

Thermochemical Conversion as the Key Step for the Production of Value-Added Products from Waste

Corona F^{1,2}, Hidalgo D^{1,2}, Díez-Rodríguez D^{1,2} and Urueña A^{1,2}

¹CARTIF Technology Centre, Spain

²ITAP Institute, Valladolid University, Spain

***Corresponding author:** Corona F, CARTIF Technology Centre, Parque Tecnológico de Boecillo 205, 47151 Boecillo, Valladolid, Spain, Tel: +34 983 546504; Fax: +34 983 546521; Email: fraenc@cartif.es

Published Date: January 10, 2016

ABSTRACT

The general aim of this paper is to review pros and cons of currently available thermochemical conversion technologies that can be applied to produce bioenergy while treating industrial, agricultural, and non-recyclable fraction proceeding from waste treatment plants. Furthermore, this review will be used to demonstrate that the sustainable management of a broad spectrum of wastes in an integrated plant is possible.

This objective is reached by means of the technological development and practical application of the “Forest integrated wood processing plant” and “Mixed plant” concepts where the thermochemical treatment becomes the key technology to support a new waste management strategy, based on the separation, pre-treatment, recycling and valorisation steps.

Keywords: Combustion; Gasification; Liquefaction; Multi-Waste; Pyrolysis; Thermochemical processes; Valorisation

INTRODUCTION

The pace of life in today's society has led to an increase in the consumption of resources, particularly those with a short lifecycle. This in turn has resulted in an exponential increase in the quantity of waste going to landfill. In the European Union countries, over 250 Mt of Municipal Solid Waste (MSW) are produced each year, with an annual growth of 3%. In 1990, each individual in the world produced an average of 250 kg of MSW generating in total 1,300 Mt of MSW [1]. Ten years later, this amount almost doubled leveling at 2,300 Mt. In US, Plastic Waste (PW) found in MSW has increased from 11% in 2000 [2] to 12.7% in 2011 [3].

Different MSW treatment options have different type of impacts; however, environmental soundness of the technology should be accounted in the long time perspective. Thermochemical process is one of the emerging technologies which have lower environmental impact than the traditional incineration process, and, at the same time, generates valuable products from waste. Sanitary landfill with energy generation has the least environmental impact among other thermal treatment technologies. However, due to the socio-economic and environmental perspective landfill is not a favorable waste treatment option.

Also biomass can be a source of valuable products. Biomass is considered as a renewable energy source because its supplies are not limited. Trees and crops can be always grown, and waste will always exist. Biomass from agricultural and forestry processes can be converted into more valuable energy forms via a number of processes including thermal, biological, and mechanical or physical processes. While biomass biological processing is usually very selective and produces a small number of discrete products in high yield using biological catalysts, thermal conversion frequently gives multiple and complex products, in very short reaction times with inorganic catalysts often used to improve the product quality or spectrum.

The bulky and inconvenient form of wastes is a major barrier to a rapid shift from fossil to biofuels. Unlike gas or liquid, solid wastes cannot be handled, stored, or transported easily, especially in its use for transportation. This provides a major motivation for the conversion of solid wastes into liquid and gaseous fuels.

Thermochemical conversion is a high-temperature chemical reforming process that breaks apart the bonds of organic matter and reforms these intermediates into biochar (solid), synthesis gas and highly oxygenated bio-oil (liquid).

The benefits of the thermochemical process are numerous: small footprint, efficient nutrient recovery, no gas emissions, short reaction time and capability of handling a variety of wastes and blends, among others.

Production of thermal energy is the main driver for this conversion route that has four broad ways: combustion, pyrolysis, gasification and liquefaction.

Table 1 shows a comparative of thermochemical processes for waste-to-energy conversion.

Table 1: Comparative of thermochemical processes.

Process	Temperature (°C)	Pressure (MPa)	Products
Combustion	700-1400	0.1	Thermal energy
Pyrolysis	500-800	0.1	Biochar Gas Bio-oil
Gasification	500-1300	0.1	Syngas
Liquefaction	250-350	5-20	Liquid biofuel

Combustion involves high-temperature conversion of waste in excess air into carbon dioxide and steam. Combustion is an exothermic reaction between oxygen and the hydrocarbon in waste. Here, the waste is converted into two major stable compounds: H_2O and CO_2 . The process takes place using more oxygen than pyrolysis or gasification, so higher air emissions are produced. As much as 30% of the processed solid waste remains as ash. This ash is also a solid waste and could be sometimes categorised as hazardous solid waste.

Unlike combustion, pyrolysis takes place at a relatively low temperature in the total absence of oxygen. Pyrolysis is a thermal decomposition of the waste into gas, liquid, and solid. In pyrolysis, large hydrocarbon molecules of waste are broken down into smaller hydrocarbon molecules. Fast pyrolysis produces mainly liquid fuel, known as bio-oil; slow pyrolysis produces some gas and solid charcoal (char or biochar). Pyrolysis is promising for conversion of waste into useful gas or liquid fuels and biochar. Unlike combustion, it is not exothermic [4].

Gasification involves a chemical reaction in an oxygen-deficient environment. This process converts fossil or non-fossil fuels (solid, liquid, or gaseous) into useful gases and chemicals. It requires a medium for reaction, which can be gas or supercritical water. Gaseous mediums include air, oxygen, subcritical steam, or a mixture of these.

Presently, gasification of fossil fuels is more common than of non-fossil fuels like biomass for production of synthetic gases. It essentially converts a potential fuel from one form to another. There are three major motivations for such a transformation: 1) To increase the heating value of the fuel by rejecting non-combustible components like nitrogen and water.

2) To remove sulphur and nitrogen such that when burnt the gasified fuel does not release them into the atmosphere.

3) To reduce the Carbon-To-Hydrogen (C/H) mass ratio in the fuel.

Waste gasification into CO and H_2 provides a good base for production of liquid transportation fuels, such as gasoline, and synthetic chemicals, such as methanol or to obtain thermal energy and power from syngas [4].

Liquefaction of solid waste into liquid fuel can be done through pyrolysis, gasification as well as through hydrothermal process. In the latter process, waste is converted into an oily liquid by contacting the waste with water or organic solvents at elevated temperatures (250–350 °C) with high pressure (5–20 MPa).

This paper makes an in-depth review of thermochemical conversion technologies able to treat a variety of wastes with the focus on the final valorisation of these residual streams.

COMBUSTION

Biomass can be burned directly in waste-to-energy plants without any chemical processing to produce steam for making electricity. Direct combustion and co-firing with coal for electricity production from waste has been found to be a promising method in the nearest future. Also wastes can be burned to provide heat for industries and homes [5].

Combustion can ideally be defined as a complete oxidation of the fuel. The hot gases from the combustion may be used for direct heating purposes in small combustion units, for water heating in small central heating boilers, to heat water in a boiler for electricity generation in larger units, as a source of process heat, or for water heating in larger central heating systems. Drying and pyrolysis/gasification will always be the first steps in a solid fuel combustion process [6].

Influencing Factors in Combustion

Air preheating

According to Van Kessel et al. [7] preheating of the primary air acts as a catalyst for the ignition on a grate rather than only drying of the waste. Zhao et al. [8] investigated the effect of air preheating in the fuel on combustion characteristics of corn straw. The average burning rate and ignition front propagation velocity increased with increasing primary air preheating temperature. The total burning time was shorter under the higher primary air preheating temperature and the higher primary air preheating temperature produced a lower ignition front flame temperature in the bed. The variation of the flue gas O_2 , CO and CO_2 concentrations with time was more intensive at a higher primary air preheating temperature during the ignition front propagation period and the char oxidation period.

Moisture content

The moisture will be released in the devolatilisation phase, and the moisture content decreases as a function of burnout.

According to several authors [8-10] fuel moisture is an important parameter to be considered. How wet or dry the fuel is will greatly influence combustion. Some amount of moisture seems to be needed in fuel in order to minimize emissions, while too much moisture can result in longer combustion time, greater fuel use and higher emissions. 5% waste moisture, although desirable, is normally not available. A typically air-dried waste is likely to have around 15 to 20% moisture in the best of circumstances (e.g. biomass). The combustor design also plays a role in determining the behavior of the fuel when burnt, whether it is dry or wet. Combustors with combustion chambers seem to burn waste more effectively at varying moisture content.

Ash

The waste contents of ash forming elements influence the choice of an appropriate combustion. They affect deposit formation, fly ash emissions and ash handling as well as ash utilisation/disposal options. Major ash forming elements (Al, Ca, Fe, K, Mg, Na, P, Si) are of relevance for the ash melting behaviour and deposit formation. Volatile ash forming elements such as Cl, S, Na, K, As, Cd, Hg, Pb or Zn play a major role regarding gaseous and especially aerosol emissions as well as concerning deposit formation, corrosion and ash utilisation/disposal. Aerosols are very small sized particles with diameters $<1 \mu\text{m}$ formed during the combustion of biomass fuels. They are mainly composed of alkali and heavy metal salts and cause particulate emissions, which can only be reduced with highly advanced gas cleaning devices such as electrostatic and fibrous filters. Due to fly ash and aerosol depositions on surfaces of boiler tubes, the efficiency of heat transfer decreases [11].

Ash effect during combustion has been widely studied [12,13]. Combustion of petrochemical fuels produced fly ashes rich in Ca, Si and Fe minerals, as well as K and Na minerals in the case of biomass samples. However, blending of the fuels resulted in a reduction of Ca, Fe, K and Na, while an increase of Si and Al elements in the fly ashes as compared to lignite combustion, suggesting lower deposition and corrosion problems in boilers firing these mixtures. The use of bauxite as an additive enriched bottom ash in calcium compounds. Under the conditions of the combustion tests, no signs of ash deposition or bed agglomeration were noticed [14].

Particle size and excess air

The waste particle size and excess air have important effects on formation of the pollutants at the combustor bottom and their oxidation (for CO and C_xH_y) or reduction (for NO) in the freeboard, and consequently, on the combustion efficiency and emissions of the combustor. The emissions of both CO and C_xH_y can be effectively mitigated by decreasing the waste particle size and/or increasing excess air, whereas the NO emission can be reduced by increasing the waste particle size and/or via lowering the amount of excess air [6].

Ninduandee and Kuprianov [15] obtained the best combustion and emission results of palm kernel shell with a particle size of about 5 mm via maintaining excess air at 40–50%.

According to [16] the particle size shows most significant impacts on char oxidation, followed by heating and devolatilisation and while less impacts of particle size is noticed on drying process.

Raw material (co-combustion)

Co-combustion waste with coal simultaneously provides among the most effective means of reducing net CO_2 emissions from coal-based power plants and among the most efficient and inexpensive uses of waste. Reviews of co-combustion [17,18] experience use essentially every major type of waste (herbaceous biomass, woody biomass, animal-wastes and anthropomorphic wastes) combined with essentially every rank of coal and combusted in every major type of boiler.

Waste-coal co-combustion represents a near-term, low-risk, low-cost, sustainable, renewable energy option that promises reduction in net CO₂ emissions, reduction in SO_x and often NO_x emissions, and several societal benefits [19].

Combustion Technologies

There are many combustion technologies available for biomass combustion such as: fixed bed combustion, fluidized bed combustion and pulverised bed combustion.

Fixed bed combustion

Fixed-bed combustion systems include grate furnaces and underfeed stokers. Primary air passes through a fixed bed, where drying, gasification, and charcoal combustion take place in consecutive stages. The combustible gases are burned in a separate combustion zone using secondary air. Grate furnaces are appropriate for burning fuels with high moisture content, different particle sizes, and high ash content. Usually, the capacity goes up to around 20 MW_{th}. The grate and walls can be water-cooled to avoid slagging problems. Underfeed stokers represent a cheap safe technology for small- and medium-scale systems up to about 6 MW_{th}. The fuel is fed into the combustion chamber by screw conveyors from below and is transported upwards on a grate. Underfeed stokers are suitable for fuels with low ash content and small particle sizes.

Fluidised bed combustion

In a fluidised bed, fuel is burned in a self-mixing suspension of gas and solid bed material (usually silica sand and dolomite) in which air for combustion enters from below. Depending on the fluidisation velocity, bubbling and circulating fluidised bed combustion can be distinguished. The intense heat transfer and mixing provide good conditions for complete combustion with low excess air demand. Using internal heat exchanger surfaces, flue gas re-circulation, or water injection, a relatively low combustion temperature is maintained in order to prevent ash sintering in the bed. Due to the good mixing achieved, fuel flexibility is high, although attention must be paid to particle size and impurities contained in the fuel. Low NO_x emissions can be achieved by good air-staging, good mixing, and a low requirement for excess air. Moreover, additives (e.g. limestone for sulphur removal) work well due to the good mixing conditions. The low excess air amounts required reduce the flue gas volume flow and increase combustion efficiency. Fluid bed combustion plants are of special interest for large-scale applications (normally exceeding 30 MW_{th}). For smaller plants, fixed bed systems are usually more cost-effective. One disadvantage is the high dust loads in the flue gas, which make efficient dust precipitators and boiler cleaning systems necessary. Bed material is also lost with the ash, making it necessary to periodically add new bed material.

Dust combustion

Dust combustion is suitable for fuels available as small, dry particles such as wood dust. A mixture of fuel and primary combustion air is injected into the combustion chamber. Combustion

takes place while the fuel is in suspension; the transportation air is used as primary air. Gas burnout is achieved after secondary air addition. An auxiliary burner is used to start the furnace. When the combustion temperature reaches a certain value, waste injection starts and the auxiliary burner is shut down. Due to the high energy density at the furnace walls and the high combustion temperature, the muffle (cylindrical furnace) should be water-cooled. Fuel gasification and charcoal combustion take place at the same time because of the small particle size.

Table 2 shows a comparative between waste combustion technologies.

Table 2: Advantages and disadvantages of waste combustion technologies. Adapted from Van Loo and Koppejan [6].

Technology	Advantages	Disadvantages
Fixed bed	<p>Low investment costs for plants < 20MW_{th}.</p> <p>Low operating costs.</p> <p>Low dust load in the flue gas.</p> <p>Less sensitive to slagging than fluidised bed furnaces.</p> <p>Simple and good load control due to continuous fuel feeding and low fuel mass in the furnace.</p> <p>Low emissions at partial load operation due to good fuel dosing.</p> <p>Low flexibility in regard to particle size.</p>	<p>Usually no mixing of fuels is possible.</p> <p>Efficient NO_x reduction requires special technologies (Combination of primary and secondary measures).</p> <p>High excess oxygen (5–8 v%) decreases efficiency.</p> <p>Combustion conditions not as homogeneous as in fluidised bed furnaces.</p> <p>Low emission levels at partial load operation require a sophisticated process control.</p> <p>Suitable only for fuels with low ash content and high ash-melting point.</p>
Fluidised bed	<p>No moving parts in the hot combustion chamber.</p> <p>NO_x reduction by air staging works well.</p> <p>High flexibility concerning moisture content and kind of fuels used.</p> <p>Low excess oxygen (3–4 v %) raises efficiency and decreases flue gas flow.</p> <p>Homogeneous combustion conditions in the furnace if several fuel injectors are used.</p> <p>High specific heat transfer capacity due to high turbulence.</p> <p>Easy use of additives.</p>	<p>High investment costs, interesting only for plants > 20MW_{th}.</p> <p>High operating costs.</p> <p>Reduced flexibility with regard to particle size (< 80 mm).</p> <p>Utilisation of high alkali fuels is critical due to possible bed agglomeration without special measures.</p> <p>High dust load in the flue gas.</p> <p>Loss of bed material with the ash without special measures.</p> <p>High sensitivity concerning ash slagging.</p>
Dust combustion	<p>Low excess oxygen (4–6 v%) increases efficiency.</p> <p>High NO_x reduction by efficient air staging and mixing possible if cyclone or vortex burners are used.</p> <p>Very good load control and fast alteration of load possible.</p>	<p>Particle size of biomass fuel is limited (< 10–20mm).</p> <p>High wear rate of the insulation brickwork if cyclone or vortex burners are used.</p> <p>An extra start-up burner is necessary.</p>

PYROLYSIS

Pyrolysis is thermal cracking of biomass feedstock without or with limited supply of oxidant-yielding volatile products and solid residue. Usual temperature of pyrolysis operation ranges within 500–800 °C. Gas, liquid, and char are three major products of pyrolysis process. The relative amount of each product depends upon operating parameters, properties of biomass and type of pyrolysis process. Usually, decomposition of waste at medium temperature (400–550 °C) favours the production of liquid oils at short residence times. At higher temperatures, probability for production of gaseous products increases. At low temperature, char is a dominant product [20].

There are two main processes for waste pyrolysis: fast pyrolysis and slow pyrolysis.

According to Bridgwater [21], in fast pyrolysis, waste decomposes very quickly to generate mostly vapours and aerosols and some charcoal and gas.

The essential features of a fast pyrolysis process for producing liquids are: very high heating rates, pyrolysis reaction temperature of around 500 °C, short hot vapour residence times, rapid removal of product char and rapid cooling of the pyrolysis vapours.

The main product, bio-oil, is obtained in yields of up to 75 wt% on a dry-feed basis, together with by-product biochar and gas which can be used within the process to provide the process heat requirements so there are no waste streams other than flue gas and ash.

Slow pyrolysis is characterised by slower heating rates, relatively long solid and vapour residence times and usually a lower temperature than fast pyrolysis, typically 400 °C. The target product is often the solid fraction (biochar), but this will always be accompanied by liquid and gas products although these are not always recovered.

Current processes led to slow pyrolysis technologies of most interest for biochar production.

Influencing Factors in Pyrolysis

Pyrolysis products yield depends on several factors: temperature, size of feed particles, rate of biomass heating, sweeping gas flow rates, mineral matter contents, type of waste.

Table 3 shows the effect of operating variables (heating rate, temperature, and gas residence time) on pyrolysis yield products maximisation.

Table 3: Effect of operating variables on pyrolysis yield. Adapted from Basu [4].

Yield maximised	Temperature	Heating rate	Gas residence time
Biochar	Low	Slow	Long
Bio-oil	Low	High	Short
Gas	High	Low	Long

Temperature

Temperature is the most influencing parameter in pyrolysis. Intermediate pyrolysis temperatures (500–550°C) usually maximise the liquid oil yield. Low and very high temperatures lead to the formation of char and gases, respectively. Higher temperatures stimulate volatile cracking reactions that decrease the yield of bio-oil and increase the production of non-condensable gases. Final pyrolysis temperature can cause 10–20% variations in yield of liquid oils. Final temperature range of 500–550 °C usually leads to the formation of higher yield of aqueous fraction. For loosely structured waste this range tends to vary from 470–550 °C. Lignin compounds (e.g. lignocelulosic biomass) require higher temperature 550–650 °C. Even at very high temperature (800–900 °C), pyrolysis of lignin does not yield more than 60% conversion.

Reaction temperature in the pyrolysis process affects both composition and yield of products.

Amutio et al. [22] studied temperature influence in pyrolysis process of the pine wood sawdust. The maximum liquid yield was obtained at 500 °C, which accounts for 75 wt% (on a wet basis). Temperature has great influence on product distribution by increasing gas yield and decreasing bio-oil and biochar yields. The gas fraction is mainly composed of carbon dioxide and monoxide, so its heating value is rather low. CO₂ concentration in the gas decreases with temperature whereas that of CO increases. As pyrolysis temperature is higher, biochar quality and surface properties are improved due to the formation of narrower pores by the release of higher volatiles. Similar results are obtained by Xiao et al. [23] from pyrolysis of rice straw and by Azargohar et al. [24] from wheat straw, sawdust, flax straw and poultry litter.

López et al. [25] carried out pyrolysis of plastic wastes. As pyrolysis temperature is raised, gas yields significantly increase to the detriment of liquid yields. 500 °C was established as the optimal temperature for plastic waste pyrolysis, in terms of both, conversion and quality of the pyrolysis liquids. Char yield was insignificant.

Size of feed particles

Feed particle size is another parameter to consider in pyrolysis process. When particle size increases temperature gradients inside the particles improves and the core temperature particles is lower than the surface which causes higher and lower bio-oil and gas yields and higher biochar yield.

It has been reported that particle size less than 5 mm does not have significant effect on the process rate [26].

In recent works, the effect of particle size on the product yields obtained by pyrolysis of biomass was experimented by Shen et al. [27] and by Aysu et al. [26]. Change in particle size did not significantly affect pyrolysis yields. Luo et al. [28] obtained smaller particle size results in higher gas yield with less tar and biochar for pyrolysis of municipal solid wastes.

Rate of waste heating

Rate of waste heating is another important factor that defines the types of decompositions products. In fast pyrolysis, heating rates are usually higher. Fast heating rates cause quick fragmentations of wastes and enhance the yield of volatiles. At high heating rates, high yield of liquid oil mainly owes to short time available for secondary reactions: tar cracking and repolymerisation. However, at high temperatures gases are the major products [20]. On the other hand, in slow pyrolysis, heating rates are lower. These heating rates led to obtain a high yield of solid fraction because of slow decomposition of biomass.

Pütün et al. [29], Şensöz, et al. [30] and Greenhalf et al. [31] researched the effect of heating rate on the products yields of the pyrolysis. The yield obtained for the fast pyrolysis (high heating rates) process was higher for bio-oil fraction. Nevertheless, the higher fraction in slow pyrolysis

(low heating rates) was obtained for biochar. On the other hand, Aboulkas et al. [32] obtained for plastic pyrolysis, when the heating rate was increased, that the conversion degree and the yield of gases increased and the yields of oils and biochar decreased. These results presents the same tendency that the obtained by Williams et al. [33], Mastral at al. [34] and Encinar and González [35] in the pyrolysis of plastics and tires.

Sweeping gas flow rates

According to previous works [36,37], the inert gas removes volatile from pyrolysis medium. Therefore, the secondary reactions such as thermal cracking, repolymerisation and recondensation are minimised, while the liquid yield is maximized. Note that the nitrogen flow affects the residence time of the vapour phase produced by pyrolysis so that higher flow rates cause rapid removal of products from the reaction medium and minimise secondary reactions such as biochar formation. The short residence time of the volatiles in the reactor as well as the increased sweeping gas flow rates cause a decreasing of secondary decomposition of higher molecular weight products [38-41].

Pütün [42] studied the influence of the sweeping gas flow rate in the pyrolysis of cotton seed. The gas yield increased with increasing nitrogen flow rate; whereas the biochar yield decreases since uncondensed volatiles are removed from the reaction zone by the nitrogen stream. These results are according to [43].

Mineral matter contents

Biomass and other wastes contain trace amounts of inorganic compounds metals (K, Na, P, Ca, Mg) which appears in pyrolysis ash. In fact, the ash has a greater effect on the pyrolysis than on the degree of crystallinity and polymerization [44]. Some elements of the ash can catalyse pyrolysis process resulting changes in pyrolysis product distribution [45]. Besides, ash removal can increase bio-oil yield and decrease gas yield [46].

Williams and Horne [47] carried out experiments to determine the influence of typical metals present in the ashes on the pyrolysis products. The influence of added metal salt was to decrease the percentage mass of derived liquid and increase the percentage mass of biochar. Consequently, biochar formation by secondary tar repolymerisation or cracking reactions were deemed to be minimised. However these secondary reactions to produce increased biochar have not been completely eliminated.

More recently, the influence of mineral matter on palm oil wastes pyrolysis was investigated by Yang et al. [48]. It was found that the addition of K_2CO_3 inhibited the pyrolysis of hemicelluloses.

Initial moisture

The presence of water in wood influences its behavior during pyrolysis and affects the physical properties and quality of the pyrolysis liquid. It is necessary to dry waste because the pyrolysis systems can handle waste typically having 30% moisture. Energy is used in endothermic

evaporation of moisture of the waste particle and decomposition reactions while pyrolysis process is carried out. The rate of moisture removal depends on the pyrolysis temperature and the heating rate. The initial moisture of the waste increases pyrolysis reaction temperature and the energy requirements to dry the biomass.

Burhenne [49] studied the effects of initial wood water content. The biochar yield did decrease significantly with increasing wood water content. The gaseous products followed a similar trend. The condensable products increased when the wood water content was higher. These results are in accordance with Demirbas [50].

Catalyst

Pyrolysis process presents some disadvantages for products application as fuel [21,51]. Bio-oil, gas and biochar improvements can be reached through several actions before, during and after pyrolysis [21]. One simple solution in pyrolysis is the introduction of catalysts to eliminate and to substitute oxygen and oxygen-containing functionalities, increasing the hydrogen to carbon ratio of the final liquid products. In general, different high cost catalysts have been mainly tested for biomass catalytic pyrolysis such as microporous zeolites, mesoporous M41S and mesoporous alumino silicates [52,53]. All these catalysts lead to a bio-oil with improved characteristics. Samolada et al. [54] have used ZSM-5 zeolites as catalysts for pyrolysis of biomass and found that introduction of these led to a decrease of the concentration of liquid products and to an increase of the quantity of gaseous products.

On the other hand, some other cheap catalysts such as bulk metal oxides [55] or supported sulphide/oxide and metal catalysts, mainly on alumina, have been also tested for biomass catalytic pyrolysis [56]. A wide review about catalysis for conversion of biomass to fuels via pyrolysis was achieved by Bulushev and Ross [57].

Type of raw material

The composition of the raw material plays a very important role in the distribution and quality of pyrolysis products. In accordance with Adrados et al. [58] the inorganic compounds do not contribute to the formation of liquid or gaseous products. The presence of cellulosic components in the samples gives rise to an increase in biochar formation which is greater as higher is the cellulosic content of the biomass. Also cellulosic components increase CO and CO₂ contents in the gases; yielding as a consequence lower HHV (Higher Heating Value) of the gases.

Several authors have studied plastics pyrolysis and have demonstrated the potentialities of this technology to process plastic wastes [25,59,60]. Pyrolysis of a mixture containing Polyethylene (PE), Polypropylene (PP) and Polystyrene (PS) in different blendings, showed that total conversion in all tests was higher than 80%, the main product being liquid (at normal conditions of temperature and pressure) with yields around 75 wt% and gas yields were always lower than 10 wt%, though products yields depended on the nature of plastic input [61].

Waste tyres can be an interesting feedstock to valorise by pyrolysis [62,63]. Choi et al. [64] studied waste tyres pyrolysis obtaining around 37 wt% of solid residue, 40 wt% of oil fraction and 23 wt% of gases. In general plastic waste pyrolysis allows the production of higher liquid products yields than those obtained with tyres pyrolysis.

Pyrolysis Technologies

Pyrolisers can be generally grouped into two groups depending on the kind of pyrolysis.

In slow pyrolysis, the pyrolisers used are fixed bed reactor and rotary kiln reactor.

Fixed bed reactor

Fixed bed reactors were traditionally used for the production of biochar and gas. Gas production depends on reactor configuration. Poor and slow heat transfer resulted in very low liquid yields. These gasifiers are divided into downdraft and updraft fixed bed reactors. Their technology is simple, reliable and proven for fuels with a relative uniform size. In a down draft fixed bed reactor, solid moves slowly down and a vertical shaft and air introduced and reacts at a throat that supports the gasifying waste. The solid and product gas move downward in a co-current mode. A relatively clean gas is produced with low tar and usually with high carbon conversion. In contrast, the updraft fixed bed reactor is characterised by solid moving down a vertical shaft and contacting a counter-current mode. The product gas is very dirty with high levels of tars although tar crackers have been developed to alleviate this problem.

Rotary kiln reactor

These reactors are the type best suits for pyrolysis simultaneously producing quality biochar and high calorific gas (suitable for the production of electricity). There are two kinds of pyrolisers: drum and screw.

Drum pyrolisers move waste through an externally heated, horizontal cylindrical shell by the action of paddles before it enters the drum to assure good biochar and gas quality. Some of the gas produced is burned in a firebox below the drum to heat the waste to pyrolysis temperatures. The process is characterised as “slow pyrolysis”, taking several minutes for the waste to travel through the drum [65].

Screw pyrolisers move waste through a tubular reactor by the action of a rotating screw. Some screw pyrolisers are externally heated while others use a heat carrier such as sand to heat the waste as it is transported through the tube. The screw pyrolyser is an attractive option due to its potential to operate at relatively small scales, being used in recent years to convert waste into bio-oil and biochar.

In fast pyrolysis, typical pyrolisers are: fluidized bed reactor, rotating cone reactor, ablative pyrolysis reactor, pyrolysis reactor vacuum.

Fluidised bed reactor

Fluid beds are the most popular configurations, due to their ease and reliable operation and ease of scaling to commercial plant sizes. They provide good temperature control and very efficient heat transfer to waste particles. The residence time of the reactants can be controlled by the flow of fluidizing gas, while special attention must be given to the system separating coke from the reaction products.

A typical bubbling fluid bed reactor uses the by-product gas and biochar to provide the process heat. In the circulating fluidised bed reactor, biochar particles have the same residence time with reaction products [66].

Rotating cone reactor

In the rotating cone reactor the pyrolysis reaction takes place upon mechanical mixing of waste and hot sand, instead of using inert gas. The waste feedstock and sand are introduced at the base of the cone while spinning causes centrifugal force to move the solids upward to the lip of the cone. As the solids spill over the lip of the cone, pyrolysis vapours are directed to a condenser. The char and sand are sent to a combustor where the sand gets re-heated before again being introduced at the base of the cone with the fresh waste feedstock [67].

Ablative pyrolysis reactor

This process involves creation of high pressure between a waste particle and a hot reactor wall. This allows uninhibited heat transfer from the wall to the waste, causing the liquid product to melt out of the waste. The waste sliding against the wall leaves behind a liquid film that evaporates and leaves the pyrolysis zone, which is the interface between waste and wall. As a result of high heat transfer and short gas residence time, a liquid yield as high as 80% is reported [68].

Pyrolysis reactor vacuum

For this reactor, waste is thermally decomposed under reduced pressure. The vapours produced are quickly removed from the vacuum and recovered as bio-oil as condensation. This pyrolysis reactor is characterised by longer residence time of solid. Other important feature in this reactor includes ability to produce larger particles than most fast pyrolysis reactors and there is less char in the liquid product due to lower gas velocities. There is also no requirement for carrier gas and the process is mechanically complicated. The typical liquid yields for dry waste feed obtained in this process are from 35 to 50% [67].

Table 4 shows a comparative between waste pyrolysis technologies.

Table 4: Advantages and disadvantages of waste pyrolysis technologies.

Technology	Advantages	Disadvantages
Fixed bed	Simple construction and operation. Good temperature control. Biomass size independent. High relative velocity between the fluid and solid phase.	High carbon conservation. Long solid residence time. Low ash carry over. Difficult to remove char. Large-scale systems have to be studied carefully due to scale-up limitations.
Rotatory kiln	No carrier gas required. A wide variety of different types and sizes of waste are accepted. Easy control of solids residence time.	Low heat transfer efficiency. Scale-up limitations.
Fluidised bed	Good solids mixing. High heat transfer rates. Good temperature control. Ease of scaling.	Heat transfer to bed must be proven at large scale. Max particle sizes up to 6 mm. If circulating increased complexity of system, char attrition and reactor wear.
Rotating cone	Good solids mixing. No carrier gas required. Ease of scaling. Small investment cost.	Heat transfer to bed must be proven at large scale. Small particle sizes required.
Vacuum reactor	No carrier gas required. Lower temperature required. Can process larger particles.	Low heat transfer rates. Solids residence time high. Liquid yield rather low.
Ablative reactor	Heat transfer gas not required. Lower temperature required. Can process larger particles. Compact design and intensive system.	Reaction rates limited by heat transfer to the reactor. Char abrasion. Scaling is costly.

GASIFICATION

Gasification is a thermochemical process that converts carbonaceous feedstock into a fuel gas through partial oxidation. The fuel gas generated is a gas comprising Carbon Monoxide (CO), Hydrogen (H₂), Carbon Dioxide (CO₂), Methane (CH₄) and light hydrocarbons. This gas mixture can be subsequently used to produce electricity, heat or synthesis of various products.

In electricity production waste is thermally converted by gasification into a fuel gas that can be used in a gas engine or turbine with electricity as well as heat as products. In the production of fuels and chemicals the fuel gas (syngas) is used in a catalytic process to synthesise the desired product.

Influencing Factors in Gasification

The generated fuel gas is very dependent on a wide variety of variables: feed particle size, moisture, gasifying agent, equivalent ratio and gasification temperature.

Feed particle size

Higher energy efficiency is obtained with smallest feed particle size but it also increases the gasification plant cost. On the other hand, an increase in feed particle size reduces the milling costs, but the residence time increases and fixed cost increases [69].

Moisture

Feedstock moisture must be reduced before use because it represents a large drain on a plant's deliverable energy. Every kilogram of moisture needs about 2,300 kJ of heat to vaporise

and an additional 1,500 kJ to be raised to a typical gasifier temperature of 700 °C. Therefore, lower moisture leads to higher heat available in the product gas [4].

Gasifying agent

Wastes gasification can be performed using several gasifying agents such as: air, steam, steam-oxygen mixture, steam-air mixture, air enriched with oxygen and oxygen-air-steam mixture [70].

- Air

Air gasification, is most commonly used because air is very cheap and readily available [71]. Air gasification increases the viability of the gasification process, and nowadays it is developed for industrial use. However, air gasification produces a fuel gas with a high concentration of nitrogen, with a Lower Heating Value (LHV) of 4-6 MJ•Nm⁻³ and a H₂ content of 8-14 v% [70,72].

- Oxygen

Oxygen gasification allows to obtain a fuel gas with higher LHV (10-15 MJ•Nm⁻³) [4], since the fuel gas will have a very low concentration of N₂. The disadvantage of oxygen gasification is the additional cost of its generation. According to Grezin et al. [73], the energy consumption of extracting oxygen from air is ~ 2.18 MJ•kg⁻¹ O₂

- Steam and air-steam

Biomass steam gasification can produce a fuel gas with a LHV of 10.16 MJ/Nm³, and a H₂ content of 30-60 v% [74]. Similar results were obtained by Balu et al. [75].

Lv et al. [76] studied the characteristics of biomass air-steam gasification in a fluidised bed. This experimental study has confirmed that the introduction of steam to biomass gasification is favourable for improving gas quality. However, excessive steam would lower gasification temperature and so degrade product gas quality. Over the ranges of the experimental conditions used, the fuel gas yield varied between 1.43 and 2.57 Nm³•kg⁻¹ biomass and the LHV of the fuel gas was between 6,741 and 9,143 kJ•Nm⁻³

Equivalence Ratio (ER)

The Equivalence Ratio (ER) is one of the most important operating parameters which are involved in the gasification of carbonaceous feedstock. ER is obtained by dividing the actual oxygen (or air) to biomass molar ratio to the stoichiometric oxygen (or air) to biomass molar ratio.

Higher ER contributed to the increment of gas yield and the decrement of tar in the raw gas. However, higher or lower ER both degraded the quality of gas and gasification efficiency [77].

Higher equivalence ratios lead to complete combustion of the feedstock and combustion of the fuel gas in the reactor resulting in low heating value of the exit gas. The heating value of the gas decreases with increasing ER after reaching its peak at about 0.26 [78].

Gasification temperature

The gasification temperature is not an independent variable, moreover temperature is consequence of different characteristics of the process: type of gasifying agent (air, oxygen), type of waste (moisture and ash content, LHV), ER, heat loss to the surroundings.

On the other hand, the gasification temperature directly affects the fuel gas composition, since temperature modify the thermodynamic behavior of the reactions. High temperatures improve product formation in endothermic reactions whereas they favour reactants in exothermic reactions [4, 69].

Gasification Technologies

Types of gasifiers can be classified according to the flow configurations. The primary configurations are: fixed bed or moving bed, fluidized bed and entrained bed.

Fixed bed or moving bed reactors

There are two types of moving bed reactor:

- Updraft or countercurrent: In this type of gasifier, the waste to be treated is fed in from the top of the reactor and the gasifying agent is fed in from the bottom of the reactor. Thus, solid and gasifying agent counter currently flowing along successive and different areas of the bed (drying, pyrolysis, reduction and oxidation).

- Downdraft or co-current: In downdraft reactor, the fuel is fed in from the top of the reactor and drops downwards, while the gasifying agent is injected from one side. Then, both gas and solid move down in parallel streams through the reactor.

Fluidised bed

In a fluidised bed reactor, the waste is fed in from one side of the gasifier. Inside the reactor, it is mixed with an inert material that promotes the suspension of the biomass, the thermal homogeneity and gas-mixing conditions in the bed. The gasifying agent is fed in from the bottom of the reactor and hold up solid particles. The ash produced is extracted from the bottom, while the gas exits through the top of the reactor.

Entrained flow

Entrained bed gasifiers operate with pulverised solid particles. The solid waste is injected in the reactor along with the gasifying agent. The ash generated melted due to the high operation temperatures ($\sim 1.400\text{ }^{\circ}\text{C}$) and is removed through the bottom of the reactor.

Table 5 shows a comparative between waste gasifying technologies.

Table 5: Advantages and disadvantages of waste gasifying technologies.

Technology		Advantages	Disadvantages
Fixed bed	<i>Updraft</i>	Simple construction and use. Low temperature of the gas produced. High thermal efficiency gasification. Size, shape and moisture content of waste particles are not critical.	Quality of the gas is generally quite low. A cleaning gas system is necessary. High quantity of tar produced. Low efficiency.
	<i>Downdraft</i>	Quantity of tar produced is low. High amount of ash in the gas. Simple and relatively low-cost technology.	High temperature of the gas produced. Pretreatment of the waste is necessary. High amount of ash in the gas. Low thermal efficiency gasification. Possibilities of ash fusion in the reactor grill.
Fluidised bed		Higher efficiency than fixed bed gasifiers. Greater variety of wastes could be fed. Low tar content in the gas. Tolerant to particle size and fluctuations in feed quantity and moisture.	Relatively low temperatures. Highly corrosive ash generated. Particles could be entrained by the gas.
Entrained bed		Almost tar free syngas. Leach-resistant molten slag.	High consumption of primary air. Spraying /atomisation of the waste is needed. High energy is needed.

LIQUEFACTION

Liquefaction is a low temperature and high pressure thermochemical process during which biomass is broken down into fragments of small molecules in water or another suitable solvent. These light fragments, which are unstable and reactive, can then repolymerise into oily compounds with various ranges of molecular weights [79]. At near-critical and supercritical temperature and pressure (374 °C, 22.1 MPa) water undergoes significant changes in solubility, density, dielectric constant, ionic properties and reactivity [80]. Hot compressed water is a powerful hydrothermal media for depolymerisation and repolymerisation of lignins, celluloses, lipids, and proteins into biocrude oil, water soluble organics, gas and biochar [81].

Influencing Factors in Liquefaction

Liquefaction products are determined by various factors, including raw material type, temperature, pressure, reaction time, solvent type and catalyst.

In recent years, liquefaction has been demonstrated with or without the presence of catalysts for a range of wastes including lignocellulosic biomass [82-84], microalgae [85-87], sewage sludge [88-90] and so on.

Raw material type

Lignocellulosic biomass is the most widely used raw material for bio-oil production through liquefaction. However, alternative raw materials are likely to be used for obtaining bio-oil by liquefaction: e.g. microalgae can be rich in proteins or rich in lipids or have a balanced composition of lipids, sugars and proteins. Sewage sludge produced in municipal wastewater treatment plants is composed mainly of bacterial constituents (nucleic acids, proteins, carbohydrates and lipids) and their decay products, undigested organic material (cellulose) and inorganic material.

Huang et al. [91] studied thermochemical liquefaction of three different raw materials: rice straw, sewage sludge and algae (*Spirulina* spp) at identical conditions. The higher conversion rate was obtained in *Spirulina* spp liquefaction. However, sewage sludge produced the highest bio-oil yield. The volatility distribution of major hydrocarbons for sewage sludge and *Spirulina* were similar (mainly at C_{17} and C_{20}), whereas a distinct trend was observed in rice straw-derived bio-oil (mainly at C_8).

Temperature

Brand et al. [92] studied the effect of reaction temperature on biomass conversion, yields of biocrude, solid residue, and gas composition. With temperature increases from 280 to 400 °C, a significant increase in the conversion from 34.0% to 98.1% and biocrude yield from 15.8 to 59.9 wt%, as well as a significant decrease in solid residue from 66.0 to 1.9 wt% was observed. With temperature increases, gas yield was increased from 18.2% to 36.0%. The gas composition varied with reaction temperature, but it had a general trend in the following order: $CO > CO_2 > C_2H_4 > CH_4 > C_2H_6$ [93]. These results are according to Jena et al. [94] and Chan et al [95].

Pressure

Brand et al. [92] tested the initial N_2 pressure effect. It was found to have a negligible effect on the conversion and the yields of biocrude, gas and solid liquefaction products. Biomass conversion and products yield remained practically unaltered over the entire pressure range. Behrendt et al. [96] conversely, stated that biocrude yield increases with pressure according to Le Chatelier's principle.

Apart from this, initial pressure had an important effect on the gas composition. As expected, amounts of all species (CO , CO_2 and light hydrocarbons) decrease with increase in head pressure. The ratio of decarbonylation to decarboxylation (CO/CO_2) decreased when the pressure increased.

Reaction time

Brand et al. [92] increased reaction time to 60 min. The conversion was found to increase up to 89.6% and biocrude yield was found to increase up to 52.0 wt%. Further increases in reaction times, were found to enhance conversion and product yield to some extent 93.6% and 59.2 wt% respectively. This result complies with previously reported studies [97]. No enhanced biochar/tar formation was observed at extended reaction times in supercritical EtOH-based liquefaction, as opposed to that during subcritical H_2O - or supercritical H_2O -based liquefaction owing to condensation and/or repolymerisation [98,99]; the hydrogen generated from supercritical EtOH may quench active intermediates to retard the polymerisation reaction. Gas composition does not strongly dependent on reaction time.

Solvent type

Besides water, organic solvents, such as ethanol, methanol, acetone, etc., have been utilised as the reaction medium [86,87,91,97]. Among these organic solvents, ethanol may be the most

promising solvent for biomass liquefaction from the viewpoint of efficiency, environmental friendliness and reproducible ability [100,101].

Singh et al. [102] carried out the hydrothermal liquefaction of the algae *U. Fasciata* using various solvents (H_2O , CH_3OH and $\text{C}_2\text{H}_5\text{OH}$). The use of alcoholic solvents significantly increased the bio-oil yield. Use of alcoholic solvents increased the aliphatics percentage in bio-oil and aliphatic ester compounds were present in bio-oil.

Catalyst

Catalyst has been found to be one of the most important variables that affect liquefaction reactions. So, the optimum selection of the catalyst is essential for the liquefaction process yield. A wide range of catalysts have been tested in liquefaction process. These catalysts includes alkali catalysts such as carbonates and hydroxide forms of Na, K [85,87,103-106] and Ni in sulfate form [107] and on $\text{SiO}_2/\text{Al}_2\text{O}_3$ support [108], sulfides of Fe [106,109] and noble metal catalysts including Ru, Mo and Pt [108,110]. Catalysts generally reduce the activation energy and increase oil yields and conversion efficiency. An increase of 10–50% has been obtained by catalytic conditions over non-catalytic conditions, depending on the catalyst type [81].

Liquefaction Technologies

Hydrothermal liquefaction processes have the potential to become an important group of technologies for converting wet biomass or organic waste into bio-oil for fuel or other applications. The various development projects that have been concluded without commercialisation underline the difficulties. However, in spite of this and remaining technical hurdles, significant progress has been made through process development performed at several pilot and demonstration plants: Hydrothermal Upgrading (HTU), Lawrence Berkeley Laboratory (LBL), CatLiq (Catalytic Liquefaction), TDP process (Thermo-Depolymerization), SlurryCarb process and PERC-process (Pittsburgh Energy Research Center) [111].

NEW TENDENCIES FOR WASTE TREATMENT

Integral Plant for Multi-Waste Valorisation

The “Mixed Plant” concept proposes the treatment and recovery, at the same facility, of a wide range of waste types: farm/livestock waste, industrial waste, agricultural and forest biomass and the non-recyclable fraction from waste treatment centres (Figure 1). For waste recovery, the inclusion of an anaerobic digestion system was proposed to convert easily biodegradable organic waste into biogas while the digestate was valorised as struvite in a crystallisation module. A thermochemical treatment system was proposed for the biomass and the non-recyclable waste fraction (mainly plastic waste and organic fraction mixed with other materials).

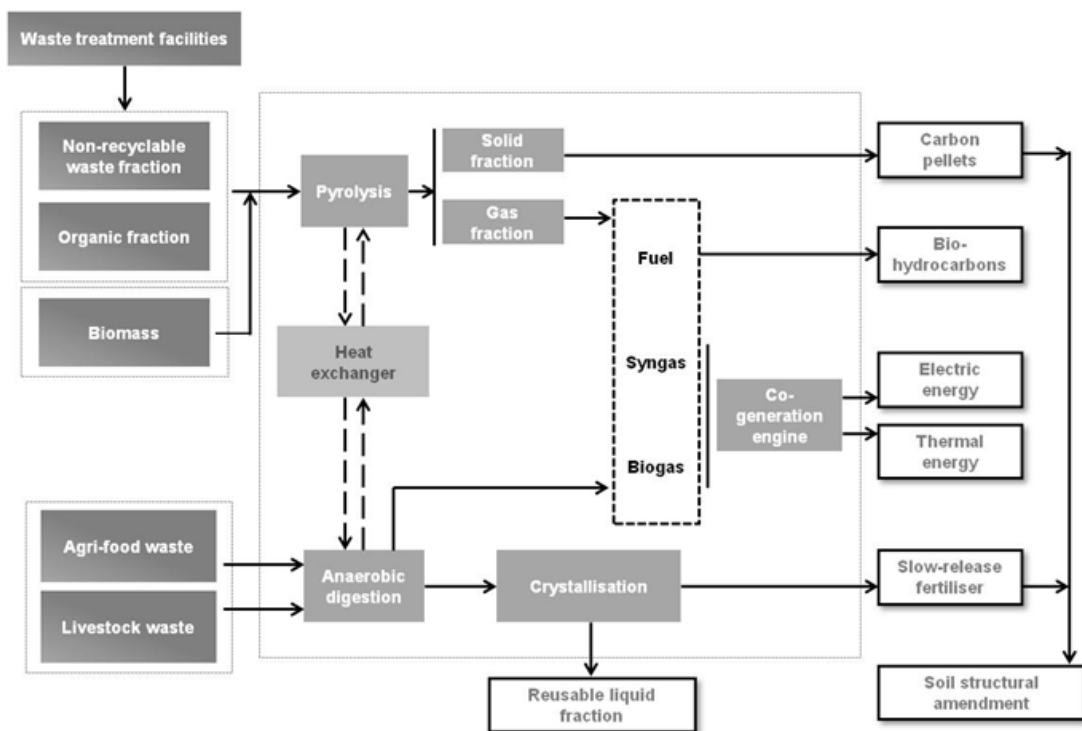


Figure 1: Schematic diagram of the integrated “Mixed Plant”.

The construction and operation of this plant is the main objective of LIFE REVAWASTE project (www.revawaste.eu), currently under development.

The results obtained from this study will provide fundamental information for scaling up a high-performance integrated mixed plant in the future. This model agrees with the rules established in the Directive 2008/98/EC, on waste, that promotes a new waste hierarchy as a priority order in waste prevention and management legislation and policy: prevention, re-use, recycling and final disposal.

Forest Integrated Wood Processing Plant

Another application of the rotary kiln pyroliser, is the use of this technology to improve the sustainability of forest plantations. So, rotary kiln pyroliser can be used to produce electricity and heat as well as biochar for soil application as fertiliser. A schematic diagram of this process is showed in (Figure 2).

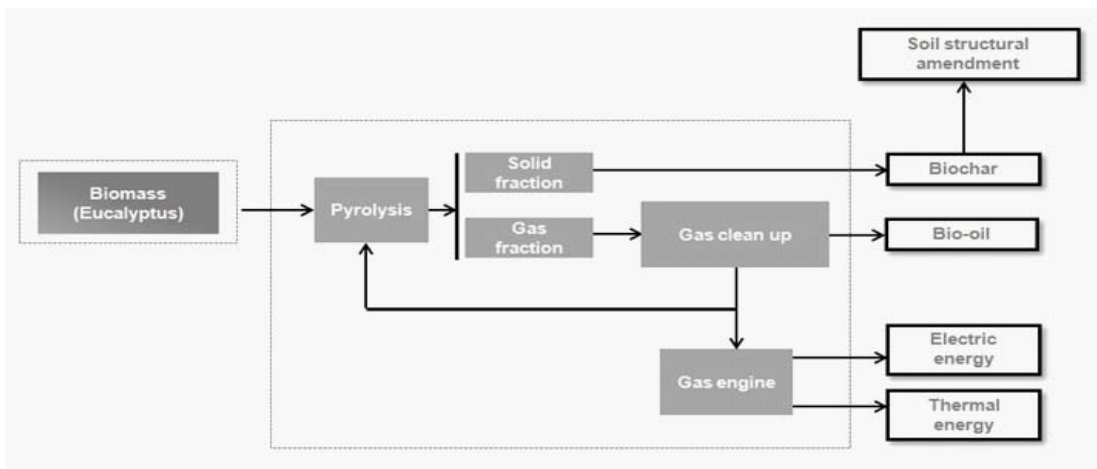


Figure 2: Schematic diagram of the “Forest Integrated Wood Processing Plant.”

An example of this kind of technology is the developed in the LIFE EUCALYPTUS ENERGY project (www.eucalyptusenergy.com).

Eucalyptus plantations in the north of Spain mainly produce trunks for cellulose extraction. Tree branches and leaves are left on the field and many times they are left behind or burned. This management burns the carbon content of the soils, promote soil erosion and increase the emission of pollutants. Frequently, these problems are incremented because the eucalyptus plantations are situated in fields with high slope. The use a rotary kiln pyrolyser fed with this kind of biomass waste can avoid these problems and produce value products.

CONCLUSIONS

The thermochemical conversion processes (combustion, pyrolysis, liquefaction and gasification) have all the capability of converting waste into value-added products like gaseous fuels, combustible oils and solids soils amendment, although catalyzed pyrolysis shows the better results from the technical, environmental and financial point of view.

ACKNOWLEDGMENTS

The authors gratefully acknowledge support of this work by the LIFE+ Program under the responsibility of the Directorate General for the Environment of the European Commission through the agreement LIFE 12 ENV/ES/000727-REVAWASTE project and LIFE 12 ENV/ES/000913-EUCALYPTUS ENERGY project.

References

1. Beede DN, Bloom DE. Economics of the generation and management of MSW, NBER Working Papers 5116, National Bureau of Economic Research, Inc. 1995.
2. USEPA. Municipal Solid Waste in the United States: 2000 Facts and Figures. Executive Summary, Office of solid waste management and emergency response (5305W), EPA530-S-02-001. 2002.
3. USEPA. Municipal Solid Waste in the United States: 2011 Facts and Figures. Executive summary, Office of solid waste management and emergency response (5306P), EPA530-R-13-001. 2013.

4. Basu P. Biomass gasification and pyrolysis. Practical design and theory. USA: Academic Press. Elsevier. 2010.
5. Saidur R, Abdelaziz EA, Demirbas A, Hossain MS, Mekhilef S. A review on biomass as a fuel for boilers. *Renewable and Sustainable Energy Reviews*. 2011; 15: 2262-2289.
6. Van Loo S, Koppejan J. The handbook of biomass combustion and co-firing. USA: Earthscan. 2007.
7. Van Kessel LBM, Arendsen ARJ, de Boer-Meulman PDM, Brem G. The effect of air preheating on the combustion of solid fuels on a grate. *Fuel*. 2004; 83: 1123-1131.
8. Zhao W, Li Z, Zhao G, Zhang F, Zhu Q. Effect of air preheating and fuel moisture on combustion characteristics of corn straw in a fixed bed. *Energy Conversion and Management*. 2008; 49: 3560-3565.
9. Patumsawad S, Cliffe KR. Experimental study on fluidised bed combustion of high moisture municipal solid waste. *Energy Conversion and Management*. 2002; 43: 2329-2340.
10. Yuntunwi EA, MacCarty N, Still D, Ertel J. Laboratory study of the effects of moisture content on heat transfer and combustion efficiency of three biomass cook stoves. *Energy for Sustainable Development*. 2008; 12: 66-77.
11. Biedermann F, Obernberger I. Ash-related problems during biomass combustion and possibilities for a sustainable ash utilization. In *Proceedings of the International Conference "World Renewable Energy Congress" (WREC)*, May 2005. Aberdeen: Elsevier. 2005.
12. Vassilev SV, Baxter D, Andersen LK, Vassileva CG. An overview of the composition and application of biomass ash. Part 1. Phase 1: mineral and chemical composition and classification. *Fuel*. 2013; 105: 40-76.
13. Vassilev SV, Baxter D, Andersen LK, Vassileva CG. An overview of the composition and application of biomass ash.: Part 2. Potential utilisation, technological and ecological advantages and challenges. *Fuel*. 2013; 105: 19-39.
14. Vamvuka D, Pitharoulis M, Alevizos G, Repouskou E, Pentari D. Ash effects during combustion of lignite/biomass blends in fluidized bed. *Renewable Energy*. 2009; 34: 2662-2671.
15. Ninduangdee P, Kuprianov VI. Combustion of palm kernel shell in a fluidized bed: Optimization of biomass particle size and operating conditions. *Energy Conversion and Management*. 2014.
16. Li J, Paul MC, Younger PL, Watson I, Hossain M, et al. Characterization of biomass combustion at high temperatures based on an upgraded single particle model. *Applied Energy*. 2015.
17. Baxter L. Biomass cofiring overview. In *2nd World Conference and Exhibition on Biomass for Energy, Industry and Climate Protection*. 2004.
18. Koppejan J. Introduction and overview of technologies applied worldwide. In *2nd World conference and Technology Exhibition on Biomass for Energy, Industry and Climate Protection*, Rome, Italy. 2004.
19. Baxter L. Biomass-coal co-combustion: opportunity for affordable renewable energy. *Fuel*. 2005; 84: 1295-1302.
20. Akhtar J, Saidina Amin N. A review on operating parameters for optimum liquid oil yield in biomass pyrolysis. *Renewable and Sustainable Energy Reviews*. 2012; 16: 5101-5109.
21. Bridgwater AV. Review of fast pyrolysis of biomass and product upgrading. *Biomass and Bioenergy*. 2012; 38: 68-94.
22. Amutio M, Lopez G, Artetxe M, Elordi G, Olazar M, et al. Influence of temperature on biomass pyrolysis in a conical spouted bed reactor. *Resources, Conservation and Recycling*. 2012; 59: 23-31.
23. Xiao R, Yang W. Influence of temperature on organic structure of biomass pyrolysis products. *Renewable Energy*. 2013; 50: 136-141.
24. Azargohar R, Jacobson KL, Powell EE, Dalai AK. Evaluation of properties of fast pyrolysis products obtained, from Canadian waste biomass. *Journal of Analytical and Applied Pyrolysis*. 2013; 104: 330-340.
25. Lapez A, De Marco I, Caballero BM, Laresgoiti MF, Adrados A. Influence of time and temperature on pyrolysis of plastic wastes in a semi-batch reactor. *Chemical Engineering Journal*. 2011; 173: 62-71.
26. Aysu T, M Maşuk Küçük. Biomass pyrolysis in a fixed-bed reactor: Effects of pyrolysis parameters on product yields and characterization of products. *Energy*. 2014; 64: 1002-1025.
27. Shen J, Wang XS, Garcia-Perez M, Mourant D, Rhodes MJ, et al. Effects of particle size on the fast pyrolysis of oil mallee woody biomass. *Fuel*. 2009; 88: 1810-1817.
28. Luo S, Xiao B, Hu Z, Liu S. Effect of particle size on pyrolysis of single-component municipal solid waste in fixed bed reactor. *International Journal of Hydrogen Energy*. 2010; 35: 93-97.
29. Ayşe E Pütün, Esin Apaydın and Ersan Pütün. Rice straw as a bio-oil source via pyrolysis and steam pyrolysis. *Energy*. 2004; 29: 2171-2180.

30. Sensöz S, Angin D . Pyrolysis of safflower (*Charthamus tinctorius* L.) seed press cake: part 1. The effects of pyrolysis parameters on the product yields. *Bioresour Technol.* 2008; 99: 5492-5497.
31. Greenhalf CE, Nowakowski DJ, Harms AB, Titiloye JO, Bridgwater AV. Sequential pyrolysis of willow SRC at low and high heating ratesâ€”Implications for selective pyrolysis. *Fuel.* 2012; 93: 692-702.
32. Aboulkas A, Makayssi T, Bilali L, Nadifiyine M, Benchanaa M. Co-pyrolysis of oil shale and plastics: Influence of pyrolysis parameters on the product yields. *Fuel Processing Technology.* 2012; 96: 209-213.
33. Williams PT, Besler S, Taylor DT. The pyrolysis of scrap automotive tyres: the influence of temperature and heating rate on product composition. *Fuel.* 1990; 69: 1474-1482.
34. Mastral AM, Murillo R, Callen MS, Garcia T, Snape CE. Influence of process variables on oils from tire pyrolysis and hydrolysis in a swept fixed bed reactor. *Energy & fuels.* 2000; 14: 739-744.
35. Encinar JM, Gonzlez JF. Pyrolysis of synthetic polymers and plastic wastes. Kinetic study. *Fuel Processing Technology.* 2008; 89: 678-686.
36. K El harfi, A Mokhlisse, M Ben Chana. Effect of water vapor on the pyrolysis of the Moroccan (Tarfaya) oil shale. *Journal of Analytical and Applied Pyrolysis.* 1999; 48: 65-76.
37. Senoz S, Angin D, Yorgun S. (2000). Influence of particle size on the pyrolysis of rapeseed (*Brassica napus* L.): fuel properties of bio-oil. *Biomass and Bioenergy.* 19: 271-279.
38. Piskorz J, Majerski P, Radlein D, Scott DS, Bridgwater AV. Fast pyrolysis of sweet sorghum and sweet sorghum bagasse. *Journal of Analytical and Applied Pyrolysis.* 1998; 46: 15-29.
39. Zanzi R, Sjoström K, Bjornbom E. Rapid pyrolysis of agricultural residues at high temperature. *Biomass and Bioenergy.* 2002; 23: 357-366.
40. Miao X, Wu Q, Yang C. Fast pyrolysis of microalgae to produce renewable fuels. *Journal of analytical and applied pyrolysis.* 2004; 71: 855-863.
41. Luo Z, Wang S, Liao Y, Zhou J, Gu Y, et al. Research on biomass fast pyrolysis for liquid fuel. *Biomass and Bioenergy.* 2004; 26: 455-462.
42. Ersan Pütun. Catalytic pyrolysis of biomass: effects of pyrolysis temperature, sweeping gas flow rate and MgO catalyst. *Energy.* 2010; 35: 2761-2766.
43. zen N, Kar Y. Pyrolysis of black cumin seed cake in a fixed-bed reactor. *Biomass and Bioenergy.* 2011; 35: 4297-4304.
44. Antal MJJ, Varhegyi G. Cellulose pyrolysis kinetics: the current state of knowledge. *Industrial & Engineering Chemistry Research.* 1995; 34: 703-717.
45. Richards GN, Zheng G. Influence of metal ions and of salts on products from pyrolysis of wood: applications to thermochemical processing of newsprint and biomass. *Journal of Analytical and Applied Pyrolysis.* 1991; 21: 133-146.
46. Raveendran K, Ganesh A, Khilar KC. Influence of mineral matter on biomass pyrolysis characteristics. *Fuel.* 1995; 74: 1812-1822.
47. Williams PT, Horne PA. The role of metal salts in the pyrolysis of biomass. *Renewable Energy.* 1994; 4: 1-13.
48. Yang H, Yan R, Chen H, Zheng C, Lee DH, et al. Influence of mineral matter on pyrolysis of palm oil wastes. *Combustion and flame.* 2006; 146: 605-611.
49. Burhenne L, Messmer J, Aicher T, Laborie MP. The effect of the biomass components lignin, cellulose and hemicellulose on TGA and fixed bed pyrolysis. *Journal of Analytical and Applied Pyrolysis.* 2013; 101: 177-184.
50. Demirbas A. Effect of initial moisture content on the yields of oily products from pyrolysis of biomass. *Journal of Analytical and Applied Pyrolysis.* 2004; 71: 803-815.
51. Oasmaa A, Czernik S. Fuel oil quality of biomass pyrolysis oils state of the art for the end users. *Energy & Fuels.* 1999; 13: 914-921.
52. Taarning E, Osmundsen CM, Yang X, Voss B, Andersen SI, et al. Zeolite-catalyzed biomass conversion to fuels and chemicals. *Energy & Environmental Science.* 2011; 4: 793-804.
53. Perego C, Bosetti A. Biomass to fuels: The role of zeolite and mesoporous materials. *Microporous and Mesoporous Materials.* 2011; 144: 28-39.
54. Samolada MC, Papafotica A, Vasalos IA. Catalyst evaluation for catalytic biomass pyrolysis. *Energy & Fuels.* 2000; 14: 1161-1167.
55. Lin Y, Zhang C, Zhang M, Zhang J. Deoxygenation of bio-oil during pyrolysis of biomass in the presence of CaO in a fluidized-bed reactor. *Energy & Fuels.* 2010; 24: 5686-5695.

56. Veses A, Aznar M, Martínez I, Martínez JD, López JM. Catalytic pyrolysis of wood biomass in an auger reactor using calcium-based catalysts. *Bioresour Technol.* 2014; 162: 250-258.
57. Bulushev DA, Ross JR. Catalysis for conversion of biomass to fuels via pyrolysis and gasification: a review. *Catalysis Today.* 2011; 171: 1-13.
58. Adrados A, De Marco I, Lopez-Urionabarrenechea A, Caballero BM, Laresgoiti MF. Pyrolysis behavior of different type of materials contained in the rejects of packaging waste sorting plants. *Waste Management.* 2013; 33: 52-59.
59. Adrados A, de Marco I, Caballero BM, López A, Laresgoiti MF. Pyrolysis of plastic packaging waste: A comparison of plastic residuals from material recovery facilities with simulated plastic waste. *Waste Manag.* 2012; 32: 826-832.
60. Sharma BK, Moser BR, Vermillion KE, Doll KM, Rajagopalan N. Production, characterization and fuel properties of alternative diesel fuel from pyrolysis of waste plastic grocery bags. *Fuel Processing Technology.* 2014; 122: 79-90.
61. Kim JS, Kaminsky W, Schlesselmann B. Pyrolysis of a fraction of mixed plastic wastes depleted in PVC. *Journal of analytical and applied pyrolysis.* 1997; 40: 365-372.
62. Quek A, Balasubramanian R. Liquefaction of waste tires by pyrolysis for oil and chemicals. A review. *Journal of Analytical and Applied Pyrolysis.* 2013; 101: 1-16.
63. MartÁñez JD, Murillo R, GarcÁa T, Arauzo I. Thermodynamic analysis for syngas production from volatiles released in waste tire pyrolysis. *Energy Conversion and Management.* 2014; 81: 338-353.
64. Choi GG, Jung SH, Oh SJ, Kim JS. Total utilization of waste tire rubber through pyrolysis to obtain oils and CO₂ activation of pyrolysis char. *Fuel Processing Technology.* 2014; 123: 57-64.
65. Brown R. *Biochar production technology.* 2009.
66. Vamvuka D. Bio-oil, solid and gaseous biofuels from biomass pyrolysis processes: An overview. *International Journal of Energy Research.* 2011; 35: 835-862.
67. Jahiril MI, Rasul MG, Chowdhury AA, Ashwath N. Biofuels production through biomass pyrolysis: a technological review. *Energies.* 2012; 5: 4952-5001.
68. Diebold J, Power A. Engineering aspects of the vortex pyrolysis reactor to produce primary pyrolysis oil vapors for use in resins and adhesives. In: *Research in Thermochemical Biomass Conversion.* Netherlands: Springer. 1988; 609-628.
69. Alauddin ZABZ, Lahijani P, Mohammadi M, Mohamed AR. Gasification of lignocellulosic biomass in fluidized beds for renewable energy development: A review. *Renewable and Sustainable Energy Reviews.* 2010; 14: 2852-2862.
70. Campoy M, Gmez-Barea A, Vidal F, Ollero P. Air steam gasification of biomass in a fluidised bed: process optimisation by enriched air. *Fuel Process Technology.* 2009; 90: 677-685.
71. Panopoulos K, Fryda L, Kakaras E. Atmospheric fluidized bed gasification of promising biomass fuels in southern European Regions. *Thermal Science.* 2007; 11: 5-15.
72. Schuster G, Löffler G, Weigl K, Hofbauer H. Biomass steam gasification—an extensive parametric modeling study. *Bioresour Technol.* 2001; 77: 71-79.
73. Grezin AK, Zakharov ND. Thermodynamic analysis of air separation equipment with a throttling refrigerating cycle. *Chemical and Petroleum Engineering.* 1988; 24: 223-227.
74. Su S, Li W, Bai Z, Xiang H. A preliminary study of a novel catalyst Al₂O₃· Na₂O· xH₂O/NaOH/Al (OH) ₃ for production of hydrogen and hydrogen-rich gas by steam gasification from cellulose. *International journal of hydrogen energy.* 2008; 33: 6947-6952.
75. Balu E, Lee U, Chung JN. High temperature steam gasification of woody biomass: A combined experimental and mathematical modeling approach. *International Journal of Hydrogen Energy.* 2015; 40: 14104-14115.
76. Lv PM, Xiong ZH, Chang J, Wu CZ, Chen Y. An experimental study on biomass air-steam gasification in a fluidized bed. *Bioresour Technol.* 2004; 95: 95-101.
77. Gai C, Dong Y. Experimental study on non-woody biomass gasification in a downdraft gasifier. *International Journal of Hydrogen Energy.* 2012; 37: 4935-4944.
78. Van den Eenden PJ, Silva Lora EB. Design approach for a biomass fed fluidized bed gasifier using the simulation software CSFB. *Biomass and Bioenergy.* 2004; 26: 281-287.
79. Zhang L, Xu CC, Champagne P. Overview of recent advances in thermochemical conversion of biomass. *Energy Conversion and Management.* 2010; 51: 969-982.
80. Savage PE. *Organic Chemical Reactions in Supercritical Water.* Chem Rev. 1999; 99: 603-622.
81. Jena U, Das KC, Kastner JR. Comparison of the effects of Na₂CO₃, Ca₃(PO₄)₂, and NiO catalysts on the thermochemical liquefaction of microalga *Spirulina platensis.* *Applied Energy.* 2012; 98: 368-375.

82. Yuan XZ, Li H, Zeng GM, Tong JY, Xie W. Sub-and supercritical liquefaction of rice straw in the presence of ethanol water and 2-propanol water mixture. *Energy*. 2007; 32: 2081-2088.
83. Sun P, Heng M, Sun S, Chen J. Direct liquefaction of paulownia in hot compressed water: Influence of catalysts. *Energy*. 2010; 35: 5421-5429.
84. Ye Y, Fan J, Chang J. Effect of reaction conditions on hydrothermal degradation of cornstalk lignin. *Journal of Analytical and Applied Pyrolysis*. 2012; 94: 190-195.
85. Shuping Z, Yulong W, Mingde Y, Kaleem I, Chun L, et al. Production and characterization of bio-oil from hydrothermal liquefaction of microalgae *Dunaliella tertiolecta* cake. *Energy*. 2010; 35: 5406-5411.
86. Yuan X, Wang J, Zeng G, Huang H, Pei X, et al. Comparative studies of thermochemical liquefaction characteristics of microalgae using different organic solvents. *Energy*. 2011; 36: 6406-6412.
87. Huang H, Yuan X, Zeng G, Wang J, Li H, et al. Thermochemical liquefaction characteristics of microalgae in sub-and supercritical ethanol. *Fuel Processing Technology*. 2011; 92: 147-153.
88. Xu C, Lancaster J. Conversion of secondary pulp/paper sludge powder to liquid oil products for energy recovery by direct liquefaction in hot-compressed water. *Water Res*. 2008; 42: 1571-1582.
89. Li H, Yuan X, Zeng G, Huang D, Huang H. The formation of bio-oil from sludge by deoxy-liquefaction in supercritical ethanol. *Bioresour Technol*. 2010; 101: 2860-2866.
90. Vardon DR, Sharma BK, Scott J, Yu G, Wang Z, et al. Chemical properties of biocrude oil from the hydrothermal liquefaction of *Spirulina* algae, swine manure, and digested anaerobic sludge. *Bioresource technology*. 2011; 102: 8295-8303.
91. Huang HJ, Yuan XZ, Zhu HN, Li H, Liu Y, et al. Comparative studies of thermochemical liquefaction characteristics of microalgae, lignocellulosic biomass and sewage sludge. *Energy*. 2013; 56: 52-60.
92. Brand S, Susanti RF, Kim SK, Lee HS, Kim J, et al. Supercritical ethanol as an enhanced medium for lignocellulosic biomass liquefaction: Influence of physical process parameters. *Energy*. 2013; 59: 173-182.
93. Yang Y, Gilbert A, Xu CC. Production of bio-crude from forestry waste by hydro-liquefaction in sub-/super-critical methanol. *AIChE Journal*. 2009; 55: 807-819.
94. Jena U, Das KC, Kastner JR. Effect of operating conditions of thermochemical liquefaction on biocrude production from *Spirulina platensis*. *Bioresour Technol*. 2011; 102: 6221-6229.
95. Chan YH, Yusup S, Quitain AT, Tan RR, Sasaki M, et al. Effect of process parameters on hydrothermal liquefaction of oil palm biomass for bio-oil production and its life cycle assessment. *Energy Conversion and Management*. 2015.
96. Behrendt F, Neubauer Y, Oevermann M, Wilmes B, Zobel N. Direct liquefaction of biomass. *Chemical engineering & technology*. 2008; 31: 667-677.
97. Xu C, Etcheverry T. Hydro-liquefaction of woody biomass in sub-and super-critical ethanol with iron-based catalysts. *Fuel*. 2008; 87: 335-345.
98. Qu Y, Wei X, Zhong C. Experimental study on the direct liquefaction of *Cunninghamia lanceolata* in water. *Energy*. 2003; 28: 597-606.
99. Yilgin M, Pehlivan D. Poplar wood water slurry liquefaction in the presence of formic acid catalyst. *Energy conversion and management*. 2004; 45: 2687-2696.
100. Chumpoo J, Prasassarakich P. Bio-oil from hydro-liquefaction of bagasse in supercritical ethanol. *Energy & Fuels*. 2010; 24: 2071-2077.
101. Chen Y, Wu Y, Zhang P, Hua D, Yang M. Direct liquefaction of *Dunaliella tertiolecta* for bio-oil in sub/supercritical ethanol-water. *Bioresour Technol*. 2012; 124: 190-198.
102. Singh R, Bhaskar T, Balagurumurthy B. Effect of solvent on the hydrothermal liquefaction of macro algae *Ulva fasciata*. *Process Safety and Environmental Protection*. 2014.
103. Ogi T, Yokoyama SY, Koguchi K. Direct liquefaction of wood by alkali and alkaline earth salt in an aqueous phase. *Chemistry letters*. 1985; 1199-1202.
104. Yang YF, Feng CP, Inamori Y, Maekawa T. Analysis of energy conversion characteristics in liquefaction of algae. *Resources, conservation and recycling*. 2004; 43: 21-33.
105. Ross AB, Biller P, Kubacki ML, Li H, Lea-Langton A, et al. Hydrothermal processing of microalgae using alkali and organic acids. *Fuel*. 2010; 89: 2234-2243.
106. Nazari L, Yuan Z, Souzauchi S, Ray MB, Xu CC. Hydrothermal liquefaction of woody biomass in hot-compressed water: Catalyst screening and comprehensive characterization of bio-crude oils. *Fuel*. 2015; 162: 74-83.

107. Goldman Y, Garti N, Sasson Y, Ginzburg BZ, Bloch MR. Conversion of halophilic algae into extractable oils. *Fuel*. 1980; 59: 181-184.
108. Duan P, Savage PE. Hydrothermal liquefaction of a microalga with heterogeneous catalysts. *Industrial & Engineering Chemistry Research*. 2010; 50: 52-61.
109. Matsui TO, Nishihara A, Ueda C, Ohtsuki M, Ikenaga NO, et al. Liquefaction of micro-algae with iron catalyst. *Fuel*. 1997; 76: 1043-1048.
110. Ikenaga NO, Ueda C, Matsui T, Ohtsuki M, Suzuki T. Co-liquefaction of micro algae with coal using coal liquefaction catalysts. *Energy & fuels*. 2001; 15: 350-355.
111. Toor SS, Rosendahl L, Rudolf A. Hydrothermal liquefaction of biomass: a review of subcritical water technologies. *Energy*. 2011; 36: 2328-2342.