature range of 300 ÷ 700 ° C, and with heating characterized by very slight thermal gradients, in the order of tenths of a degree per second. The reaction time, on the other hand, exceeding hours, is very high, which allows feeding with raw material of also significant dimensions.

Flash Pyrolysis: in complete opposition to conventional pyrolysis requires high temperatures (around 1000 ° C), very high heating speed (above 200 ° C / sec.) And residence times of less than one second. The treated particles should have infinitesimal dimensions.

Fast Pyrolysis: it is a managed process with intermediate operating conditions between the two previous technologies.

Conventional pyrolysis achieves a more uniform distribution between the phases produced. The other processes favor the formation of the distilled phases (liquid and gas) at the expense of the solid residue: higher temperatures facilitate the gasification reactions of heavy chain organic species and char, with the production of a gas rich in H_2 and CO and, then, a higher calorific value, and the consequent reduction of the residual solid carbonaceous.

The application of pyrolysis has clear advantages resulting from the particular type of process, which can be summarized as:

- Use on a small scale
- Possibility of final recovery of chemical species with commercial value.
- Significant reduction in the amount of gas that undergoes purification treatment.

Pyrolysis, that is, heat treatment in the absence of oxygen or air (environment, which is, even if incorrectly, called reducing compared to one in which oxidative combustion processes occur) is the most innovative technological proposal how many among many presented in the field of biomass treatment in general.

COMPARISON WITH INCINERATION PLANTS

The proposed pyrolysis process is in clear competition to the thermal destruction technology (Incineration).

The incineration takes place in a special furnace, generally of the type with a mobile grid, specially designed to burn the particular "fuel" characterized by low calorific value and by qualitative and dimensional inhomogeneities.

Direct combustion undoubtedly has a number of advantages, including:

- reduction of up to 90% and up to 70%, respectively, in initial volume and weight
- the residual material is completely sterile and stabilized
- the possibility of recovering the contained energy

However, in direct comparison with the proposed pyrolysis process, its limitations are surely evident. Traditional incineration processes are exothermic and characterized by including combustion temperatures in a wide range (800�1400 ° C). Due to the variability of the decomposition of the materials, the temperature adjustment in the incinerator is the result of the continuous changes in the power flow and is therefore difficult to manage: the consequence is a plant run frequently away from optimal operating conditions.

Add to this is that all studies have confirmed in the gas emissions from incineration plants, the presence of different classes of organic compounds and halogenated derivatives, including some classes of highly toxic substances such as benzodiossine (PCDD) and polychlorinated benzofurans. (PCDF). Harmful organochlorine products are generated in the combustion gas cooling phases (in the furnace the high temperatures inhibit their formation), catalyzed by the ever-present ash: the incineration process actually favors the presence of significant amounts of particles in the gaseous effluents, constituting among the other, a great problem for their treatment. The presence of heavy metals in high concentration was found in the dragged ashes. Those skilled in the art have addressed many critics for conventional incinerators, contending for the reasons stated, in addition to the difficulty of conduction and operation, the possibility that highly polluting products can be dispersed in the atmosphere. The presence of monumental and expensive reduction systems for slaughter and purification of fumes, in addition to considerably increasing the value of the investment and the increase in management and maintenance costs, does not guarantee, however, environmental safety.

PYROLYSIS	INCINERATION
▪ Minimum environmental impact and high Reliability. Simple and reliable disposal systems	▪ Doubtful environmental compatibility (especially in relation to emissions micro-pollutants) and uncertain reliability. ▪ Chilling systems that are characterized due to complicated engineering and heavy plant management, as well as many high costs
▪ Treatment of the gaseous stream before of its combustion and, therefore, not yet being diluted from the combustion air, in limited quantity. Waste pyrolysis produces a quantity of gas over 10 times less than that produced by combustion	▪ Treatment of gaseous effluents below combustion and therefore in a massively important stream (diluted from the combustion air). To obtain a complete combustion, it is operated with an excess of air of 1.5 to 2.5 times the stoichiometric amount required.
▪ The endothermic pyrolysis process is leads to relatively low temperatures (next to 500 ° C). This facilitates the control of the temperature, and then of the process, drastically reduces the amount of gaseous effluents, avoids the formation of unwanted products.	▪ Oxidative exothermic processes are characterized by combustion temperatures higher than 1000 ° C. The temperature control is difficult to handle because it appears only through the variation of the feed flow (high inertia of the system)
▪ The stream purification operation Gas is extremely simple since the pyrolysis gas produced in a reducing environment, and not yet burned, is characterized by structurally simple molecules and absolutely free of chlorinated organic compounds (PCDD-PCDF). The Distillation in the absence of air converts the halogens and sulfur into hydrogenated acidic compounds that are knocked down and removed from the pyrolysis gas stream prior to combustion.	▪ Complications in training control of PCDD-PCDF: difficulties arise both in the design phase and in the combustion management phase and affect the reliability of the system with respect to organochlorine micro-pollutants. Difficult to combat the phenomenon of the reform of the PCDD-PCDF.
▪ Water treatment section for the recovery with economic benefits obvious.	▪ Necesidad de una sección importante para el tratamiento de residuos líquidos, con todos los problemas relacionados
▪ Partial gasification of C, the rest remains	▪ Complete oxidation of all contained C

PYROLYSIS	INCINERATION
in the residue like coal mixed with inorganic components.	in waste in CO2 and its subsequent dispersion in the atmosphere with the possibility
▪ The low temperature and the practical absence of convective movements inside the reactor avoid the entrainment of particulate.	▪ Significant presence of dust and particles in the fumes, due to the movement of the residues on the grill and the considerable excess air.
▪ Easy combustion management linked to the fuel type (gas phase pyrolysis gas).	▪ Direct combustion of a product heterogeneous, with formation of various combustion products characterized by complex molecules and presence of unburned.
▪ Complete recovery of metals in non-oxidized form.	▪ Loss in metal slag low point melting (aluminum) and decrease in value due to the oxidation of ferrous metals. Formation of metallic nanopowders.
▪ The carbonaceous component, a residue of the pyrolysis of organic components, it is easy to use as a fuel (PCI ~ 5,200 kcal / kg) making the recovery of flexible energy.	▪ Energy recovery system no Flexible, with a link between the production of electrical energy on site and the consumption of auxiliary fuel in the afterburner.
▪ Low process temperature that favors life of refractory linings and mechanical parts. The type and amount of gas in the circuit prevents erosion and corrosion and drastically reduces maintenance costs.	▪ Direct combustion of waste with formation of aggressive compounds. High maintenance costs.
▪ Almost universal layout system, can be applied to various categories of input materials.	▪ Sensitivity of networks to waste with a high calorific value (used tires).
▪ Limited investment costs.	▪ Considerable investment costs.
▪ Low cost of management.	▪ Management expenses at the middle levels.
▪ Plant simplicity.	▪ Complex plants, especially in the smoke treatment system.
▪ Simplicity in managing the process.	▪ Complex management of the process that The problem of the qualification of exercise personnel.
▪ Long-term reliability.	▪ Need for frequent.
▪ Possibility of varying the scale of the modular way.	▪ Scale stiffness (large plants).
▪ Delivery, installation and commissioning relatively short.	▪ Delivery, installation and commissioning with long times.

The great defects of incineration, which can be summarized in the incomplete combustion of solid waste, large volumes of fumes to be treated, dangerous emissions into the atmosphere, impossibility of storing the energy produced, loss of value of inorganic components, etc. place in evidence the peculiarities of the proposed pyrolysis process.

STATE OF THE ART

Many pyrolysis and / or gasification installations with combustion of the gas obtained (boiler) for the production of both thermal and electrical energy are known and operational. In time, few pyrolysis and / or gasification plants are capable of supplying the gas produced by combustion engines. It is well known that internal combustion engines have conversion efficiencies of approximately twice that of common and small turbines (steam, ORC, etc.) and are therefore of considerable interest in relation to the incentivized production of electricity from biomass. E ', however, also known that the problems related to the purification of the synthesis gas produced by not totally degraded components that accompany it have effectively limited even today the effective application of these technologies. In fact, in the last ten years, our company has actions not so much in the pyrolysis and / or gasification phase (already thoroughly developed) as in the search for sustainable systems adapted to purify the synthesis gas, complete the cycle of energy, avoid polluting emissions, so that currently our process is completed with:

- catalytic treatment of synthesis gas, with purification and formation of other synthesis gas
- complete reuse of liquid biofuels derived from the gas condensation phase.

In view of the above, and the fact that pyrolysis is the heart of the entire system, our Company is capable of providing, in the field of biomass energy conversion, a plant a simple and, above all, reliable and efficient plant.

ADVANTAGES OF PYROLYSIS TECHNOLOGY

- High efficiency of transformation of biomass into energy
- Does not produce dioxins, PM 10, polycyclic aromatic hydrocarbons, furans and benzofurans
- Produce biochar strongly applied for in agriculture
- It allows transforming a wide range of dry or wet materials, such as municipal solid waste and derivatives, sewage sludge, etc.
- It makes possible the construction of large, medium and small plants that are also inserted in the urban context to allow exploiting the thermal energy produced by heating or cooling
- It involves an irrelevant environmental impact
- It is not a facility for combustion or incineration, but for processing biomass into hydrogen, carbon monoxide and light hydrocarbons
- Has no residual

PROJECT GENERAL DESCRIPTION

The document in question intends to present a specific technology for the combined production, for each line of operation, of electricity (1,200 kWe) and heat (1,600 kWt) through the use of internal combustion engines in cogeneration configuration, powered with the gas produced by a biomass or MSW pyrolysis process.
The document frames the process in its 4 reference sections:

- **Biomass storage**

  Biomass is made up of organic-based waste that is stored in dedicated environments and vacuumed to prevent bad odors from leaking into the atmosphere.

- **Material pre-treatment**

  The biomass at the outlet, due to its physical characteristics, requires a previous treatment in order to optimize the pyrolysis process. This will require a crushing process to reach a size of <20 mm.

- **Pyrolysis**

  The material comes out of the pre-treatment and is introduced into the pyrolysis reactor; Three products are obtained from the process: gas, condensate and carbonaceous structure. The pyrolysis gas, characterized by a high calorific value, is sent to the storage system (gasometer) for its subsequent use in cogeneration engines. The carbonaceous structure is partially recycled at the top of the pyrolysis reactor in order to reduce the carbon content and the remaining part is sent to large bags for later use as biochar / special waste, after any possible selection of metals present.

- **Production of electricity and heat**

  The pyrolysis gas is partly recycled in the pyrolysis reactor to maintain a constant production rate, partly for the power system that has the same temperature pyrolysis reactor and, finally, for the most significant part it is used to feed internal combustion engines for the generation of electricity. The engines, which operate in cogeneration, guarantee a total amount of thermal energy equal to 1,600 KWt in the form of water at 85 ° C and hot fumes at 500 ° C. The recovered heat can serve both adjacent industrial activities and other specific uses to locate.

The proposed system is clearly different from the common processes of exploitation of the energy of organic materials currently in use. In particular, it is distinguished by the high quality of the pyrolysis products, due to the specific process adopted and therefore to the possibility of assigning them to energy recovery through the most efficient technologies.

The advantages offered by this technology are due both to the type of pyrolysis process applied, and to the particular design implemented of the plant. The choice of an endothermic process, carried out at relatively low temperatures (around 450 ° C), allows an easier and better control of the distillation process, and avoids the formation of unwanted products and the carry-over of particles.

The limited amount of fumes to purify compared to traditional combustion reduces the investment costs of the abatement system and favors the same purification phase, with increased yields.

The low operating temperatures, in addition to bringing advantage to the plant implementation level, promote the life of the insulating coatings and of all mechanical organs in general, consequently reducing maintenance costs.
In addition, the system installation configuration also has inherent advantages:

- High process efficiency, thanks to the peculiarities of the reactor, its internal configuration and the use of the most efficient energy conversion systems (internal combustion engines);
- Reduction of investment and management costs;
- Easy installation and commissioning;
- Easy adjustment and control of the process parameters, also thanks to the reduced capacity of the system;
- Easy management;
- Easy to carry out modular plant;
- Adjustable reaction temperature depending on the quantities and types of output products;
- Minimum system maintenance with planned interventions;
- Request for personnel exclusively for fuel loading and surveillance, since the system is automated and equipped with electronic control systems;
- Thermal independence of the process, if not only for the start-up periods or, in special cases, for example, the drying of the material;
- High intrinsic safety, as the system works with a slight overpressure, which is a key element of intrinsic safety; in fact, in case of leaks in the system, contact between the pyrolysis products and the air occurs outside the reactor, and this does not constitute a risk factor.

CALIBRATION FOR EACH 1200 kWe LINE

Each line is dimensioned to guarantee a nominal electrical production per hour of 1,200 kWh (assuming an electrical conversion efficiency in the motor of 30%). The crushing phase involves only a reduction in the size of the material until it reaches a size such as to favor the subsequent drying and pyrolysis processes. The material size is <20x20mm.
In these conditions you get around:

• 850/950 kg / h of pyrolysis gas with L.H.V. = 4,200 kcal / Nm3 (4.8 kWh / Nm3);

• 100 kg / h of the carbonaceous structure;

• 80 kg / h of condensate with a water content of 70/80%.

The pyrolysis process including the drying line can bind up to 850,000 kcal / h (990 kW)
available in part, using syngas produced by gasification of the carbonaceous structure.
680/720 Kg/h of gas are sent to the gasometer with an average LHV of 4.8 / 4.9 kW / Nm3, with contributions then to cogeneration of approximately 3.6 kWt / h.
Assuming an electrical conversion efficiency of 33/34% and thermal conversion of 45%, 1,200 kWe and 1,600 kWt of installed power are obtained.
Total operating hours: 7,500 hours / year under normal conditions.
η el (the overall efficiency of the system): 25%.

ENVIRONMENTAL ASPECTS

The system operates the conversion of organic materials into electricity and heat, in fact, avoiding the consumption of fossil fuels. In addition to the strategic benefits for the energy market, fuel savings (through the use of renewable resources and cogeneration) result in avoided CO2 emissions, that is, in a contribution to the achievement of the objectives set by the Kyoto Protocol and the national energy policy.

- **Emissions to the atmosphere**

  The plant is designed to comply with the emission limits prescribed by Italian and European law.

- **Liquid Emissions**

  Liquid emissions are those derived by the recovery system of the content of energy of the pyrolysis condensates. The resulting maximum flow can be equal to 150/200 liters / h; Such waters will be treated inside the plant for the total recovery of the organic substance.

- **Solid Emissions**

  Solid waste is managed in accordance with current legislation. Solid waste from the plant is the ash generated by the gasification stage.

- **Noise**

  The limits of the law are respected by the adoption of measures such as:
  - setting limits on the sound level of its components in order to ensure a sound level that does not exceed the limits;
  - the arrangement of components and structures in order to protect those with higher emissions compared to the most critical receivers;
  - the adoption of soundproof booths and low-noise equipment;
  - the sound pressure will be in accordance with the values defined by the Zoning Plan Acoustics prepared by the Municipal Administration.

- **Firefighting**

  Fire regulations - Firefighters
  Project examination instance for the issuance of the compliance opinion.

- **CO2 emissions avoided**

  The annual avoided emissions of CO2 by the line for the production of electricity, or the carbon dioxide emitted by a traditional plant powered by fossil fuels in the production of an equivalent amount of electrical energy, is equal to about 6,500 t / year.

METHANE PRODUCTION

After producing the synthesis gas, as an alternative to its use to power combustion engines and to produce electricity, a catalytic reaction can be carried out for the production of methane at approximately 95% purity in principle, its commercialization and distribution .
In this case, the section of the electrical energy production plant is replaced by a section of medium pressure catalysis.