Chapter 2
Recent Advances in the Catalytic Co-pyrolysis of Lignocellulosic Biomass and Different Polymer Wastes from Laboratory Scale to Pilot Plant

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Abstract Nowadays, it is generally accepted that the production of biofuels through the pyrolysis of lignocellulosic biomass may be an interesting alternative to fossil fuels. The appeal of this renewable resource is due to its worldwide availability and its environmentally friendly nature. The liquid fraction obtained from pyrolysis processes, bio-oil, is the most valuable product given its further application as biofuel, although it contains many oxygenated compounds and has a low heating value and high acidity, which hinders its direct application or even storage. To improve its quality, a dual strategy combining the two well-known upgrading approaches of cracking catalyst addition and waste plastics co-feeding has recently emerged as a promising solution since positive synergistic effects are achieved that are more suited to the production of upgraded biofuels. The upgrading reaction mechanism has mainly been associated with the presence of plastic wastes, which serve as H_2 donors to promote hydrocracking and hydrodeoxygenation catalytic reactions, and accordingly, highly significant results have been achieved using this dual strategy. This chapter discusses the most important of these results as reported in the literature obtained in facilities ranging from thermogravimetric reactors (technology readiness level (TRL) 2) to pilot plants in a relevant environment (TRL 5).

Keywords Biomass · Polymer wastes · Catalytic co-pyrolysis · Thermogravimetry · Laboratory scale · Pilot plants

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Abbreviations

CC	Catalytic Cracking
DAEM	Distribution activation energy model
FCC	Fluid Catalytic Cracking
GC-MS	Gas Chromatography –Mass Spectrometry
GS	Grape seeds
HDO	High Pressure Hydrodeoxygenation
HDPE	High Density Polyethylene
HHV	High Heating Value
LDPE	Low Density Polyethylene
PET	Polyethylene terephthalate
PLA	Polylactic acid
PP	Polypropylene
PS	Polystyrene
PUR	Polyurethane
PVC	Poly (vinyl chloride)
RSO	Rubber Seed Oil
TGA	Thermogravimetric Analysis
TRL	Technology readiness level
WT	Waste tire

2.1 Introduction

The use and extraction of fossil fuels, associated with high levels of greenhouse gas emissions [1, 2], come with a hugely negative environmental impact. They are the world's primary source of energy and owing to the high energy demand created by the economic and social development of contemporary society, fossil fuels are also becoming more costly. To counteract this, much scientific research is focused on the search for alternative fuels or energy sources that are more widely available, economic, and environmentally friendly. Great efforts have been made in recent decades to satisfy the need for a sustainable development strategy with the potential to reduce the environmental impact of energy production while favoring economic and social development. In this sense, the use of biomass as a feedstock is emerging as an attractive renewable energy resource [1, 3, 4]. Processing of biomass to produce fuels began in the late nineteenth century, although it was only at the end of the twentieth century that biomass started to be used as an energy resource. The growth, development, and expansion of these processes were closely related to the phenomenon of globalization. The surge in the use of biomass as an energy resource came after the oil crisis of 1973, a consequence of the global repercussions felt by the skyrocketing price of crude oil, particularly in countries without petroleum reserves. The use of lignocellulosic biomass has grown considerably in recent years as it represents an opportunity to obtain value-added products from a renewable source, with a significant reduction in environmental impact compared with the processing of fossil fuels. Furthermore, the use of this renewable energy source can advance the energy independence of non-oil-producing countries [5]. In particular, the use of residual lignocellulosic biomass from forestry and agricultural residues, among others, is considered to be of interest because it can be used as a raw material at a local and regional level, thus providing a potential market for by-products, generating employment, and contributing to the sustainable forest management. Finally, from an environmental perspective and when compared to fossil fuels, the use of lignocellulosic biomass represents a reduction in greenhouse gas emissions, due to its almost neutral character in CO_2 emissions.

For all these reasons, the use of lignocellulosic biomass in thermochemical processes such as pyrolysis, combustion, and gasification has achieved great importance in recent years. In particular, not only does pyrolysis provide an opportunity to obtain biofuels (liquid, solid or gas) and chemical products of reasonable quality from a renewable source, but a number of authors have also demonstrated that this process is more environmentally friendly. Consequently, the pyrolysis of lignocellulosic biomass is receiving renewed interest as it has the potential to become a viable option for transforming a great variety of waste materials such as industrial, agricultural, and forestry residues into value-added products in a profitable and decentralized manner [1, 6, 7]. Interestingly, the development of small-scale production units capable of efficiently processing a few tons of biomass per day could reduce the costs associated with handling and transporting biomass to the end user. In a pyrolysis process, the biomass is treated in a non-oxidizing atmosphere, usually at temperatures between 400 °C and 700 °C [4, 8]. As a result, three fractions are obtained: a solid fraction, also called biochar; a gas fraction, and a liquid fraction, also called bio-oil [3, 9, 10]. A general schematic of the pyrolysis mechanism involving the different endothermic and exothermic reactions of its main structural components (cellulose, hemicellulose, and lignin) using grape seed as biomass is shown in Fig. 2.1.

The origin of the lignocellulosic biomass strongly determines its characteristics and composition, and in turn, its behavior under pyrolysis conditions. Structurally, the basic composition of biomass is 25–50% cellulose, 15–40% hemicellulose, 10–40% lignin, 0–15% extractives, and a small fraction of inorganic minerals [11]. The relationship between the organic and inorganic components of the biomass depends on the environment in which it develops and the time at which it is harvested. These main components of biomass can be seen in Fig. 2.1.

It should be also noted that the physicochemical properties of the biomass (fixed carbon, volatile matter, moisture, and ash content), the type of reactor and its operating conditions (temperature, pressure, gas and vapor residence time, and heating rate) would also be factors that strongly influence product distribution [8, 12] after pyrolysis. Accordingly, ultimate and proximate analyses are common methods used to study biomass composition for further thermal processing. An example of the composition of two representative lignocellulosic biomasses (derived from forestry residues and agricultural residues) can be seen in Table 2.1. Volatile

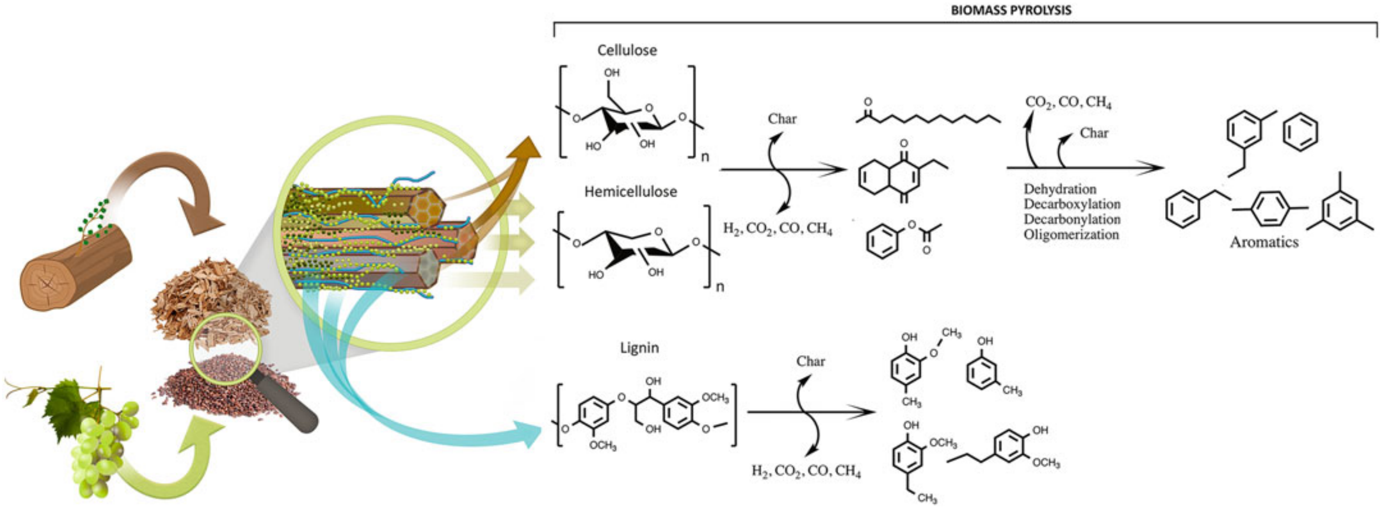

Fig. 2.1 Schematic of biomass pyrolysis

Table 2.1 Characterization of GS (grape seeds), Pine, PS (polystyrene), PP (polypropylene), HDPE (high density polyethylene), PET (polyethylene terephthalate), PLA (polylactic acid), and WT (waste tire) by ultimate and proximate analyses. All these samples came from waste sources (e. g., polystyrene from food packaging and polyethylene terephthalate from waste liquid containers) and were determined following standard methods

Properties	GS[a]	Pine[a]	PS[a]	PP[a]	HDPE[a]	PET[a]	PLA[a]	WT[a]
Proximate analysis (wt%)								
Moisture	6.3	6.3	0.5	0.2	0.1	0.4	0.4	1.1
Ash	4.6	0.5	0.1	0.1	0.0	0.1	0.0	3.8
Volatile matter	69.5	84.5	97.7	99.8	100.0	89.2	99.3	63.6
Fixed carbon	25.9	15.0	0.5	0.00	0.0	10.3	0.3	31.8
Ultimate analysis (wt%)								
C	57.6	52.5	90.3	85.4	85.5	62.7	51.1	87.9
H[b]	6.3	6.3	9.1	14.5	14.5	4.4	5.8	7.4
N	2.5	0.1	0.3	0.0	0.0	0.0	0.0	0.3
S	0.2	0.0	0.0	0.0	0.0	0.0	0.0	1.1
O[c]	33.4	41.2	0.3	0.0	0.0	32.8	44.0	3.3
HHV (MJ/kg)	23.5	20.6	42.1	43.1	43.1	22.2	17.2	38.6

Analyses performed at Instituto de Carboquímica

HHV Higher heating value

[a] Air-dried basis

[b] Hydrogen of moisture are contained

[c] Calculated by difference

matter is the fraction that is released as condensable and non-condensable organic compounds under pyrolysis conditions. Moisture is associated with the presence of physically and chemically bound water. The amount of moisture is a parameter that must be controlled since is closely related to the final quality of the bio-oil (values lower than 10 wt% are commonly considered acceptable for pyrolysis processes). Therefore, drying units should be integrated into pyrolysis installations, which increases the energy requirements of the full process. Ash is the inorganic residue resulting from the complete combustion of the biomass, which mainly comprises Na, K, Ca, Mg, Si, and Fe. It should be noted that ashes can affect the pyrolysis process and product distribution, given that this inorganic matter can act as a catalyst to reduce the liquid yield [12]. Finally, fixed carbon is the organic matter that remains after the moisture and volatile matter from the biomass have been devolatilized [13], becoming the predominant component of the solid product.

In relation to pyrolysis conditions, a very important variable in the pyrolysis process is temperature. The highest liquid yields are normally obtained in the range of 400–600 °C. Above 600 °C, the liquid yield decreases because bio-oil is converted into gas by secondary cracking reactions. Additionally, temperatures higher than 700 °C further decrease the yield in liquid products since formation of heavy polycyclic aromatic hydrocarbons (tars), which are deposited on the biochar surface, is also promoted as a result of both decarboxylation and dehydration reactions [3, 7, 8, 10]. Likewise, biomass particle size strongly influences heat transfer rate, and therefore the distribution of final products. Large particles lead to the presence of a large thermal gradient in the particle, so that longer solids residence times are needed to complete the devolatilization of biomass. Additionally, a slower devolatilization rate is achieved, decreasing vapor residence time, and therefore promoting secondary reactions through the increased contact time between primary vapors and hot char [12, 14]. Consequently, the use of biomass with large particle size reduces liquid production. Related to this, the residence time of volatiles inside the reactor is another parameter of considerable importance in a pyrolytic reaction. This parameter depends on the inert gas flow used to perform the pyrolysis process. A low inert gas flow leads to lower liquid yields caused by the promotion of cracking and retrogressive reactions, which increase the amount of both light gases and tars. Similarly, an increase in gas pressure could also lead to lower liquid yields since an increase occurs in the concentration of volatiles inside the reactor, favoring the presence of secondary reactions. A final key parameter in any pyrolysis process is heating rate. As in the case of large biomass particles, low heating rates increase the contact time between primary vapors and hot char, promoting secondary reactions and therefore leading to lower liquid yields. Both vapor residence time and heating rate also depend on the reactor design and will define the type of pyrolysis process. Generally, pyrolysis can be classified into three different types, referred to as slow pyrolysis, fast pyrolysis, and flash pyrolysis processes. The choice of the preferable option depends on the required product. Slow pyrolysis is focused on maximizing the solid product, whereas fast pyrolysis and flash pyrolysis maximize the liquid fraction, as can be seen in Table 2.2. At this point, it should be also highlighted that the liquids obtained from slow pyrolysis and fast/flash pyrolysis are remarkably different and cannot be processed in the same manner. For this reason, fast pyrolysis and bio-oil are carefully defined in standard specifications (ASTM D7544–12 (2017)).

The pyrolysis process has been studied in different types of reactors. At lower scales (TRL (technology readiness level) 2), the most widely used reactors are the thermogravimetric analyzer and the analytical pyrolyzer coupled with gas chromatography mass spectrometry (GC/MS) [16, 17]. At laboratory-scale (TRLs 3 and 4) the most prevalent are fixed-bed, autoclave, ablative, microwave, and entrained flow reactors. At higher scales, pilot plant or commercial plants, fluidized bed (circulating and bubbling), spouted bed, rotating cone, and auger reactors (single and twin) are the most prominent [7, 18]. In particular, fluidized bed, rotating cone, and auger

Table 2.2 Types of pyrolysis [3, 15]

	Slow	Fast	Flash
Yield	For biochar production. Low liquid yields (~30–35 wt%)	Liquid is the majority product (~50 wt%)	Higher liquid yields (up to 75 wt%)
Heating rate	0.1–1 °C/s	~100 °C/s	10–1000 °C/s
Residence time	>30 min	<2 s	>0.5 s
Temperature	300–700 °C	400–650 °C	800–1000 °C

reactors have the greatest commercial potential due to their robustness and attractiveness on the market [4]. Fluidized bed reactors have good temperature control and high heat transfer to biomass particles due to the high density of the solids [4]. However, biomass particles of small size are required for high heat transfer, necessitating additional pretreatment that significantly contributes to total operating costs. The system for operating rotating cone reactors can be considered similar, considering that the transport of sand and biomass is performed by means of centrifugal forces operating in a rotating cone. An advantage of their design is that intense mixing is possible without the use of an inert carrier gas, and the size of the equipment required downstream is minimal. On the other hand, auger reactors have a simple design, which allows their operation with low gas flows, and show high reproducibility and stability [19, 20]. A limiting factor for the scaling up the use of auger reactors is heat transfer owing to the use of external heating. Nevertheless, heating rates can be significantly improved by using sand, stainless steel beads, or even inexpensive minerals with catalytic properties, such as ilmenite, sepiolite, bentonite, attapulgite, calcite, and dolomite, as heat carrier materials [21, 22].

As previously explained, the pyrolysis of biomass produces three types of products: bio-oil, biochar and gas [3, 7]. The gas fraction has a low calorific value (8–9 MJ/m^3) [23] because it is basically composed of H_2, CO, CO_2, and light hydrocarbons (e.g., methane (CH_4) and ethane (C_2H_6)). Although this fraction can be easily used for energy generation, its application is basically limited to meeting the energy requirements of the actual process. Biochar is essentially the fixed carbon and ashes (mineral fraction) derived from the biomass [3], although if the secondary mechanisms of pyrolysis (cracking and polymerization) were to take place, part of the volatile matter from the biomass would also contribute to increasing the char fraction. The char has a relatively high caloric value (~30 MJ/kg) [24, 25], which makes this product attractive for gasification and combustion applications, even replacing coal for the generation of electricity. This fraction has a heating value equivalent to that of coal, with the advantage that the SOx and NOx emissions produced by its application as a fuel (by combustion) are lower than those produced by conventional mineral carbons [26]. In addition, its textural properties give it the potential for use as both as a natural fertilizer [27], contributing to fixed CO_2, and as a precursor for activated carbons [28]. At the commercial scale, its most common use is to supply the energy required by the pyrolysis process. Finally, bio-oil is considered the most valuable product as it can be used as a fuel or as precursor for chemicals. The bio-oils obtained from fast pyrolysis processes are dark brown, corrosive liquids that consist of polar organic compounds (ca. 75–80 wt%) and water (ca. 15–30 wt%). The chemical composition of bio-oils is very complex as they are made up of a mixture of more than 400 compounds, including carboxylic acids, alcohols, aldehydes, esters, ketones and aromatic species, certain polymeric carbohydrates, and lignin-derivative compounds. In addition, lignocellulosic biomass-derived bio-oils usually have a high H_2O content (15–30 wt%) and high density (in the range of 1.15–1.25 kg/m^3), and they may contain some solids in the form of fine char particles and ash (in the range of 0.1–1 wt%). Bio-oils have a high oxygen content (35–40 wt%), which, together with its acidity, (pH 2.5–3.5) makes it corrosive and also accelerates its degradation (increased viscosity) by polymerization and oligomerization reactions, leading to difficulties during storage and transport [11]. Furthermore, its higher heating value (~15–20 MJ/kg) is generally less than half of that of mineral oils (~40 MJ/kg) [3, 29, 30] and, unfortunately, bio-oils and mineral oils are not miscible.

The point should be made at this stage that the application of bio-oils is basically limited to the substitution of heavy fuel oils in boilers [29, 31, 32]. It is of note, however, that very interesting research is underway focusing on long-duration experiments and accurate analytical test methods to allow the standardization of fast pyrolysis bio-oils as a fuel, paving the way towards the future marketing of this product. Nonetheless, the poor properties shown by bio-oil as a fuel and all the negative issues associated with its use have led to the conclusion that bio-oil quality should be improved by different upgrading strategies before it can be efficiently used as a transportation fuel or source of high-value chemical products. For this reason, a number of promising strategies have been postulated in recent decades to improve bio-oil properties. These upgrading strategies are generally based on physical treatments (such as the removal of light volatiles with acids, solvent addition, fractionation, and filtration of hot vapors) and chemical treatments (such as esterification, catalytic pyrolysis and co-pyrolysis, and co-processing of bio-oil in fluid catalytic cracking facilities). In general, chemical upgrading methods can be divided in two groups [15, 33, 34]: (i) ex situ (those produced after the pyrolysis process, where there is no contact between the biomass and catalyst), and (ii) in situ (those produced during the pyrolysis process itself, where the biomass and catalysts are in contact). Both strategies can be adapted to existing pyrolysis systems [11, 32, 34, 35]. Within the ex-situ strategies, we would highlight high pressure hydrodeoxygenation (HDO) [10, 36] and catalytic cracking (CC) [10, 36]. HDO is a complicated process that requires complex equipment, a high-performance catalyst, and pressurized H_2. This route leads to the partial deoxygenation of the bio-oil by the elimination of water molecules and the CO_2 generated by C–O bond breakage [12]. On the other hand, CC is a process in which high-molecular-weight molecules are broken down into low-molecular weight molecules, with the removal of the oxygen in the bio-oil components, such as water, CO, and CO_2. This upgrading process is usually performed in either fixed or fluidized bed reactors, and it also makes use of high-performance catalysts (usually tailor-made zeolites) [10]. This CC is based on the fluid catalytic cracking (FCC) process designed for the oil refining industry, which is an essential part of the refining process, transforming heavy crude oil into light compounds, including liquefied petroleum gas (LPG) and transportation fuels. In the FCC process, specific zeolite-based catalysts have demonstrated to be highly efficient. Unfortunately, FCC catalysts have shown a limited performance for the ex situ upgrading of bio-oils, mainly due to their fast deactivation and limited regeneration. Therefore, new tailor-made catalysts should be developed for bio-oil upgrading purposes [37, 38].

In-situ strategies require lower capital investment and offer better technical benefits than ex-situ ones, given that higher efficiencies can be achieved. The most popular in-situ upgrading strategy is catalytic pyrolysis, where the biomass devolatilization process is performed in the presence of a catalyst [15, 32, 34]. A lower quantity of liquid product (~50 wt%) is usually obtained in a catalytic pyrolysis process, but a good choice of catalyst allows improved bio-oils to be obtained. A pyrolytic liquid obtained by catalytic upgrading usually has two differentiated phases: an aqueous phase, which comprises mainly water, polysaccharides, organic acids, hydroxyacetone, hydroxyacetaldehyde, furfural, and small amounts of guaiacols [39]; and an organic phase, which comprises oxygenated compounds (organic acids, aldehydes, ketones, alcohols, esters, furans, sugar derivatives, and phenols, among others) [28, 29] and aliphatic and aromatic hydrocarbons [40]. These two phases are easily separable, thus enabling valuable products to be obtained from both phases and the economy of the process to be improved. As an example, different industrial chemicals, including acids, levoglucosan, hydroxyacetaldehyde, and furfural, can be recovered by solvent extraction of the water phase. Moreover, catalytic steam reforming of the aqueous fraction is also considered a potential route for renewable H_2 production. As the different routes for application of the aqueous phase are not the aim of this work, more information can be found in the following references [41–43]. On the other hand, the organic phase could be used as a low-quality biofuel for boilers or as source of chemical products. However, as in the case of raw bio-oils from conventional fast pyrolysis processes, a significant amount of oxygenated compounds remain and cause many of its negative properties, such as low heating value, high corrosiveness, high viscosity, and instability. All these issues greatly limit its further application, particularly as a transportation fuel. Therefore, the introduction of further improvement processes is strongly advised.

The catalytic pyrolysis process is not only affected by the same factors that condition fast pyrolysis (reaction temperature, gas and solids residence time, heating rate, physicochemical properties of the biomass, type of reactor) but also by those of biomass-to-catalyst ratio and type of catalyst, which should be selected following certain guidelines [44]: high activity in the production of non-oxygenated compounds; resistance to deactivation due to coking, sintering, or fouling; stability and reusability; mechanical strength; low cost; and wide availability. As a result, current research is focused on the search for new catalysts that are able to meet these criteria. Despite this, the most widely studied catalysts for this process are zeolites, which are costly materials that present an important problem of deactivation resulting from coke deposition in the active sites [45]. Although a thermal regeneration of the zeolites can be postulated by ex-situ calcination together with biochar, as already performed in FCC processes, deactivation by ash deposition (from the inorganic content of biomass), in addition to their hydrothermal instability at high temperature, prevents the feasible regeneration of their catalytic properties. An interesting alternative to the use of zeolites could be readily available natural minerals or commercially available metal oxides. This line of research has studied different types of low-cost materials with relative success, including the use of different metal oxides, such as MgO, ZnO, NiO, Fe_2O_3, and TiO_2 [46–50], and different low-cost minerals, such as sepiolite, bentonite, attapulgite, ilmenite, calcite, and dolomite [22, 51–53]. While acid catalysts, such as bentonite, promote bio-oil deoxygenation and aromatization through the Diels–Alder reaction and hydrocarbon pool mechanism, basic catalysts, such as MgO, calcite, and dolomite, can promote bio-oil deoxygenation through ketonization, aldol condensation, and hydrogen transfer reactions, thus minimizing acidity while enhancing light hydrocarbon components. In summary, the use of low-cost materials has also demonstrated notable improvements in the physicochemical properties of the organic fraction resulting in a bio-oil with lower acidity, lower O_2 content, and increased higher heating value, proving the potential of this type of materials. Finally, it should be added that the biomass-to-catalyst ratio is another important factor in a catalytic pyrolysis process because optimum contact between both materials must be ensured. While a high biomass-to-catalyst ratio could promote excessive cracking reactions that lead to the formation of heavy polycyclic aromatic compounds, an insufficient biomass-to-catalyst ratio would hardly improve the quality of the liquids [48, 50, 51].

Another in-situ upgrading strategy that has been receiving special attention in recent decades is the incorporation of oxygen-free materials, such as waste polymers, into the biomass pyrolysis process. It is well known that the demand for polymers is increasing every year owing to their use in different applications, such as toys, cars, packaging, electronics, and a wide variety of others. This demand has also led to an increase in the amount of waste leftover from these applications. Plastic waste consists mainly of high-density polyethylene (HDPE), low-density polyethylene (LDPE), polyethylene terephthalate (PET), polypropylene (PP), polystyrene (PS), polyurethane (PUR), and polyvinyl chloride (PVC). The structures of the different polymer repeating units can be seen in Fig. 2.2. The utilization of these type of waste materials is of great interest, for example, about 17.8 million metric tons of end-of-life plastics were collected for treatment in Europe in 2018, of which 42% were recycled, 39.5% were used for energy recovery, and 18.5% ended up in landfills [54, 55]. This represents a huge environmental problem because of their non-degradable nature; their potential health risks to water, land, and animals; and their impact on environmental pollution. Furthermore, it has recently been reported that end-of-life plastics that are not recycled will be subject to higher taxes. In response to this problem, different solutions have been proposed for the management of plastic waste, such as incineration and mechanical recycling [56]. Because incineration negatively contributes to pollution through harmful and toxic emissions, other alternatives need to be developed. On the other hand, the main drawbacks of mechanical recycling are its high economic costs and the low quality of the final products when pure streams are not used, emphasizing the key role to be played by advanced pretreatment sorting and cleaning processes for efficient mechanical recycling.

The global challenges for sustainable development in relation to plastic waste management, clean energy, and efficient use of resources can be simultaneously addressed by the production of high-value liquids by the pyrolysis of polymer wastes. Unlike biofuels, these liquids can have fuel properties similar to those of fossil fuels, particularly for the pyrolysis of polyolefins [57], where the absence of oxygen, together with their high carbon and hydrogen content, does away with the need for further improvement processes [58]. Compared to lignocellulosic biomass,

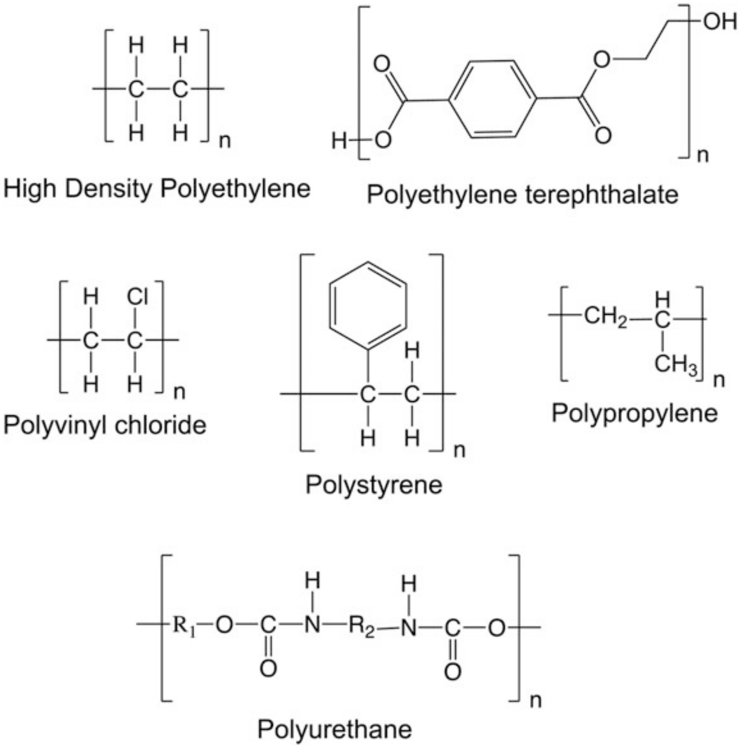

Fig. 2.2 Structures of the different polymer repeating units

see Table 2.1, the oxygen content in waste polymer materials can be considered negligible, with the exception of PET and biopolymers such as PLA. Additionally, synthetic waste polymers present a higher content in carbon (60–90 wt%) and hydrogen (4.5–14.5 wt%), achieving higher heating values (40 MJ/kg). Again as an exception, PLA and PET have a chemical composition similar to that of biomass. Therefore, there is potential to produce high-quality liquid oils with high calorific value and rich in compounds compatible with standard fuels by the pyrolysis of these polymers [57, 58]. In a similar way to biomass pyrolysis, waste plastics are heat-treated at temperatures ranging between 500 °C and 700 °C [59]. During the pyrolysis of waste plastics, devolatilization takes place through radical mechanisms (initiation, propagation, and termination), leading to a high liquid yield (higher than 80 wt% for PS and polyolefins). Obviously, catalytic pyrolysis processes have been also studied for waste polymers, for which zeolites are again the most commonly used catalysts. Under these pyrolysis conditions, higher yields to aromatic-rich oils are usually obtained, likely related to the fact that zeolites significantly promote the cracking of large aliphatic and olefin molecules and their further aromatization [60].

At this point, we would like to remark that liquids obtained from the pyrolysis of biomass and waste plastic are completely immiscible owing to their different polarity (polar for biomass and nonpolar for polymer). Therefore, a simple blending strategy for the upgrading of bio-oil characteristics is not viable. However, a co-pyrolysis strategy for the formation of a new, upgraded bio-oil through the interaction of the radicals released by both feedstocks does seem to be a potential solution and can be seen as a promising in-situ upgrading approach to enhance both the efficiency of the process and the properties of bio-oil as fuel. At the same time, the addition of waste plastics to biomass pyrolysis processes would also not only contribute to mitigate their accumulation in the marine environment, or even in landfills, where they are a source of greenhouse gas emissions [10], but could also contribute to reducing processing costs and solve problems related to biomass availability. Interestingly, this initial hypothesis has been already demonstrated in several studies [61–63] that show the co-feeding of plastic wastes with biomass significantly improve the quality of pyrolytic oils. Bio-oil upgrading using this strategy was reflected in the formation of an organic fraction with improved properties (lower oxygen content and higher in value-added compounds, mainly cyclic hydrocarbons and aromatics) and a higher calorific value [57]. The upgrading mechanism was associated with the fact that waste plastics could act as hydrogen donors to enhance hydrodeoxygenation and hydrocracking reactions [61–63]. Accordingly, Brebu et al. [64] found that the addition of PS, LDPE, and PP to the pyrolysis of pine sawdust (1:1 weight ratio) in a fixed bed reactor at 500 °C produced a higher amount of bio-oil with lower oxygen content and a remarkable higher calorific value. Suriapparao et al. [65] recently studied the addition of PS to five different types of biomass (peanut shells, bagasse, rice husk, *Prosopis juliflora*, and mixed wood sawdust) in a microwave reactor. They found that a co-pyrolysis approach led to higher yields of an aromatic-rich bio-oil with a high calorific value (38–42 MJ /kg^{-1}), particularly when using sawdust and rice husk. They also found that bio-oil viscosity was remarkably lower than that obtained by the conventional fast pyrolysis of biomass. Finally, Akancha et al. [66] investigated the co-pyrolysis of rice bran wax and PP in a semi–batch reactor. They also found that not only higher liquid yields were obtained (using a 1:3 blend of PP and biomass) but also higher aliphatic compounds were found in the final liquid, thus improving its quality. Although different mixtures have been successfully studied in co-pyrolysis processes, as can be seen in Table 2.3, the selection of feedstock components is also an important factor as both raw materials should be devolatilized in the same temperature range under process conditions [10]. Further tools for the proper selection of feedstock components in a catalytic co-pyrolysis process will be provided in this chapter.

As could be expected, the use of a reasonable ratio of both feedstocks also plays a crucial role in the catalytic co-pyrolysis process from the sustainability and technical perspectives [67, 68], meaning that it is another parameter to be optimized. As an example of the importance of the biomass-to-plastic waste ratio, Stančin et al. [68] observed that although a high sawdust-to-PS ratio (25/75 wt%) led to higher liquid yields, these conditions generated a larger amount of polycyclic aromatic hydrocarbons (PAHs) [68]. These compounds are considered hazardous to health and harmful to the environment, thus limiting further bio-oil applications. Likewise, special attention should be paid to the use of high proportions of polymers with a significant

Table 2.3 Some representative studies of biomass/plastics co-pyrolysis

Biomass	Polymer	Biomass/ polymer ratio	T (°C)	Scale	Reactor	Reference
Pine woodchips	WT	90/10 80/20	500	Laboratory Demonstration	Fixed bed Auger	[67]
Sawdust	PS	75/25 50/50 25/75	600	Laboratory	Stainless steel fixed reactor	[68]
Palm shells	PS	50/50	500	Laboratory	Fixed bed	[70]
Karanja and niger seeds	PS	50/50	500	Laboratory	Stainless steel semi-batch operation	[62]
Palm shells	Truck tires	25/75	500	Laboratory	Fixed bed	[63]

content in certain heteroatoms (e.g., sulfur and chlorine), since their thermal decomposition could lead to the formation of compounds that pose a risk to human health (dioxins formation from PVC pyrolysis) [69]. Therefore, although the quality of bio-oil could be remarkably improved by co-pyrolysis, there are still some crucial points to be resolved.

Against this background, a dual upgrading strategy involving the simultaneous incorporation of catalyst and waste plastics into the biomass pyrolysis process has recently emerged as a very promising approach for the production of upgraded bio-oils in a relatively simple one-step process, enabling some of the previously described problems observed in the conventional fast pyrolysis, catalytic pyrolysis, and co-pyrolysis processes to be solved. This statement is supported by the increasing number of articles regarding this process published in the last 10 years, as shown in Fig. 2.3, in which catalytic co-pyrolysis processes for the production of high-quality biofuels have been widely studied. The following sections of this chapter will present a critical overview of the field of the catalytic co-pyrolysis of biomass with waste polymers in facilities ranging from bench and laboratory scale (thermogravimetric analysis and lab-scale reactors) to pilot scale, providing insights into the potential of this technology for the production of high quality bio-oils in a single-stage process. We will show, with some representative examples carried out in our research group, how a proper selection of process conditions and feedstocks could facilitate the direct integration of catalytic co-pyrolysis bio-oils in the energy market as drop-in fuels. The use of drop-in fuels would increase the potential market for this product as a fuel that is fully interchangeable and compatible with conventional fossil fuels. This is advantageous because no costly adaptation of the fuel distribution network would be required.

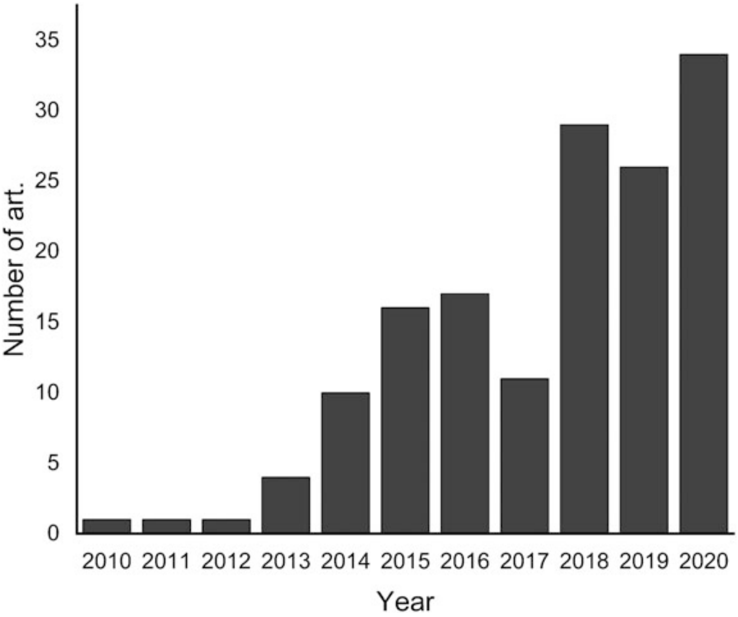

Fig. 2.3 Evolution of the number of articles on catalytic co-pyrolysis in the last 10 years. Articles found in Scopus using the keywords "catalytic co-pyrolysis biomass"

2.2 Recent Advances in the Catalytic Co-Pyrolysis Process

The potential of catalytic co-pyrolysis processes for the production of high-quality bio-oils has been addressed by several authors. It is generally accepted that the main process parameters, such as temperature, heating rate, and gas and vapor residence time, together with the selection of an optimum ratio between biomass, waste polymer and catalyst, are crucial and must be carefully studied from laboratory scale to pilot plant facilities, paving the way toward the development of commercial catalytic co-pyrolysis processes. In accordance, this overview has been divided into three different sections, depending on the technology readiness level (TRL) used [71–73], hopefully providing the reader with the appropriate tools for the development of catalytic co-pyrolysis processes able to produce high-quality bio-oils.

2.2.1 TRL 2: Bench-Scale Experiments in Microreactors

A useful tool for analyzing the first insights at TRL 2 of any catalytic co-pyrolysis process is thermogravimetric analysis (TGA), which is an effective study to identify the potential of any biomass/waste plastic/catalyst mixture. It should be pointed out, that although this technique is limited to micro scales, it is a simple, inexpensive, and effective way to obtain useful data regarding the potential of the process. Accordingly, numerous research groups have conducted TGA studies to determine the thermal behavior of different materials, such as biomass, plastic wastes, and their mixtures [16, 74–76]. This characterization technique determines the percentage of mass loss of any material during heating and, in turn, its behavior during the pyrolysis (devolatilization) process. Additionally, TGA is a very useful system to determine the pyrolysis kinetic parameters under isothermal and non-isothermal conditions. It is interesting to highlight that the TGA of lignocellulosic biomass generally shows two ranges of decomposition that are linked with their main constituents: 150–350 °C for the decomposition of cellulose and hemicellulose, and 250–500 °C for lignin decomposition. However, this technique may present several limitations when using heterogeneous samples such as municipal solid waste [77], which contains numerous components including cellulose, hemicellulose, lignin, PE, PP, PVC, and PET, whose correct identification can be limited due to the overlapping of the devolatilization curves. As a guideline, however, it can be considered that in the form of individual components, cellulose degrades at the temperature range of 260–400 °C, lignin at 150–750 °C, PVC at 250–550 °C [77], PP at 400–500 °C [77], PET at 375–500 °C [77], PE at 450–550 °C [77], PLA at 315–375 °C [78], PS at 300–500 °C [79], and WT at 450–550 °C [80]. Interestingly, devolatilization profiles of the isolated components show that there is an operational window where some of these feedstocks are simultaneously devolatilized, and their devolatilization could therefore lead to interactions between the released compounds under co-pyrolysis conditions.

In line with this, as can be seen in Fig. 2.4, the first insights obtained by our group [81] using TGA studies applied to individual compounds already evidenced that the devolatilization of lignocellulosic biomass and waste polymers, such as HDPE, PP,

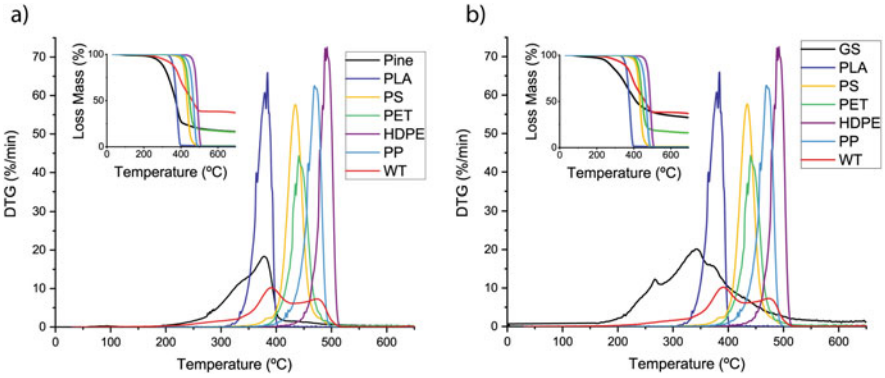

Fig. 2.4 Experimental TGA (insets) and derivative thermogravimetry (DTG) curves at 20 °C/min heating rate for (**a**) pine wood and plastic wastes (PLA (polylactic acid), PS (polystyrene), PET (polyethylene terephthalate), PP (polypropylene), HDPE (high-density polyethylene), WT (waste tire)), (**b**) grape seeds (GS) and plastic wastes

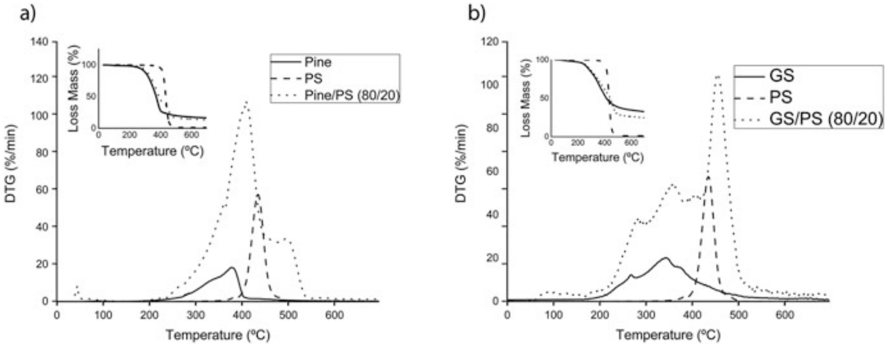

Fig. 2.5 TGA and DTG curves at 20 °C/min heating rate during co-pyrolysis of: (**a**) pine/PS (80/20), (**b**) TGA and DTG of co-pyrolysis of GS/PS (80/20)

PET, PS, PLA and WT, partially coincide within a common temperature range, and therefore potential interactions between the radicals released during the pyrolysis process could be taking place [16]. However, while a broad operational window is observed in the case of some waste plastics, such as WT, PLA, and PS, this zone is quite limited in the case of PET and polyolefins (Fig. 2.4). Very interesting results were found when experimental TGA profiles of lignocellulosic biomass/PS mixtures (Fig. 2.5) were compared to calculated profiles obtained from the sum of the individual components. Thus, it was observed that while the devolatilization of the biomass component in the mixture is highly comparable to that predicted by the individual samples, a slower decomposition rate was clearly observed for PS devolatilization, which seems to be related to the presence of biomass char preventing PS depolymerization while promoting intermolecular hydrogen-transfer reactions. Additionally, it was observed that a temperature about 600 °C could be adequate to achieve the full conversion of both feedstocks.

The co-pyrolysis of biomass with polymer-type residues using TGA has been also studied by other authors [62, 79, 80]. In line with our results, Hameed et al. [82] studied the thermal behavior of biomass and different feedstocks such as sludge, coal, and plastics. They also demonstrated that the presence of a common area where volatiles could coexist, eventually leading to interactions between the radicals released from these materials. Furthermore, Akancha et al. determined optimal reaction parameters by TGA in order to obtain maximum conversion in the co-pyrolysis of rice bran and PP [66]. Different reaction parameters were studied, such as temperature, heating rate, and the proportion of each material in the mixture, concluding that 550 °C and a biomass-to-waste plastic ratio of 1:3 were the optimum pyrolysis process conditions. Similarly, Alam et al. [83] studied the devolatilization of sawdust bamboo and LDPE. Significantly, they proposed that there could be radical interactions between those volatiles released from both feedstocks, and that the interactions would be enhanced at high waste plastic-to-biomass ratios. While cellulose and hemicellulose devolatilization was not significantly modified by the presence of LDPE, it was observed that the radicals released during LDPE devolatilization could boost lignin decomposition at temperatures ranging between 380 °C and 520 °C. Finally, Önal et al. [84] also used TGA to define the optimum temperature for the co-pyrolysis of almond shells and HDPE, ensuring the full conversion of both feedstocks at 550 °C.

The downside of all those interesting works on TGA is that they were only able to provide data on devolatilization under slow or moderate pyrolysis conditions because heating rates higher than 200 °C/min are not feasible. Interestingly, this issue could be solved by applying a kinetic model to the TGA data. Kinetic parameters, such as activation energy (Ea) and the pre-exponential factor (A), can be obtained by means of different fitting models, including the one-step global model based on the model-fitting method, global model based on the model-free method, multi-step successive model, semi-global model, distribution activation energy model (DAEM), and molecular modeling [85]. Although kinetic modeling is beyond the scope of this chapter, detailed literature can be found in the following references [85–92]. Among them, DAEM is the most widely used method to determine the kinetics of the pyrolysis process as a first stage leading to the design of the pyrolysis reactor. In this regard, very interesting results were reported by our research group [81] when conducting a kinetic study of the co-pyrolysis of lignocellulosic and different polymer wastes. In particular, forestry (pine woodchips) and agricultural (grape seeds) residues were selected as lignocellulosic biomass samples. Additionally, six different polymers were introduced into the feed for their further analysis (PLA, PS, PET, PP, HDPE and WT). It was interesting to observe that a higher process temperature than that initially foreseen from the experimental TGA data (100 °C/min) should be used to ensure the full conversion of both feedstocks under realistic fast pyrolysis conditions (1000 °C/min). Therefore, it can be concluded that DAEM could be a very useful tool to predict the behavior of biomass/waste plastic mixtures under true fast co-pyrolysis process conditions, which cannot be experimentally obtained by TGA.

TGA was also used to identify the role of different catalysts in the devolatilization of single biomass [93–95] and plastic wastes, as a further step toward the study of biomass/waste plastic/catalyst mixtures [96, 97]. An interesting example of the biomass catalytic pyrolysis using TGA was shown by Nishu et al. [95], who studied the catalytic pyrolysis of cellulose extracted from rice straw using alkali-modified zeolite as the catalyst. The biomass-to-catalyst ratio used was 1:4. Remarkably, the use of catalysts slightly decreased the temperature needed for the full devolatilization of the rice straw. Along similar lines, Lei et al. [93] studied the thermal decomposition of cellulose in the presence of nickel dispersed on HZSM-5 zeolite. They concluded that the presence of nickel also reduced cellulose devolatilization temperature. However, they observed that the devolatilization rate was slowed down by the formation of coke on the catalyst surface. On the other hand, the catalytic pyrolysis of waste plastics was studied by Durmuş et al. [96], who studied the thermal decomposition of PP using Beta, Mordenite, and ZSM-5 zeolites as catalysts. As was found for cellulose, they demonstrated that the presence of zeolite in the process also decreased the temperature for PP devolatilization and that there was

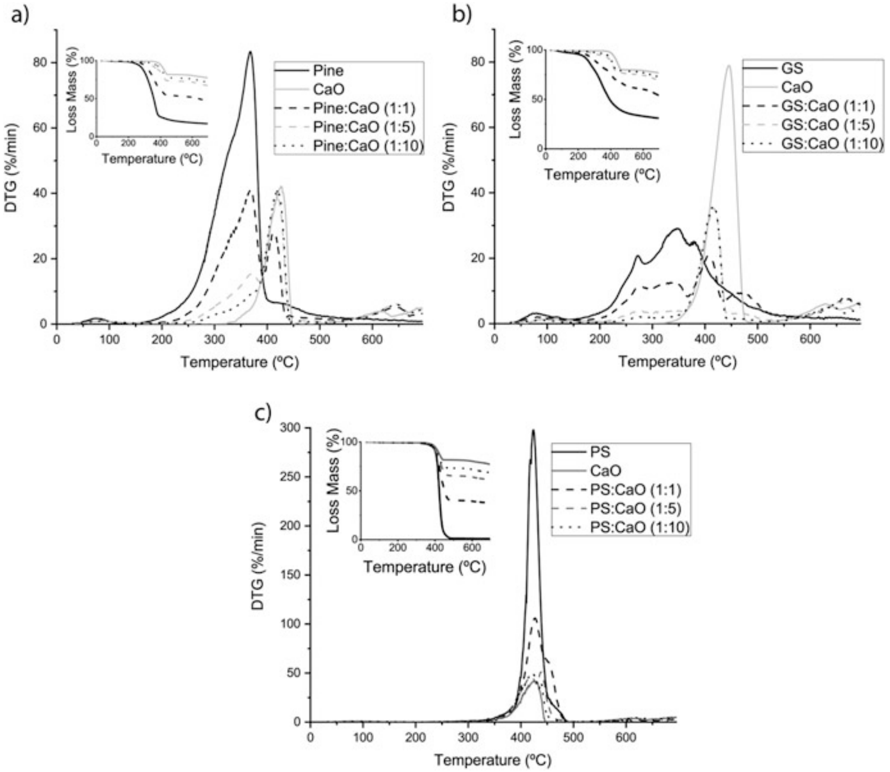

Fig. 2.6 TGA and DTG curves showing the effect of the catalyst amount on the catalytic pyrolysis of: (**a**) pine woodchips, (**b**) GS, (**c**) PS

a lower loss of mass resulting from the accumulation of coke on the surface and in the pores of the zeolites. Similarly, our research group studied the effect of CaO addition on the devolatilization of both lignocellulosic biomass and waste plastics. In this case, grape seeds and pine woodchips were selected as biomass representatives, while PS was chosen as the candidate for plastic waste. Fig. 2.6 shows the TGA and derivative thermogravimetric (DTG) curves. It can be observed that the dehydration and decarboxylation reactions of the biomass volatiles seem to have been promoted by CaO at temperatures higher than 350 °C. Interestingly, the catalytic role of CaO was not limited to these deoxygenation reactions since it was also observed that CaO could be also promoting the cracking of intermediate liquid tar to produce gas at high temperature, given that a decomposition rate higher than that theoretically expected is obtained at 400–450 °C and 450–550 °C for the pine woodchips and GS, respectively. As expected, both reactions were enhanced at a higher catalyst-to-biomass ratio. It is worth mentioning that catalyst-to-biomass ratio is a key parameter that also needs to be carefully evaluated at a higher TRL since an overbalanced cracking of the volatiles could lead to the formation of heavy tars and light gases instead of upgraded bio-oil. With this premise, we also performed TGA on PS/CaO mixtures. We observed that CaO leads to a slight decrease in the PS decomposition rate, likely related to the addition of CaO promoting intermolecular hydrogen transfer reactions instead of supporting the PS depolymerization process through intramolecular hydrogen-transfer reactions.

Once the role of the different agents in the catalytic co-pyrolysis process was identified, the performance of biomass/waste plastic/catalyst mixtures could be studied by TGA. We would like to point out that the amount of data published in the literature is somewhat limited, although there are several works of interest to be found. As an example, Kim Y. M. et al. [98] studied two types of catalysts (microporous (HZSM-5) and mesoporous (Al-MCM-41)) in the catalytic co-pyrolysis of yellow poplar and HDPE. They showed that a large quantity of HZSM-5 catalyst (10/1) significantly reduced the temperature of HDPE decomposition so that yellow poplar and HDPE devolatilization overlapped at the range of 350–450 °C, whereas their simultaneous decomposition could not be observed without the catalyst. Similar results were found by Zhang et al. [75] for the catalytic co-pyrolysis of Douglas fir sawdust and LDPE using ZSM-5 as catalyst. These authors also observed that the addition of catalyst decreased the decomposition temperature of the biomass/plastic mixture, shifting the peak corresponding to LDPE devolatilization to lower temperatures [99]. Likewise, we recently studied the thermal devolatilization of different biomass/waste plastic mixtures using CaO as catalyst, where both pine woodchips or grape seeds were selected as lignocellulosic biomass samples and PS as waste plastic, the results of which can be found in Fig. 2.7. Regardless of the biomass/waste plastic mixture, TGA data showed that the addition of CaO only changed the devolatilization profile of those peaks related to biomass decomposition (either pine woodchips or grape seeds). At temperatures higher than 350 °C, CaO seemed to be promoting dehydration and decarboxylation reactions in the hemicellulose and cellulose components of the biomass. This effect was more apparent in the GS/PS/CaO mixtures. These results were in line with those found during biomass/CaO devolatilization, as previously mentioned. Nonetheless, it should be noted that there was only a marginal shift in the main peak to a lower

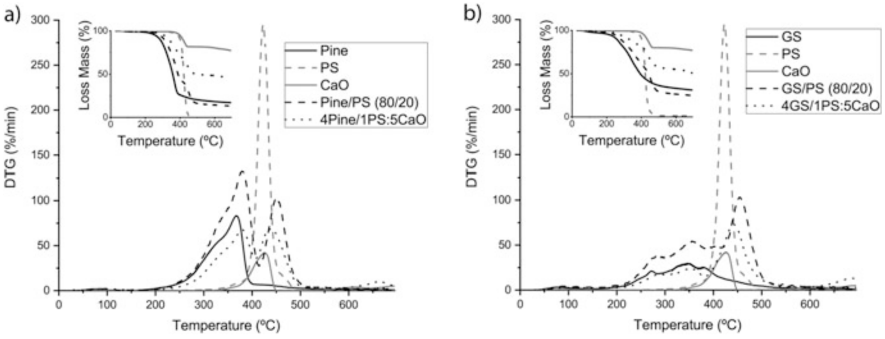

Fig. 2.7 Different catalytic co-pyrolysis experiments with: (**a**) pine/PS; (**b**) GS/PS CaO using the biomass/plastic-to-CaO ratio of 4/1:5

temperature, now involving both lignin and PS decomposition, likely pointing out that the tar cracking reactions previously observed for the devolatilization of biomass/CaO mixtures were not promoted under co-pyrolysis conditions. On the other hand, PS depolymerization seemed to be strongly affected by the presence of both CaO and biomass char, which may be explained by a significant decrease in the devolatilization rate observed at 450 °C, whereas a higher temperature is required for the full devolatilization of the PS component in the mixture. Again, it could be assumed that the presence of both CaO and biomass char could be promoting intermolecular hydrogen-transfer reactions instead of intramolecular ones, slowing down the PS depolymerization process while promoting interactions between the different volatiles in the mixture. This finding is quite important for the further design of a catalytic co-pyrolysis process involving a GS/PS/CaO mixture since it would require a higher temperature than that initially foreseen from the devolatilization of the individual components. Thus, it can be concluded that the use of TGA to study the depolymerization of biomass/waste plastic/catalyst mixtures should be established as a first step toward any scaling up of catalytic co-pyrolysis processes, given that the behavior of these complex mixtures cannot be extrapolated from the data obtained from the individual components.

Complementary to the use of TGA, analytical pyrolyzer coupled with gas chromatography mass spectrometry (GC/MS) allow information to be obtained on the composition of the volatiles. While this technique has been widely used for both the catalytic and fast pyrolysis of single biomass components [100–103], the number of works dealing with the catalytic co-pyrolysis of biomass/waste plastics is rather limited [16, 17]. An interesting example of this is the study by Sarker et al. [104], where a Pyroprobe-GC/MS was used to study the catalytic co-pyrolysis of poplar wood sawdust and HDPE using acid-modified ZSM-5 zeolites. A biomass/HDPE mixture (1:1) and a feedstock-to-catalyst ratio (1:1) were selected as experimental conditions. The catalyst was modified with an acidic solution (H_2SO_4) of different molarities (0.1, 0.3, 0.5, and 0.7 M). This treatment modified the amount and nature of the acidic sites and, in turn, the efficiency of the catalyst for the production of aromatic hydrocarbons. Interestingly, it was observed that catalytic co-pyrolysis with HDPE provided a higher relative olefin content than biomass catalytic pyrolysis, and the content of oxygenated compounds was significantly reduced, except for alcohols. The ZSM-5 sample treated with an acidic solution 0.5 M was the most selective catalyst for the formation of aromatic hydrocarbons. This behavior was linked to its higher content of Brønsted acidic sites. Another interesting example was reported by Xue et al. [105], who also used a Pyroprobe-GC/MS to assess the performance of MCM-41 silica for the catalytic co-pyrolysis of cellulose and PP mixtures. It was observed that the main products in the presence of catalyst were olefins and aromatics, whereas the main products without catalysts were oxygenated compounds. It can therefore be concluded that the use of an analytical pyrolyzer could be a very interesting alternative to assessing and optimizing the performance of different catalysts for the production of upgraded bio-oils since the composition of the volatiles could be promptly determined. Unfortunately, the use of a pyrolysis gas chromatography mass spectrometry (Py-GC/MS) is not a routine technique in most laboratories. Additionally, microreactors can provide fast useful data but they present several limitations. These are mainly related to operational conditions, mass transfer, temperature profile...etc., than differs in a great extent from those conducted at higher or industrial scale [106].

2.2.2 TRL 3–4: Laboratory-Scale Catalytic Co-pyrolysis Processes

A further step toward the development of catalytic co-pyrolysis processes at industrial scale is based on the assessment of these types of processes in laboratory-scale reactors at TRLs 3 and 4. This scale allows information to be obtained on the influence of different process parameters, such as temperature, heating rate, solid and gas residence time, biomass-to-waste plastic ratio and feedstock-to-catalyst ratio, on both the yield and the composition of the pyrolysis products. Account should also be taken of the fact that these final results will be strongly dependent on the nature of the pyrolysis reactor. There are a large number of studies in the literature related to fast and catalytic pyrolysis of a single biomass or plastic, and very interesting information on the major aspects of these processes can be found in different reviews [58, 105–109], where it is generally accepted that further upgrading processes are needed to increase the quality of the liquid product and that the addition of waste plastics is one of the most interesting alternatives. In this respect, several interesting works can be found in the literature [59, 60, 63–65] at the scale of TRLs 3 and 4 for co-pyrolysis processes. In these studies, PP, HDPE, LDPE, PS, and WT are the most commonly used polymers. Interestingly, Brebu et al. [64] studied the co-pyrolysis of plastic polymers (PE, PP, and PS) and biomass (pine woodchips) mixtures (50/50) in a semi-batch reactor at 500 °C. They observed that the liquid product yields were always higher than 60 wt%, reaching 69.7 wt% in the case of the mixture with PS. Co-pyrolysis produced three different phases: aqueous, organic, and tars. In all cases, the calorific values of the organic phase were higher than 45 MJ/kg. While oxygenated polar compounds were distributed between the tar and aqueous phases, the organic phase was predominantly composed of hydrocarbons, their nature being dependent on the type of synthetic polyolefin. PE produced saturated and unsaturated hydrocarbons; PP produced branched hydrocarbons ranging from dimers to heptamers of PP; and PS produced styrene monomers, dimers, and trimers; all were similar to those obtained from the pyrolysis of the individual waste polymers. In line with the conclusions found in microreactor studies, it should be highlighted that unless process conditions are carefully selected, the formation of three different phases will take place simultaneously and, therefore, which will not favor interactions between the radicals released from the different components of the mixture, resulting in an immiscible liquid product similar to that obtained by mixing the individual components.

Conversely, a careful selection of both process conditions and feedstock components has demonstrated to be critical for the production of an upgraded bio-oil that does not only involve products coming from the pyrolysis of both feedstock components but also the compounds obtained through the interaction of radicals released by their devolatilization. In fact, it has been observed that plastic wastes can act as hydrogen donors, upgrading the pyrolytic oil through hydrogen transfer reactions [62, 67]. However, some drawbacks remain, mainly those associated with the plastic-to-biomass ratio. As previously explained, the choice of a reasonable ratio plays a crucial role in this process, from both the sustainability and technical points of view, given that the presence of significant amounts of bio-oil contaminants such as sulfur- and chloride-containing compounds or PAHs could be greatly increased [61, 65–67].

Progress toward the production of high-quality bio-oils at TRL 3–4 reactors has been also accomplished by the incorporation of catalysts to the co-pyrolysis process. Thus, different kinds of catalysts have been studied for this purpose: zeolites such as ZSM-5 [110–112]; mesoporous silicas, such as SBA-15 [113–115] and MCM-41 [116–118]; alkaline and alkaline earth metal oxides, such as CaO and MgO [17, 119]; different metal oxides of transition metals, such as Co, Ni, Cu, and Ga [9, 120]; and even mixtures of these catalysts [38, 121]. The most widely studied and used catalysts in catalytic upgrading processes at laboratory-scale facilities are ZSM-5 zeolites owing to their high specific surface and intrinsic acidity, adsorption capacity, ion-exchange capacity, and high hydrothermal stability. In addition, ZSM-5 zeolites have a precise balance of acidic strength, micropores with appropriate dimensions to inhibit the formation of large molecules that eventually lead to coke formation, and high porosity and pore connectivity, favoring the diffusion of reactives, products, and by-products to the internal acidic active sites. However, while the ZSM-5 deoxygenation rate may be successfully improved by the incorporation of different metal active sites such as Ni, Co, Ga, and Mg, among others [122] and/or the development of mesoporosity [38], the stability of ZSM-5-based materials has been demonstrated to be very limited [123], with some of the main issues commonly observed being coke formation under reaction conditions, and fouling and sintering during regeneration processes. Nonetheless, several attempts have been made to improve the stability of these very active materials. Zheng et al. [124] studied the catalytic pyrolysis of biomass/rubber seed oil (RSO) (1:1) over HZSM-5 at a feedstock-to-catalyst ratio of 1:2. They showed that RSO addition decreased coke formation, also leading to an aromatic-rich bio-oil with a lower PAH content. Interestingly, a similar effect was observed for the co-pyrolysis of poplar wood and HDPE (50/50) using HZSM-5 zeolite as catalyst (ratio 1:1) [125], pointing to the addition of plastics to the feedstock as a way of reducing coke formation. Another approach to deal with this issue was reported by Lin et al. [126], where lower coke formation during the catalytic co-pyrolysis of corn stover/HDPE (50/50) was also achieved by the impregnation of ZSM-5 with potassium. Interestingly, it was also observed that the addition of potassium promoted the formation of alkenes and monoaromatic hydrocarbons while inhibiting PAH formation as coke precursors. In this context, it should be noted that none of these works provided relevant data on catalyst stability under cyclic operation involving catalyst regeneration, which should be carefully evaluated as coke formation was still observed, while fouling and sintering during regeneration stages could be very important during this stage. For this reason, it can be concluded that the future of zeolites in biomass catalytic pyrolysis processes seems to be quite limited unless novel materials and/or processes are developed that prevent these operational problems of paramount importance from taking place.

Therefore, novel strategies have been developed following the guidelines for the selection of new catalysts described in the introduction section [44]. Cao et al. [127] compared the performance of two mesoporous silica solids (SBA-15, MCM-41) versus acidic ZSM-5 zeolite for the co-pyrolysis of biomass/waste polymer mixtures in a fixed-bed reactor. Interestingly, they observed that mesoporous silica materials led to better results, particularly SBA-15, which enabled upgraded bio-oils with the lowest oxygen content, density, and viscosity to be obtained. The authors observed that mesoporous silicas could effectively decompose some of the large molecular compounds into smaller ones, which could not be upgraded with ZSM-5 due to limitations with their diffusion to internal acidic active sites. Another interesting alternative consisted of using alkaline and alkaline earth metal oxides as catalysts. In this respect, Ryu et al. [128] assessed the performance of MgO-supported catalysts in the co-pyrolysis of biomass/HDPE in a semi-batch reactor. Three different supports (activated charcoal, Al_2O_3, ZrO_2) were selected for MgO impregnation, with activated charcoal being the support that obtained the highest yield in an aromatic-rich bio-oil. Positive effects were also found for CaO and BaO when these metal oxides were impregnated into red mud. Mohamed et al. [129] observed that these metal oxides significantly increased the deoxygenation rate of red mud. However, the catalytic co-pyrolysis of biomass/LDPE (1/4) mixtures led to lower aromatic yields. Again, we should note that there is a lack of data regarding the stability of these catalysts under process conditions. On the other hand, red mud is a highly available waste from the aluminum industry, which is likely to eliminate the need for a regeneration stage and can be of interest from a cost standpoint. Therefore, it can be concluded that although progress is being made on very interesting synthesis strategies for the development of more active and stable catalysts, relevant data regarding catalyst stability, cyclability, and operating costs are still required.

Against this background, we have recently reported [128, 129] some interesting results from the catalytic co-pyrolysis of different biomass/plastic waste mixtures in a TRL 3 fixed-bed reactor in which the influence of different relevant parameters of the catalytic co-pyrolysis process was assessed with regard to the yield and characteristics of the bio-oil produced. A comparison was made between the experimental and theoretical results obtained by the rule of mixtures in all cases, allowing the identification of possible synergetic effects. Initial insights into the stability of the catalysts under cyclic operating conditions were also provided. Owing to the interest of this approach, we proposed the use of several low-cost materials as potential catalysts for the catalytic co-pyrolysis of biomass/waste polymer mixtures. Grape seeds were selected as the sample for lignocellulosic biomass and PS and WT were used as waste plastics. The catalytic role of CaO in the pyrolysis of the individual feedstock components was initially studied for comparative purposes. As expected, the catalytic upgrading process led to a lower yield in the organic phase, the most valuable product for further applications, and also resulted in a significantly lower gas yield. This issue was related to the partial absorption of CO_2 by the CaO material, simultaneously promoting H_2 formation through the CaO-enhanced water-gas shift reaction. This higher hydrogen content seemed to play a key role in the production of upgraded bio-oil since not only hydrodeoxygenation and hydrocracking reactions could be favored for the formation of aromatics from phenolic compounds, but also the production of olefins and cyclic hydrocarbons through hydrocracking and hydrogenation reactions. Finally, we cannot rule out an additional catalytic role of CaO given the slight increase in the number of ketones, which could be pointing to the simultaneous occurrence of a decarboxylation pathway via an acid ketonization reaction over CaO basic sites. On the other hand, the CaO addition had a minor influence on the pyrolysis of PS in terms of liquid yield. Similar results were found in the case of WT pyrolysis. However, it should be remarked that a higher hydrogen concentration was observed in the gas fraction for both waste plastics, likely associated with the promotion of light hydrocarbon cracking reactions as these compounds were simultaneously reduced. The promotion of cracking reactions was also observed in the composition of the liquid fraction, given the significant reduction in PS depolymerization molecules, styrene monomers, dimers, and trimers, which are the main oil components in non-catalytic fast pyrolysis processes, while an increase in the production of monoaromatic—mainly benzene, toluene, and xylenes—was observed. In contrast, the incorporation of CaO into the WT mainly promoted hydrocyclization reactions of linear paraffins, leading to the increase in cyclic hydrocarbons in the WT oils. These data were taken as a baseline from which the possible synergistic effects produced by a dual strategy based on the catalytic co-pyrolysis of plastic/biomass mixtures could be assessed.

In this light, in addition to CaO, our research group also assessed the applicability of other materials as economical, stable, and reusable catalysts for catalytic co-pyrolysis processes. Attapulgite [53], ilmenite [52], sepiolite [51], red mud [52], and dolomite were also evaluated. Experiments were carried out in a fixed-bed reactor using a GS/WT(80/20 wt%) mixture as the feedstock and a catalyst-to-feedstock ratio of 1:1 (except with sepiolite, for which the ratio was 5:1 due to the excessive cracking effect observed at higher ratios for biomass pyrolysis [22]). The results of these experiments were also compared with those obtained from the co-pyrolysis of grape seeds/WT (80/20 wt%). Table 2.4 provides a summary of some of the results obtained in these experiments. Significantly, the presence of the catalyst slightly increased the total liquid yield. An additional role of the catalyst as heat carrier could explain this fact since the GS/WT control experiment was carried out in absence of any inert material working as heat carrier. Additionally, some differences can be observed in the distribution between organic and aqueous phase. Thus, the organic phase yield was comparable for attapulgite, ilmenite and sepiolite, whilst this yield decreased for CaO and dolomite. This effect can be explained by the dehydrating effect of calcium-based catalysts, consequently increasing the aqueous phase yield in the liquid product. As regards the properties

Table 2.4 Yields of catalytic co-pyrolysis of GS/WT (80/20) with different low-cost catalysts and product liquid quality

	Yields (wt%)				Liquid phase distribution (wt.%)		Organic fraction quality			
Experiment	Liquid	Solid	Gas^a	Total	Org.	Aq.	O^a (wt %)	S (wt %)	HHV (MJ/kg)	pH
GS	39	33	24	96	61	39	14.3	0.0	36.6	6.4
WT	44	38	15	97	100	0	0.1	0.6	43.4	7.5
GS:CaO (1:1)	38	42	22	102	56	44	16.6	0.0	34.9	9.8
WT:CaO (1:1)	46	30	24	100	100	0	1.7	0.4	42.5	9.0
GS/WT (80/20)	40	33	26	99	69	31	10.6	0.2	38.8	6.7
Catalytic Co-pyrolysis										
GS/WT (80/20): CaO 1:1	44	40	16	100	55	45	5.3	<0.1	41.2	9.1
GS/WT (80/20): CaO.MgO 1:1	44	40	16	100	52	47	3.2	0.3	42.1	8.9
GS/WT (80/20): attapulgite 1:1	42	36	20	98	68	32	13.3	0.2	37.9	6.6
GS/WT (80/20): ilmenite 1:1	42	33	21	96	69	31	14.3	0.1	37.3	6.4
GS/WT (80/20): sepiolite 5:1	43	37	18	98	64	36	12.5	0.1	38.4	7.8
Cyclic operation										
GS/WT (80/20): CaO 1:1 C0	44	40	16	100	55	45	5.3	<0.1	41.2	9.1
GS/WT (80/20): CaO 1:1 C1	34	47	19	100	67	33	5.3	0.2	40.5	9.3
GS/WT (80/20): CaO 1:1 C2	38	45	17	100	60	40	5.2	0.3	40.5	9.0
GS/WT (80/20): CaO 1:1 C3	37	47	15	99	72	28	6.2	0.3	39.1	9.3

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[a] By difference

of the organic phase, the oxygen content, heating value, and acidity of this phase were only remarkably improved after the addition of CaO or dolomite, with oxygen values remaining similar to those found in the non-catalytic experiments with the other catalysts. In addition, a reduction was achieved in the sulfur-containing compounds derived from the pyrolysis of WT, particularly when CaO was used, simultaneously increasing the calorific value of the bio-oil. In fact, HHVs were achieved close to those obtained for WTs (43.4 MJ/kg) and remarkably higher than those obtained from non-catalytic co-pyrolysis (38.8 MJ/kg). Finally, the chemical composition of this valuable fraction was also determined by GC/MS. Cyclic hydrocarbons and single ring aromatics were observed to have been synergistically increased. Concurrently, there was a noticeably reduction in oxygenated compounds, mainly phenols, esters, and fatty acids. This behavior was associated with the additional promotion of hydrodeoxygenation, hydrocyclization, and aromatization reactions resulting from the availability of a significant amount of H_2 produced through both the catalytic cracking of light hydrocarbons and the CaO-enhanced water-gas shift reaction. Finally, calcium-based sorbents also promoted decarboxylation reactions, leading to a slight increase in the number of ketones. Therefore, a reaction mechanism comparable to those observed for the catalytic pyrolysis of the individual components was attained, although synergetic effects were observed in terms of fuel properties (lower oxygen and sulfur contents and higher calorific value), as shown in Table 2.4.

As previously stated, another important issue to be assessed is the performance of the catalyst under cyclic operation. In this case, the regeneration stage was carried out by combustion of the CaO/char mixture at 800 °C in air atmosphere. As a preliminary study, three consecutive cycles were performed involving pyrolysis + catalyst regeneration. We would highlight the fact that although the total liquid yields significantly decreased after the first cycle, the yield to the organic fractions were always close to that obtained in the initial experiment (about 25 wt%) since higher fraction of organic phase was attained. Positively, the CaO deoxygenation rate was maintained throughout the cyclic operation, leading to an upgraded bio-oil with comparable properties in terms of oxygen content, HHV, and acidity, see Table 2.4. Some significant differences were observed in the composition of the non-condensable gas since the CO_2 concentration increased while the H_2 content simultaneously decreased. As expected, this phenomenon could be associated to the well-known decline in the CO_2 absorption capacity of CaO natural sorbents, suppressing the CaO-assisted water-gas shift reaction. Fortunately, negligible differences were found in the composition of the bio-oil since cyclic hydrocarbons, aromatics, phenols, and ketones remained at similar values in this fraction during cyclic operation. These results corroborate the exceptional potential of CaO for use in catalytic co-pyrolysis processes, as already observed in biomass pyrolysis.

As the results from the catalytic co-pyrolysis of grape seeds/WT mixtures using CaO as catalyst were very encouraging, the applicability of this solid to other biomass/waste plastic mixtures was also evaluated. Thus, we modified either the nature of the polymer waste, using waste PS as biomass co-feedstock, or the type of lignocellulosic biomass, using pine woodchips as feedstock. Again, higher liquid yield was obtained in the upgrading process under catalytic co-pyrolysis conditions, although the organic phase yield was lower than that of the co-pyrolysis experiment (73.2 vs. 58.7 wt%). Regardless of the feedstock mixture, synergy between both upgrading strategies was similarly observed through this dual approach in the quality of the organic phase, leading to an upgraded bio-oil with a lower oxygen content and higher calorific value than theoretically expected, as can be appreciated in Table 2.5. On the other hand, GC-MS analysis of the liquid organic phase and chromatographic analysis of the gas fraction confirmed our positive results, demonstrating that the simultaneous addition of waste plastics and CaO to the biomass feedstock could lead

Table 2.5 Distribution of products and liquid quality of pyrolysis, catalytic pyrolysis, co-pyrolysis, and catalytic co-pyrolysis of GS, Pine, and PS

Experiment	Yield (wt%)			Liquid phase distribution (wt %)		Organic fraction quality		
	Liquid	Solid	Gas[a]	Org. phase	Aq. phase	Oxygen (wt%)[a]	HHV (MJ/Kg)	pH
GS	39	33	28	61	39	14.3	32.3	6.4
Pine	50	25	25	60	40	38.8	21.2	2.8
PS	82	1.0	17	100	0	2.3	40.8	3.8
GS:CaO (1:1)	38	43	19	56	44	14.4	35.8	6.6
PS:CaO(1:1)	52	28	20	61	39	0.0	40.7	4.0
Pine:CaO (1:1)	53	20	27	57	43	15.8	37.9	2.9
GS/PS (80/20)	51	27	22	80	20	5.3	39.0	5.6
Pine/PS (80/20)	62	18	20	73	26	31.5	37.9	3.0
GS/PS (80/20): CaO (1:1)	54	29	17	47	53	5.3	41.2	9.1
Pine/PS (80/20): CaO (1:1)	25	61	14	59	41	20.2	39.1	3.9

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[a] By difference

to synergetic effects since hydrodeoxygenation, hydrocracking and hydrocyclization reactions were promoted owing to the significant improvement in H_2 availability.

2.2.3 *TRL 5: Pilot Plant Catalytic Co-pyrolysis Processes*

The next step in the scale-up of the catalytic co-pyrolysis process would be its validation at TRL 5, where experiments in a relevant environment for further industrial application should be performed.

First, it should be pointed out that certain companies, such as KiOR (currently in bankruptcy proceedings), Anellotech [133], and the Gas Technology Institute (GTI) [134, 135] have already attempted to undertake projects involving the catalytic pyrolysis process at demonstration scale, and even commercial scale, with varying degrees of effectiveness. As to be expected at this magnitude, it is a difficult task to obtain specific information regarding product yields, bio-oil quality, and operational issues. In addition, companies such as ABRI-TECH (Canada), PYREG (Germany), and BIOGREEN-ETIA (France), and different research groups such as EBRI (University of Aston), IKFT-KIT (Germany), and ICB-CSIC (Spain) are developing biomass pyrolysis-based technologies at an industry-relevant scale, TRLs 5 and 7. The aim of these companies and research groups has been to demonstrate on a pilot scale level that pyrolysis, catalytic pyrolysis or even co-pyrolysis with different feedstocks can be profitable technologies for biomass valorization. Although these results are not included in this chapter for the purpose of simplicity, relevant information can be attained elsewhere [21, 22, 67, 136–141]. Unfortunately, the degree of catalytic co-pyrolysis process development currently stands at lower TRLs, since scarce study has been given to the catalytic co-pyrolysis process at TRL 5 or higher. Nonetheless, some interesting results have been already reported by our research group using a single-screw auger reactor capable of processing up to a rate of approximately 20 kg/h., providing the first insights into the viability of this process in the relevant environment. Thus, we have assessed how process variables could influence the yield and quality of the final products, significantly leading to the production of an upgraded bio-oil fully compatible with conventional fuels. More information on this facility can be found elsewhere [131].

We highlight the fact that the experimental conditions reached in the auger reactor (temperature, heating rate and gas, vapor and solid residence time) can be considered close to the operating conditions of industrial-scale plants. Significantly, the incorporation of heat carriers with catalytic properties into the pyrolysis process in auger reactors, as first proposed by our research group, has demonstrated to be a key to the resolution of certain major issues associated with biomass pyrolysis since, first, heat transfer to the biomass particles is significantly increased and, second, the bio-oil is highly upgraded because the catalytic properties of the heat carriers are in close contact with the biomass and waste plastic particles. Based on the results found in the laboratory-scale reactor, we proposed the use of different calcium-based materials as heat carriers with catalytic properties, such as calcite and dolomite. As expected, lower organic phase yields were obtained compared to the non-catalytic experiment using sand as heat carrier without catalytic properties, but the oxygen content of the bio-oil greatly decreased. It should also be noted that both acidity and calorific value were also improved compared to the non-catalytic test, evidence that CaO materials are able to promote hydrodeoxygenation, decarboxylation, and ketonization reactions, as previously demonstrated in laboratory-scale reactors. Other low-cost minerals (sepiolite, bentonite, attapulgite and red mud) were also tested at TRL 5, but the performance of these heat carriers was again notably inferior to that shown by calcium-based sorbents. We would like to mention here that although calcium-based materials are low-cost minerals, their cyclability in a two-stage integrated process consisting of, first, biomass pyrolysis in the auger reactor and, second, char combustion in a fluidized bed reactor for heating and regeneration of the heat carrier was successfully demonstrated (Fig. 2.8), proving that biomass catalytic pyrolysis in an auger reactor is a self-sustaining process [21, 141].

Based on these encouraging results for biomass catalytic pyrolysis, we have recently tested the catalytic co-pyrolysis process at TRL 5 in order to see if the process performance in a more relevant environment was consistent with that achieved in the laboratory-scale fixed-bed reactor. These experiments were conducted at atmospheric pressure using N_2 as the inert carrier gas. The vapor residence time was fixed at 2–3 seconds. As in the fixed-bed reactor, grape seeds were selected as the lignocellulosic biomass, while PS and WT were the chosen plastic wastes. GS/WT and GS/PS mixtures were used at the ratio of 80:20 and 90:10, in both the co-pyrolysis and catalytic co-pyrolysis processes. In line with

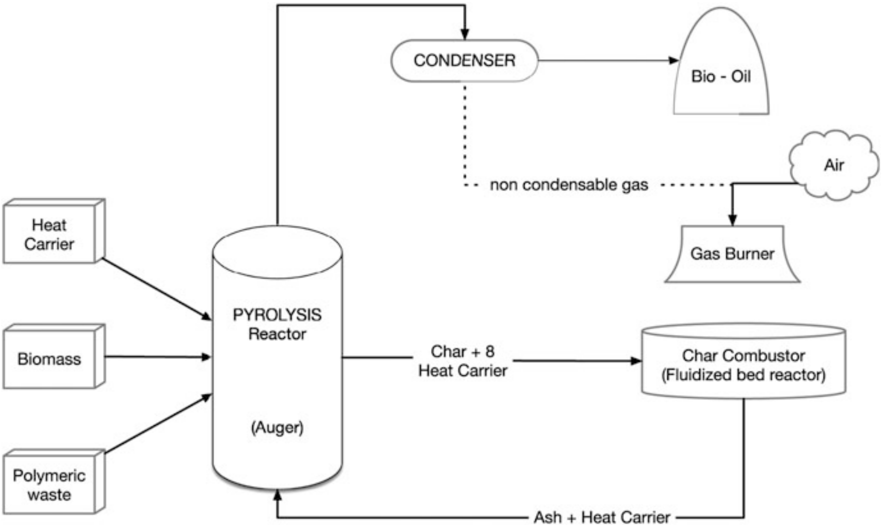

Fig. 2.8 Simple schematic of an integrated catalytic co-pyrolysis process using heat carriers

previous biomass catalytic pyrolysis results, CaO was selected as the catalyst and the feedstock-to-catalyst ratio was fixed at 2:1 since this heat carrier in recirculation was enough to meet the energy balance demand of the integrated process proposed in Fig. 2.8, while at the same time preventing the excessive cracking of volatiles observed at a higher ratio.

Fortunately, catalyst addition to the GS/PS co-pyrolysis process replicated or even enhanced those positive results observed at TRL 3 in the fixed-bed reactor. Thus, a lower organic fraction yield with upgraded properties was again obtained (Table 2.6). Significantly, the production of a fully deoxygenated organic phase with an oxygen content close to 1 wt% for the 80:20 grape seeds/PS:CaO mixture was achieved where the formation of a H_2-rich gas stream with low CO_2 concentration and high calorific value (32.2 MJ/m^3), which was again linked to the promotion of both light HC cracking and Ca-enhanced water-gas shift reactions was observed. As the addition of CaO to the GS/PS co-pyrolysis generated very promising results, the use of WT as a waste polymer was also assessed. Very encouraging results were again achieved since a higher yield in upgraded bio-oils was also obtained (Table 2.7). As expected, the results from the single-screw auger reactor again reproduced the trends observed in the TRL 3 fixed bed reactor, proving that the addition of both CaO and WT to biomass pyrolysis can also promote synergetic effects on the upgrading of bio-oil in terms of both yield and quality. In line with this, the oxygen content achieved for the organic fraction was lower than 1 wt%, resulting in a bio-oil with a very high calorific value of more than 40 MJ/m^3. Additionally, this upgraded bio-oil obtained at the TRL 5 auger facility showed very interesting physicochemical properties as a fuel since water content and acidity were significantly improved, and a high content in aromatics and hydrocarbons was obtained. It

Table 2.6 Yields, organic phase quality, and non-condensable gas composition of pyrolysis, catalytic pyrolysis, co-pyrolysis, and catalytic co-pyrolysis of GS and PS

	Yields (wt%)				Liquid phase distribution (wt%)		Organic phase quality			Non-condensable gas composition (Vol%)			
Experiment	Liquid	Char	Gas	Total	Aq.	Org.	Oxygen[a] (wt%)	HHV (MJ/Kg)	pH	H_2	CO_2	CO	CH_4
GS	42	31	23	96	62	38	11.8	35.5	8.0	15.6	34.9	16.0	17.5
PS	94	0	2.5	96	0	100	0.0	42.0	8.1	33.7	8.4	3.9	19.0
GS:CaO (2:1)	28	36	15	80	68	32	12.7	34.7	9.0	31.0	9.4	15.0	23.3
PS:CaO (2:1)	92	0	2.4	95	0	100	0.0	42.0	7.8	41.1	8.6	4.3	19.4
GS/PS (90/10)	44	30	25	99	45	55	9.2	36.9	7.4	16.0	35.2	15.9	17.5
GS/PS (80/20)	51	25	23	99	30	70	2.2	40.4	7.3	16.7	36.0	15.3	17.4
GS/PS (90/10):CaO	44	35	16	96	51	49	1.6	40.0	9.2	32.6	9.6	14.6	22.7
GS/PS (80/20):CaO	46	33	16	95	41	59	1.0	40.9	8.7	33.2	8.7	14.9	22.7

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Table 2.7 Yields, organic phase quality, and non-condensable gas composition of pyrolysis, catalytic pyrolysis, co-pyrolysis, and catalytic co-pyrolysis of GS and WT using different Ca-based catalysts

	Yields (wt%)				Liquid phase distribution (wt%)		Organic phase quality				
Experiment	Liquid	Char	Gas	Total	Aq.	Org.	Oxygen[a] (wt%)	HHV (MJ/kg)	pH	Aromatics	Phenols
GS	43	31	23	97	62	38	11.8	36.8	8.0	31.6	17.1
WT	38	38	23	99	0	100	0.7	43.3	8.3	91.8	0.0
GS/WT (90/10)	33	37	29	99	61	39	7.8	34.8	9.6	63.3	6.4
GS/WT (80/20)	36	33	26	95	51	49	3.9	37.6	9.5	64.3	4.9
GS/WT (80/20):CaO	39	37	21	97	59	41	0.5	41.2	9.1	70.9	1.3

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[a] By difference

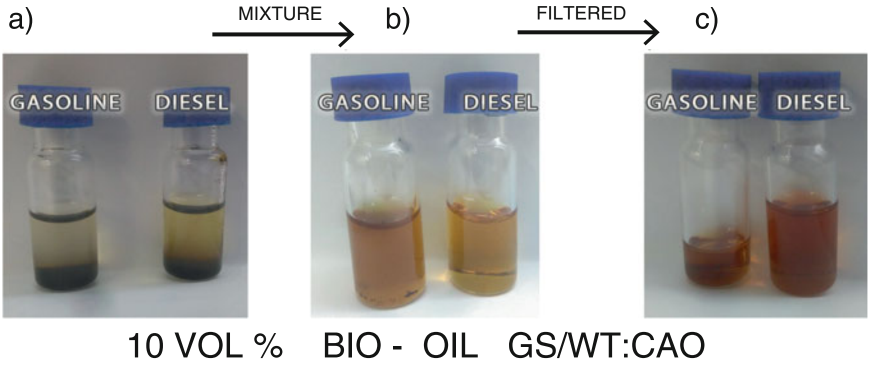

Fig. 2.9 Bio-oil with conventional fuels compatibility: (**a**) commercial gasoline and diesel mixture with bio-oil from catalytic co-pyrolysis (80 GSs/20 WTs/CaO). (**b**) Mechanical mixture of catalytic co-pyrolysis bio-oil with gasoline and diesel. (**c**) Mixture of catalytic co-pyrolysis bio-oil with gasoline and diesel after filtration process. Mixtures were prepared using a blend consisting of 90 vol% gasoline or diesel/10 vol % bio-oil. Adopted with permission from Ref. [130]. Copyright © 2018, Elsevier

should be highlighted that bio-oil upgrading process was actually more efficient in the TRL 5 auger facility compared to that performed in the TRL 3 fixed-bed reactor. Therefore, it can be concluded that although comparable upgrading routes were identified at both TRLs, better contact between volatiles and CaO active sites was promoted in the TRL 5 auger reactor, favoring the upgrading process.

Significantly, the bio-oils produced by catalytic co-pyrolysis of grape seeds with polymer wastes were highly compatible with conventional fuels, as can be observed in Fig. 2.9, showing the perfect blending achieved between this upgraded bio-oil and gasoline/diesel. Therefore, this technology could be identified as a simple and reliable solution for the production of drop-in biofuels.

2.3 Conclusions and Future Outlook

Insights into the potential of the catalytic pyrolysis of biomass and waste polymers at TRL 5 have been shown. Although further research is still necessary, focusing particularly on the optimizing of key parameters, such as i) the selection of an efficient and low-cost catalyst, ii) the biomass/waste polymer mixture, and iii) the optimization of the main operational parameters of the process (temperature and volatile residence time), the exceptional potential of this process for the production of transportation fuels in a single-stage process has been successfully revealed from laboratory scale to pilot plant scale. Significantly, this dual strategy has proven to be a robust and simple technology that enables high valuable liquids to be obtained for direct use as drop-in fuels. In fact, an almost fully deoxygenated liquid with a large proportion of valuable aromatics can be obtained using different types of biomass (grape seeds or pine woodchips), waste plastic (polystyrene or waste tire), and catalyst (calcite or dolomite) mixtures. Hopefully, these positive results will not be only limited to these mixtures, and the study of other mixtures will also lead to the efficient production of upgraded bio-oils. Therefore, the great versatility of this process, linked with the wide range of feedstocks that can be treated (both biomass and waste polymers) could enhance the potential of the catalytic co-pyrolysis process so that it can reach the commercial level.

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