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Waste tyre valorization by catalytic pyrolysis – A review

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Abstract

The environmental concern associated with waste tyre disposal and the necessity of sustainable waste management policies has promoted the development of waste tyre valorization processes in the last decades. Within this framework, this review analyzes the main advances in waste tyre valorization by catalytic pyrolysis. Waste tyre pyrolysis allows converting this solid waste into three product fractions of potential interest, as are gases, pyrolysis oil (TPO) and char, with their yield and features being conditioned by pyrolysis conditions. Catalytic pyrolysis is an interesting alternative to improve the quality of the products and the selectivity of the process. A wide range of catalysts have been proposed in the literature for waste tyre valorization, with zeolites being the most commonly used due to their capacity for the production of valuable chemicals, such as BTX and light olefins. This review approaches multidisciplinary aspects for the evaluation of the critical points in this process, such as those related to pyrolysis technologies, reaction mechanisms, catalyst design and products properties.

Keywords: waste tyres; pyrolysis; catalytic cracking; TPO; catalyst; zeolite

1. Introduction

According to estimations, the annual global tyre production is of around 1.5 billion units, which accounts for approximately 17 million tons of used tyres [1,2] and,

1 furthermore, their production rate continues growing as their demand in developing
2 countries is rapidly increasing. Implementation of environmentally friendly valorization
3 routes is required in order to solve the environmental issues associated with the
4 inappropriate management of end life tyres [3]. Moreover, the need for alternative
5 energy and fuel sources to reduce the dependency of fossil fuels increases the interest of
6 waste tyre thermochemical valorization.
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8 Thus, waste tyres are characterized by their remarkable energy content; in fact, values
9 above 30 MJ kg⁻¹ are reported in the literature [4-9]. This high heat heating value is
10 related to their high carbon content, usually between 75 and 80%, with that of hydrogen
11 ranging from 6 to 8% and that of sulfur from 1 to 2.5% [10-14]. Although tyre
12 composition varies depending on the application, they are mainly made up of different
13 rubbers, such as natural, butyl and styrene-butadiene ones, and carbon black, with their
14 contents being in the 60-65% and 25-30% range, respectively [3].
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16 Based on the aforementioned characteristics of the wastes, different management routes
17 have been assayed in the last decades, with the most common ones being landfilling,
18 direct reutilization, retreading, and material an energy recovery. A balance involving
19 these options is not straightforward and has evolved considerably in the last decades due
20 to the restrictions in the regulations for waste tyre disposal in landfills. Figure 1 shows
21 the evolution of waste tyre management in the European Union in the last two decades
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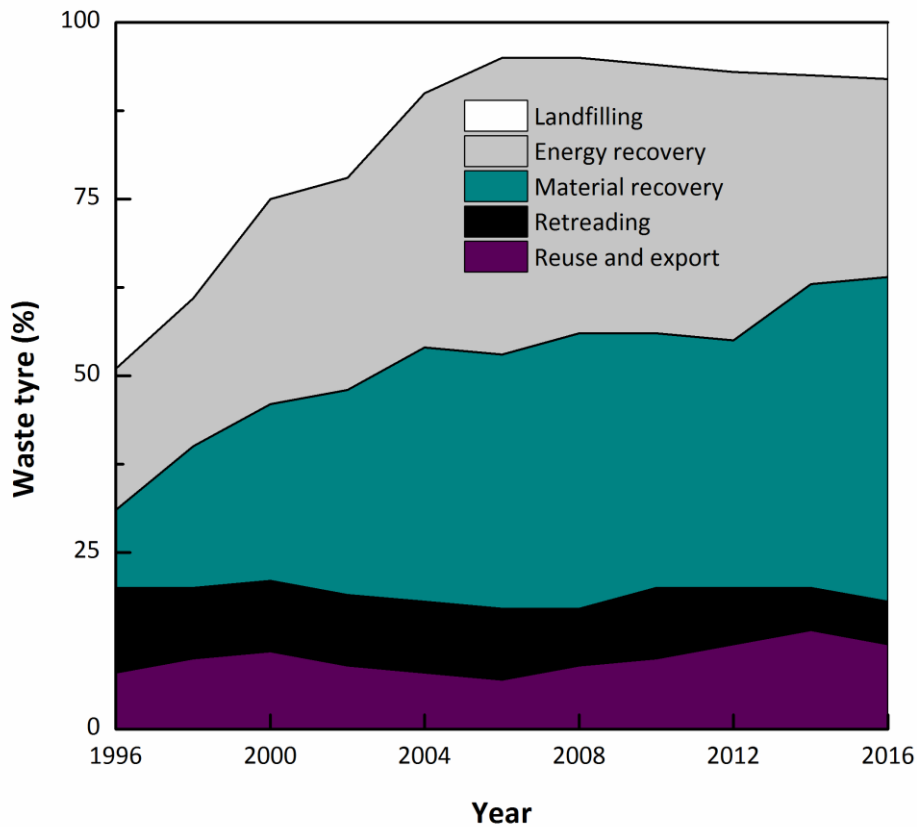


Figure 1. Evolution of waste tyre management routes in the 1996-2015 period in the European Union [15].

Although waste tyre retreading is a direct reutilization alternative for waste tyres, this option may not be of interest from an economic perspective compared to the manufacturing of new tyres and, furthermore, retreaded tyres may involve safety and performance problems, especially at high velocities [16]. Another waste tyre reutilization option lies in their use in different civil engineering applications, such as those involving manufacturing of concrete [17,18] and asphalt [19,20] or paving of playground and artificial sport pitches [21]. It should be noted that the use of waste tyres in some of these applications is conditioned by health risks associated with the release of volatile organic compounds (VOC) and polycyclic aromatic hydrocarbons (PAH) [21,22].

1 The high energy content of waste tyres has boosted their utilization in different energy
2 applications, such as direct combustion, especially in cement kilns or paper industries
3 [3,23]. However, waste tyre combustion is hindered by the hazardous emissions
4 produced, with dioxins being of especial concern [24].
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9 Within this scenario, thermochemical routes play a relevant role in waste tyre
10 management, reducing the environmental impact associated with their valorization and
11 allowing the production of high value added product. These routes are summarized in
12 Figure 2. Gasification is a thermochemical conversion process consisting in a partial
13 oxidation of the organic material at high temperatures to produce a syngas and char
14 (adulterated carbon black), with tar being the main undesired byproduct, and product
15 yields and their composition depending on the gasifying agent used (air, O₂, steam or
16 their mixtures). Thus, waste tyre gasification has been regarded as a suitable
17 valorization route [25-29]. In fact, this waste material has high carbon and hydrogen
18 content, and therefore a remarkable potential for syngas production. Thus, the interest of
19 this alternative lies not only in the production of syngas [26,28,30-32], but also in the
20 co-production of activated carbons by means of char upgrading processes [25].
21 Moreover, high hydrogen yields have been reported in the in line catalytic steam
22 reforming of waste tyre pyrolysis volatiles [33-35]. However, the great potential of the
23 pyrolysis-reforming strategy attained in the valorization of other polymeric materials,
24 such as plastics [36], is hindered in this case by the high sulfur content of waste tyres,
25 which causes fast deactivation of the reforming catalyst [37].
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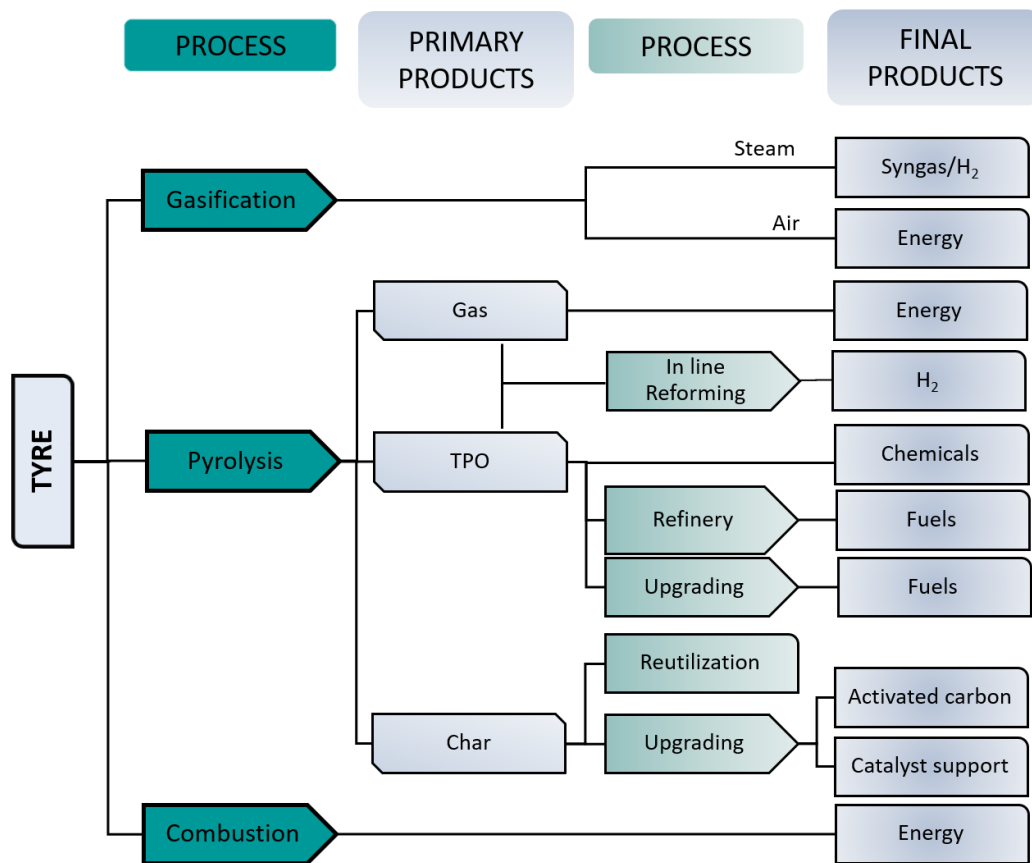


Figure 2. Summary of thermochemical processes for the valorization of waste tyres and the main products obtained.

Pyrolysis is an efficient and eco-friendly process that allows producing fuels and chemicals from waste tyres [3,38-41]. Furthermore, the versatility of this process allows for jointly valorizing waste tyres and other residues, such as biomass [42-44], coal [14], plastics [45], cooking oil [46], and microalgae [47,48]. Waste tyre pyrolysis is commonly conducted at lower temperatures than gasification and under inert atmosphere, with the main products being the tyre pyrolysis oil (TPO) and char [3,39,49,50]. TPO is a dark-brown oil made up of hydrocarbons of different nature, such as aliphatic, aromatic and heteroatomic compounds [39]. Moreover, high concentrations of specific chemicals of high value added, such as isoprene, styrene and limonene, are contained in the TPO [5,8,51-54]. The interest of this liquid as fuel lies in its high heating value, higher than that of the original tyres, i.e., in the range from 35 to 45 MJ kg⁻¹ [7,55-58].

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However, sulfur contents of around 1 wt.% [4,12,55,57,58] involve the main drawback for its direct utilization. Accordingly, different TPO upgrading processes have been proposed in the literature. Thus, hydroprocessing [40,59-61] and fluid catalytic cracking (FCC) [62-64] have been regarded as feasible TPO valorization routes, once it has been blended with conventional refinery feedstocks. In addition, several processes aimed at TPO desulfurization have been proposed for improving TPO features [65-67].

The solid product (char) obtained in the pyrolysis of waste tyres is mainly the carbon black added to its formulation to improve the antiabrasive performance, together with other inorganic additives. The yield and adulteration degree of the char or residual carbon black recovered after pyrolysis strongly depends on reaction conditions [3,39,68]. Given that its direct reutilization is a challenging route [69-73], the production of activated carbons was proposed as an alternative upgrading route [74,75]. Finally, the gaseous products are characterized by their high heating value, and they are therefore used mainly for combustion to meet the energy demand for the pyrolysis process [76].

The commercial success of tyre pyrolysis is conditioned by the quality of the product stream, i.e., the selectivity of the process. In fact, the interest of catalytic pyrolysis lies in its capacity to produce a narrower product distribution than thermal pyrolysis, and therefore improve the yield of high value added products [77-80]. Thus, use of catalysts in waste tyre pyrolysis has been proposed in the literature with following main objectives: i) Increase the TPO yield [52,81], ii) Increase the gaseous product yield [82-84], iii) Selective production of valuable chemicals, such as light olefins or aromatics [83,85-92], iv) Reduction of the sulfur content in the TPO [93-97] of v) Increase of H₂ content in the gaseous product [98,99].

1 This review analyses the main advances in waste tyre catalytic pyrolysis in recent years.
2 The influence of the catalysts used on product distribution and their composition,
3 especially that of TPO and gaseous products, is analyzed in detail. The main features of
4 the most common catalysts are described and their role in waste tyre degradation is
5 evaluated. Moreover, other fundamental aspects of the process, such as the effect the
6 catalyst has on the tyre pyrolysis mechanism, reactor design and pyrolysis conditions,
7 are discussed. Finally, the main challenges and unsolved aspects of this promising
8 valorization route are also critically evaluated.

19 **2. Waste tyre characteristics**

21 Tyres are manufactured by assembling different components, such as the tread, different
22 textile plies, steel carcass and rubbers, which have specific properties to maximize the
23 effectiveness of the assembly. Prior to pyrolysis, the tread is separated from the textile
24 and steel elements and grinded to a particle size conditioned by the pyrolysis technology
25 used.

34 The rubber is the main component of the tyres and has a complex composition including
35 several materials depending on the application. The most common ones are natural
36 rubber (NR), styrene–butadiene rubber (SBR) and butadiene rubber (BR). The
37 remaining components that make up the tyre in order to meet specific functions are as
38 follows: i) Carbon black, which is used to reinforce the rubber and increase its
39 resistance to breakage and abrasion. ii) The dispersant oil, which is a mixture of
40 aromatic hydrocarbons, with the aim being to soften the rubber in order to make it more
41 manageable. iii) Sulfur, which is used to join the polymer chains inside the rubber and
42 also harden and prevent the mixture against excessive deformation at high temperature.
43 iv) The accelerator, which is an organo-sulfur compound that acts as a catalyst in the
44 vulcanization process. v) Zinc oxide and stearic acid, which also control the

1 vulcanization process and so improve the physical properties of the rubber. vi) Silica is
2 a reinforcing load, specifically used for a long time for special tyres, due to the
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4 resistance to breakage it confers upon some mixtures, but the wear resistance or the
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6 adherence provided by carbon black is much more superior. The typical car and truck
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8 tyres have the following composition in mass percentage: natural rubber 14-30%,
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10 synthetic rubber 14-27%, carbon black 20-28%, steel 13-25% and fabric, fillers,
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12 accelerators, antiozonants and other materials 10-17% [100]. It should be noted that the
13
14 main difference between car and truck tyre composition is the higher proportion of NR
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16 in the latter.
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21 Prior to use in pyrolysis processes the tyre material must be conditioned. Thus, steel and
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23 other carcass elements (such as textiles and cords) are removed with efficiency
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25 depending on the technology used. Moreover, tyre rubber must be ground to a particle
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27 size that strongly depends on the pyrolysis technology in which it will be processed. It
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29 is to note that this is an energy intensive process and, furthermore, energy consumption
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31 grows exponentially with particle size reduction, as it is directly proportional to the
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33 newly formed surface area of the shredded particles [101]. Therefore, this point must be
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35 carefully considered in the evaluation of the potential of pyrolysis technologies.
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41 The proximate and ultimate analyses of waste tyres reported in different studies in the
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43 literature are summarized in Table 1. As observed, there are significant differences in
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45 the proximate analyses of the samples, which in turn involve differences in the product
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47 distributions obtained in their pyrolysis. The elemental analysis of waste tyres clearly
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49 reveals the potential of the pyrolysis process for their valorization, as their volatile
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51 matter ranges from 60 to 70 %. In addition, the fixed carbon content is between 20 and
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53 30 % and can be directly associated with the carbon black included in the formulation.
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Finally, the ash contents are uneven and they depend on the additives contained in the original tyre and the extension of the steel removal process.

In the same line, there are also some minor differences in the elemental composition determined in different studies (Table 1). It should be noted the high contents of carbon (above 80 %) and hydrogen (around 7%), which promote the production of hydrocarbons in their conversion by pyrolysis. However, the high sulfur content, between 1.5 and 2.5 %, conditions the direct utilization of pyrolysis products as fuel.

Table 1. Proximate and ultimate (on an ash free basis) analyses of waste tyres

Reference	Proximate analysis (wt.%)				Ultimate analysis (wt. %)				
	Moisture	Volatile matter	Fixed carbon	Ash	C	H	O	N	S
[102]	0.4	62.9	18.1	18.6	84.9	7.3	4.1	1.1	2.6
[5]	0.8	68.7	27.2	3.3	85.6	7.9	4.7	0.5	1.3
[103]	1.8	64.5	26.3	7.4	84.2	7.9	5.5	1.0	1.4
[10]	1.4	66.1	27.5	5	83.2	7.7	6.2	1.5	1.4
[104]	0.4	59.9	21	18.4	86.3	7.1	4.5	0.5	1.7
[105]	1.1	66.8	28.5	3.6	82.6	8.2	6.1	0.9	2.2
[8]	-	65.1	29.9	4.9	84.3	7.7	4.7	0.8	2.5
[106]	0.3	68.6	26.9	4.2	90.7	4.2	2.1	0.4	2.6
[107]	0.2	71.5	28.5	8.3	82.6	7.4	8.2	0.4	1.5
[9]	1.1	62.2	32.3	4.3	84.4	6.7	6.9	0.4	1.6

3. Waste tyre pyrolysis technologies

The pyrolysis of waste tyres involves a series of complex chemical reactions, including primary polymer degradation reactions and secondary ones both inside the tyre particle and in the gas phase. The pyrolysis behavior of waste tyres differs from that of other polymeric material as plastics, which is mainly due to their physical properties, i.e., different proximate analysis and composition. Therefore, waste tyres are characterized by their higher fixed carbon content, which is related to the amount of carbon black added for vulcanization, whereas the volatile products are related to the degradation of polymeric materials (rubber) included in their composition. Thus, the high fixed carbon

1 content of waste tyres leads to high yields of char (or adulterated carbon black) in their
2 pyrolysis. The removal of this solid from the reactor should be approached in the reactor
3 design, especially in reactors operating in continuous regime at full scale, as the features
4 of this product are conditioned by its residence time in the reactor [3]. Similarly to
5 waste plastics, tyres have also a poor thermal conductivity, which hinders heat transfer
6 in the pyrolysis reactor. Interestingly, waste tyres are not melted under reaction
7 conditions, and therefore do not involve the problems related to the sticky behavior of
8 waste plastics, i.e., the latter involve a great challenge for the reactor design and
9 operation in their valorization by pyrolysis [77]. However, the stability of tyre particles
10 under reaction conditions strengthens the role of particle size on the pyrolysis process
11 due to the limitations associated with heat and mass transfer.
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26 The extent of primary and secondary reactions, and therefore the product distribution
27 obtained is determined by pyrolysis conditions, particularly, temperature, heating rate,
28 residence time (of both the volatile products and the char) and tyre particle size. It is to
29 note that some of these conditions strongly depend on the reactor design, with is evident
30 in view of the wide variety of alternative technologies reported in the literature
31 [3,39,40,49]. In fact, waste tyre pyrolysis reactors are basically those applied to biomass
32 valorization [77,108,109], which is explained by certain similar characteristics of both
33 feedstocks in terms of volatile and fixed carbon content.
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46 Based on the conditions, pyrolysis technologies can be grouped into those for fast and
47 slow pyrolysis processes. Fast pyrolysis is characterized by high heating rates ($>10^3$ °C
48 s^{-1}), short residence times in the reactor (up to 3s) and rapid quenching of the volatile
49 products [110]. These conditions minimize secondary reactions and lead to high TPO
50 yields [3,111]. Thus, the most common fast pyrolysis technologies are bubbling [112-
51 114] and circulating fluidized beds [5], spouted beds [8,115,116], and rotating cone and
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ablative reactors [117,118]. Figure 3 shows a scheme with the main fast pyrolysis technologies. Moreover, the main features of these reactor designs have been summarized in Table 2.

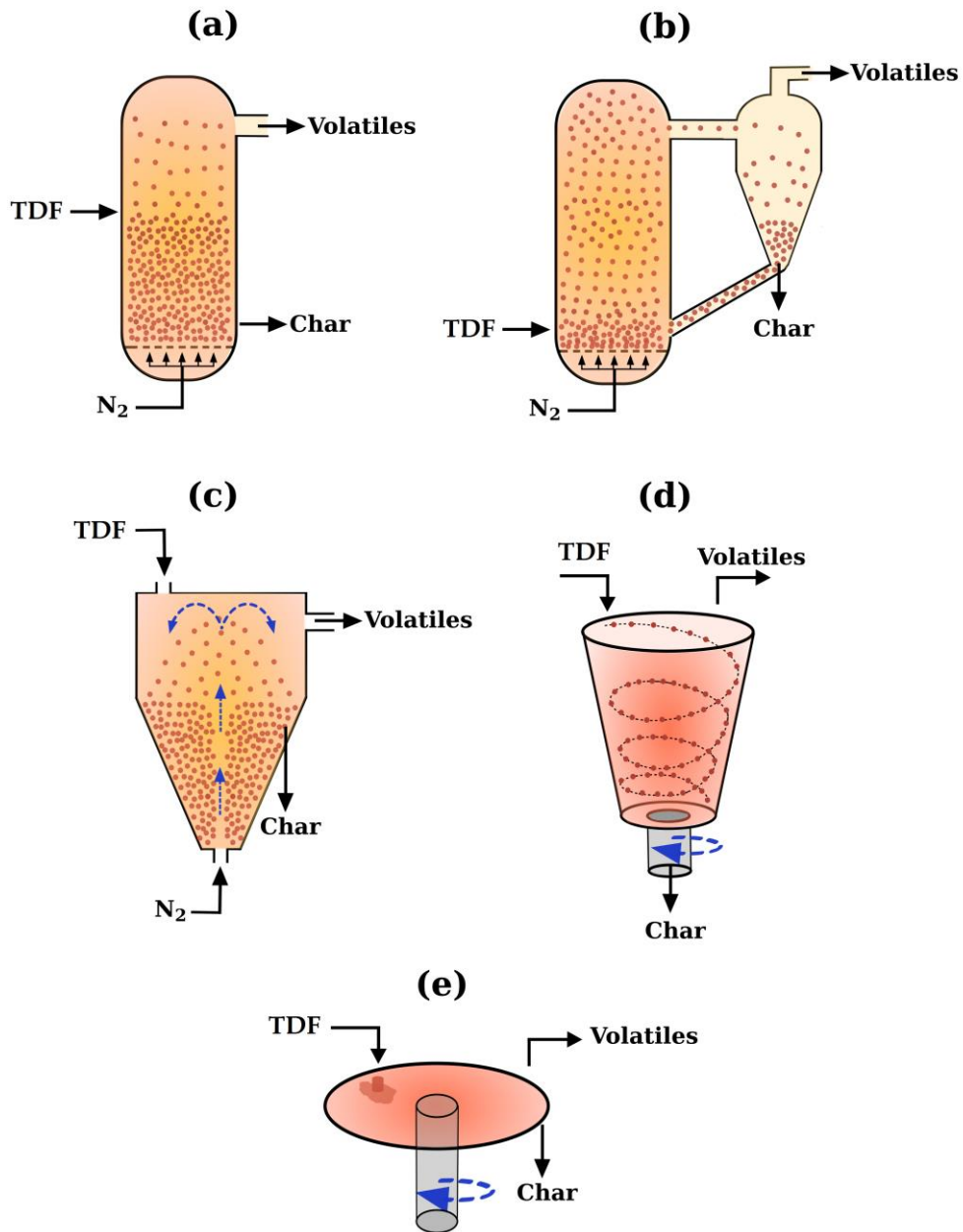


Figure 3. Different fast pyrolysis reactors applied in waste tyre pyrolysis. Bubbling fluidized bed (a), circulating fluidized bed (b), spouted bed (c) rotating cone (d) and ablative reactor (e).

1 In the slow pyrolysis processes, tyre particles undergo low heating rates (usually
2 between 5 and 50 °C min⁻¹) and the residence times of the solid and volatile compounds
3
4 are generally high (above 10 s). Furthermore, slow pyrolysis processes are commonly
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6 operated in batch regime. Thus, secondary reactions are promoted and lower yields of
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8 TPO and higher of solid residue and gases are obtained [49]. The fixed bed reactor is
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10 the most common technology for slow pyrolysis [55,119,120]. In addition, there are
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12 other technologies, such as auger reactors [121-124], rotary ovens [9,125,126] and
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14 microwave reactors [53,127,128], whose features are intermediate between those of fast
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16 and slow pyrolysis ones. Figure 4 summarizes slow and intermediate pyrolysis reactors.
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20 Among the process parameters in pyrolysis, final temperature is the most influential one
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22 [3]. As widely reported in thermogravimetric studies, waste tyre pyrolysis takes place
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24 between 300 and 500 °C [129-132]. Therefore temperatures around 500 °C are required
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26 to ensure complete devolatilization of the rubbers contained and these temperatures are
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28 the optimum ones for the maximization of TPO production [6,8,11,57,133]. It is to note
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30 that higher temperatures favor secondary reactions leading to gas production, and higher
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32 yields of char are obtained at temperatures below 500 °C, as tyre rubber is not fully
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34 converted [49]. The influence of temperature is usually less significant in batch reactors
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36 operating with low heating rates, given that waste tyres usually reach final pyrolysis
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38 temperature when they are almost completely degraded, which reduces its effect on
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40 product distribution.
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44 Although the influence of pressure is not so remarkable, the positive effect of
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46 performing tyre pyrolysis under vacuum conditions has been reported by different
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48 authors [52,133-136]. Thus, the interest of vacuum conditions lies in the minimization
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50 of secondary reactions and the enhancement of the devolatilization process, which
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52 improves TPO yield and the quality of the residual carbon black. The influence of tyre
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particle size has also been described in the literature. Thus, an increase in size usually leads to a reduction in TPO production [5,137]. Nevertheless, an optimum tyre particle size should be careful selected, as tyre grinding is an energy demanding process.

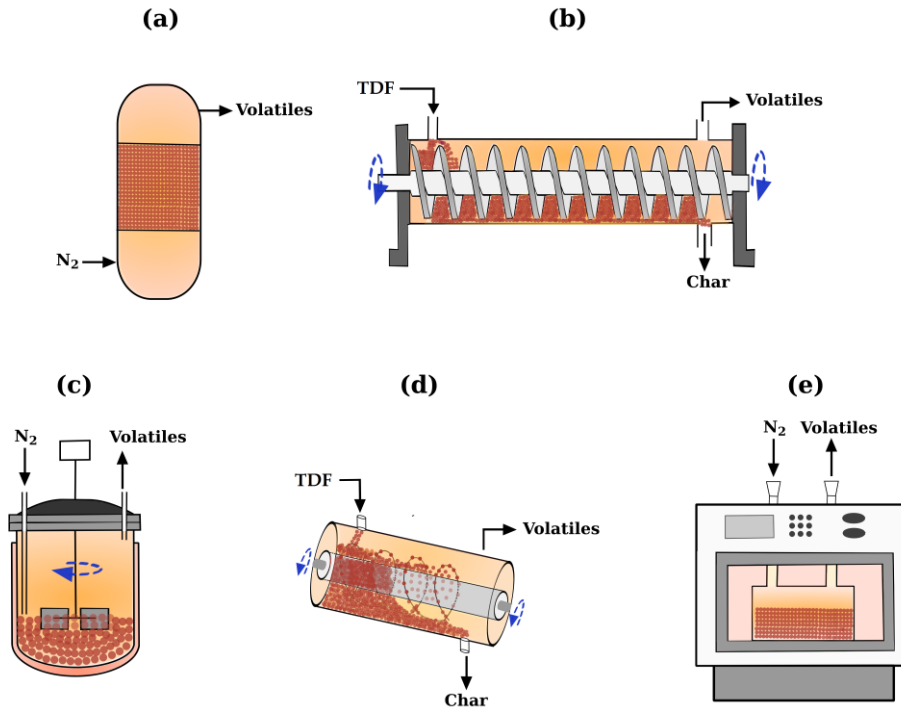


Figure 4. Different slow/intermediate pyrolysis reactors used for waste tyre pyrolysis. Fixed bed (a), auger reactor (b), stirred reactor (c), rotary oven (d) and microwave reactor (e).

In the following sections, the main features of the most relevant pyrolysis technologies are briefly revised, and aspects related to their interest and application in the in situ catalytic pyrolysis are also mentioned.

Table 2. Characteristics of the main technologies applied in tyre catalytic pyrolysis

Technology	Characteristics	Operation temperatures	Heat transfer	Heating method	Gas residence time	Scale-up
Fixed Bed	· Widely applied in WT pyrolysis	350-600 °C	Slow	Indirect	10-40 s	Difficult

	<ul style="list-style-type: none"> · Operating under batch regime · Easy design and operation · No limitation in WT particle size · Heat transfer limitations as scale is increased · Poor heat transfer rate · Complex control of operating conditions · Difficulties for operating in a continuous regime 		(5-40 °C min ⁻¹)	heating		
Fluidized bed	<ul style="list-style-type: none"> · Short residence time of volatiles · High heat and mass transfer rates · Bed isothermicity · Fast pyrolysis regime is attained (high TPO yields) · Continuous operation is possible · Complex design and operation · High investment required · Very small particle sizes of WT required 	350-800 °C	Fast (> 10000 °C min ⁻¹)	Direct with use of heating carrier and indirect heating	1-5 s	Easy
Spouted bed	<ul style="list-style-type: none"> · Alternative gas-solid contact method to fluidized beds · Very short residence time of the volatiles · Very high heat and mass transfer rates · Bed isothermicity · Fast pyrolysis regime is attained (high TPO yields) · Continuous operation is possible · More intense solid circulation than in fluidized beds · Coarse and irregular particles can be handled 	400-600 °C	Fast (> 10000 °C min ⁻¹)	Direct with use of heating carrier and indirect heating	30-500 ms	Medium
Rotary kiln	<ul style="list-style-type: none"> · Simple design and construction · WT is brought in contact with the reactor hot wall · Reactor wall transfer heat to the particles · Continuous operation is possible · Operation without heat carrier (sand) · Poor heat transfer efficiency (low TPO yields) · Poor gas-solid contact (catalyst performance limited) 	400-600 °C	Slow-Intermediate (≈100 °C min ⁻¹)	Direct with hot gases or indirect contact	≈ 30 s	Easy
Auger	<ul style="list-style-type: none"> · Simple design and construction · Solid residence time is easily controlled · Continuous operation is possible 	400-550 °C	Intermediate (1000-100 °C min ⁻¹)	Direct with hot gases or indirect	5-30 s	Medium

	<ul style="list-style-type: none"> · Operation without heat carrier (sand) · High energy consumption the mechanical drive 			contact		
Microwave	<ul style="list-style-type: none"> · Enhanced heat transfer into the tyre particles · Absence of temperature gradients in the reactor · Carbon black is a good microwave absorbent (heat carrier) · Difficulties for operating in continuous regime · Heat carrier is not needed · High electric power required 	400-700 °C	Slow-Intermediate (1-150 °C min ⁻¹)	Direct with a microwave field	20-60 s	Difficult

3.1. Fixed bed reactors

Fixed bed reactors have been widely applied in the waste tyre pyrolysis process, especially in laboratory scale units operating in batch regime, and they are in fact the most used reactors in laboratory and bench scale studies [49]. In these reactors, the tyre sample is usually subjected to a relatively slow heating rate (5-40 °C min⁻¹), while the volatiles formed are purged using an inert flow stream [4,54,55,119,138]. The main interest of fixed bed reactors lies in their easy design and operation, as they have no limitation regarding tyre particle size. However, these reactors are characterized by their poor heat transfer rate and complex control of operating conditions, especially temperature. In addition, their scaling up is a remarkable challenge, due to, on the one hand, severe heat transfer limitations as the reactor volume is increased [39] and, on the other hand, great difficulties for continuous operation. Therefore the low specific capacity limits the economic interest of fixed bed reactors for full scale applications.

Cunliffe and Williams [4] studied the influence of final temperature between 450 and 600 °C and a heating rate of 5 °C min⁻¹ using a fixed batch reactor with a capacity of 3 kg of waste tyres. Akkouche et al. [120] studied the batch pyrolysis of truck tyres in a laboratory unit (300 g), with the influence of heating rate in the 5 to 24 °C min⁻¹ range being analyzed. Similarly, Mkhize et al. [119] analyzed the influence of final

1 temperature and heating rate in the batch pyrolysis in a fixed bed reactor (40 g) in the
2 350 to 550 °C and 5 to 25 °C min⁻¹ ranges, respectively. Islam et al. [139] developed a
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4 pseudo-continuous fixed bed reactor operating by charging 750 g batches, in which they
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6 studied the influence of temperature, tyre particle size and gas residence time.
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9 In the catalytic pyrolysis studies performed in fixed bed reactors, the catalysts is
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11 commonly used in situ, and therefore physically mixed with the tyre material. However,
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13 this strategy has several drawbacks, such as the excessive coke deposition and the
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15 difficulties to separate the catalyst and solid product at the end of the reaction [140].
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17 Demirbas et al. [141] studied the pyrolysis of waste tyres om a Na₂CO₃ catalyst in situ
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19 at 600 °C. Ahoor and Zandi-Atashbar [142] analysed the influence of using in situ a
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21 MgCl₂ catalyst in a fixed bed reactor (10 g of sample) operating in batch regime with a
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23 heating rate of 20 °C min⁻¹. He et al. approached the production of light olefins in a
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25 fixed bed batch reactor (1 g of tyre sample) using γ -Al₂O₃ and nano-HZSM-5 as in situ
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27 catalysts [143].
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33 **3.2. Fluidized beds**

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35 The short residence time of the volatiles, high heat transfer rates and bed isothermicity
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37 ensure a fast tyre particle heating and degradation under controlled and reproducible
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39 conditions. Thus, fluidized bed reactors operate under fast pyrolysis conditions, which
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41 enhances TPO yield [3]. In addition, this technology eases continuous operation, which
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43 is of great relevance for the scale up of the process. However, these reactors are of
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45 complex design and operation and, furthermore, they require higher investment than
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47 other technologies, which hindered their utilization. Another point that should be
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49 carefully assessed is the small tyre particle size required.
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53 The application of fluidized bed reactors for waste tyre pyrolysis was originally
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55 proposed by Kaminsky [144], and their process known as Hamburg reached a
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1 remarkable degree of development, with different pilot plants (up to 120 kg h⁻¹) being
2 constructed for the pyrolysis of waste tyres [112,145] and plastics [146]. Other relevant
3 contributions of this research group were the use of in situ catalyst for the cracking of
4 polymeric wastes [147,148] or the pyrolysis under steam atmosphere for the selective
5 production of light olefins [149]. Dai et al. [5] studied the continuous pyrolysis of waste
6 tyres in a circulating fluidized bed reactor with a capacity of 5 kg h⁻¹, with their study
7 focusing on the influence of temperature and gas residence time in the 360-810 °C and
8 1-5 s ranges, respectively. Recently, Mkhize et al. [150] published a relevant study in
9 which the performance of a bubbling fluidized bed reactor was compared with that of a
10 fixed bed and a conical spouted bed. Thus, the influence of residence time and heating
11 rate on product yields and their composition was evaluated using the same tyre material.
12 Williams and Brindle [151] studied the continuous pyrolysis of tyres (220 g h⁻¹) in a
13 fluidized bed reactor between 450 and 600 °C. More recently, Raj et al. [152] performed
14 a wide experimental study on the pyrolysis of waste tyres in a bench scale unit provided
15 with a fluidized bed reactor operating in continuous regime (up to 25 g min⁻¹ of feed).
16 The continuous reaction system developed by Choi et al. [113] consisted in a two-stage
17 pyrolyzer, i.e., an auger reactor, in which the tyre material was partially devolatilized
18 between 230 and 450 °C, and a fluidized bed reactor operated at 510 °C.
19
20 The interest of fluidized beds for catalytic pyrolysis is related to the excellent gas-
21 particle contact and mixing regime for the solid and, moreover, strategies of catalyst
22 circulation and continuous regeneration may be implemented. Thus, continuous
23 operation may be performed, which is of great relevance for the large scale
24 implementation of the process. However, catalytic pyrolysis of tyres has scarcely been
25 studied in fluidized bed reactors and, in fact, solely Williams and Brindle [82,85]
26 studied the catalyst pyrolysis of tyres in a bench scale fluidized bed reactor with
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1 continuous feed. The influence of using HZSM-5 and HY zeolites in situ was evaluated
2 at 500 °C. In addition, Wang et al. [43] studied the co-pyrolysis of waste tyres and in
3
4 line catalytic cracking over HZSM-5 zeolite in a bench scale plant.
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7 **3.3. Rotary kilns**

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9 The main interest of rotary kilns lies in their simple design and construction.
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11 Furthermore, the residence time of the solid can be easily controlled by varying the
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13 ration speed, but their poor heat efficiency is their main shortcoming.
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17 Recently, Antoniou and Zabaniotou [153] reached a capacity of 100 kg h⁻¹ in a plant
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19 provided with a rotary kiln reactor. Ayanoglu and Yumrutas [125] studied waste tyre
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21 pyrolysis process in a pilot plant with a capacity of 4 tones (per batch) equipped with a
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23 rotary kiln reactor and operating at 400 °C under optimum conditions. Moreover,
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25 Syamsiro et al. [154] studied the influence of rotating speed on the pyrolysis of waste
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27 tyres in a bench scale unit
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31 The application of rotary ovens to waste tyre catalytic pyrolysis is limited. Luo and
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33 Feng [9] developed a process based on a rotary oven with continuous tyre feed (200 g
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35 min⁻¹), in which a blast-furnace slag was used as both heat carrier for the pyrolysis
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37 process and catalyst. Thus, this process involves a contribution from a sustainable point
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39 of view as an industrial byproduct is upgraded as heat carrier and catalyst.
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43 **3.4 Auger reactors**

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45 The auger reactor is a versatile pyrolysis technology that allows operating from fast to
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47 slow pyrolysis. In spite of being more complex than conventional rotary kilns, it can be
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49 considered of simple design. Moreover, the mixing regime created by the rotating screw
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51 ensures good heat transfer rates and suitable control of process conditions. Thus, this
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53 reactor design has reached a relatively high degree of development and has been
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55 commonly applied to the pyrolysis of biomass and different solid wastes [155].
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1 Martinez et al. [121,122,156,157] developed an auger pilot plant with a capacity of 15
2 kg h⁻¹ of continuous tyre feed. Moreover, the same authors also studied the effect of
3
4 using Ca based catalyst in situ in the same reaction unit by co-feeding mixtures of waste
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6 tyres and biomass [158]. Xu et al. [159] proposed a low temperature pyrolysis process
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8 in a screw kiln reactor for the production of asphalt from waste tyres.
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10 11 **3.5. Spouted beds**

12 Spouted beds are an alternative gas-solid contact method to fluidized beds, with both
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14 reactors sharing some characteristics, such as high heat transfer rates, bed isothermicity,
15
16 and good gas-solid contact and solid mixing regime [160]. The main differences
17
18 between spouted and fluidized beds are related to the solid phase dynamics, with more
19
20 intense solid circulation pattern in spouted beds, which eases the handling of coarse and
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22 irregular particles [161]. Accordingly, the tyre grinding requirement is not so strict in
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24 the case of the spouted bed reactor, which is of great relevance for the overall economy
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26 of the process. Interestingly, the gas residence time is shorter in spouted beds than in
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28 fluidized beds and heat and mass transfer rates higher [162]. These features allow
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30 operating under fast pyrolysis conditions and specifically the short residence times limit
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32 secondary reactions in the gas phase, which leads to an increase in the yield of pyrolysis
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34 oil [8,163,164]. Furthermore, these conditions are of special interest in waste tyre
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36 pyrolysis, given that limonene yields are enhanced [11,58]. It is to note that a biomass
37
38 pyrolysis pilot plant with a spouted bed reactor was successfully scaled up to 25 kg h⁻¹
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40 [165,166]. The recent incorporation of the fountain confiner to conical spouted beds has
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42 greatly improved its capacity for handling fine materials, allowing a successful
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44 application in drying process [167,168]. Moreover, this alternative reactor design has
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46 also demonstrated to be suitable as catalytic reactor in biomass gasification [169,170],
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48 as its outstanding gas-solid contact allows increasing the efficiency of the process using
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1 the catalyst in situ. The excellent features of conical spouted beds, equipped with recent
2 improvements, make this technology a suitable alternative for the thermal and catalytic
3 pyrolysis at full scale.
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7 Initially, the pyrolysis of waste tyres was studied in batch regime in a bench scale unit
8 provided with a conical spouted bed reactor [116]. Subsequent studies in continuous
9 regime (3 g min^{-1}) analyzed the influence of operating conditions and tyre rubber
10 composition on products yields and composition [11,115].
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14 The lack of segregation together with the mixing regime and excellent gas-solid contact
15 are interesting features for the in situ utilization of a catalyst in spouted beds, as was
16 confirmed in the catalytic valorization of different solid wastes [169,171,172].
17
18 Arabiourrutia et al. [86,87] analyzed the performance of HY and HZSM-5 zeolites in
19 the pyrolysis of waste tyres in a conical spouted bed reactor in the 425 to 500 °C range.
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21 **3.6. Microwave reactors**

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24 The interest of microwave pyrolysis lies in the enhanced heat transfer into the tyre
25 particles together with the **fact that it allows** operation under isothermal conditions in the
26 reactor, **which is** associated with the homogenous heat distribution within the bed
27 [53,173]. Moreover, this technology is especially interesting for the valorization of
28 waste tyres, as the carbon black included in their formulation is an excellent microwave
29 absorbent, and therefore no carbonaceous material is required as in the treatment of
30 other polymeric materials [174].
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34 Song et al. have studied the microwave pyrolysis of a waste tyre in a reactor operating
35 in batches with samples of 30 g [53,128,173,175]. Thus, these studies focused on the
36 influence operating conditions (such as specific microwave power) have on the
37 composition of TPO and gaseous products. Moreover, these authors analyzed the effect
38 the presence of steel wires and the promoted discharges have on the microwave
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pyrolysis of waste tyres [176]. Undri et al. [127] used a similar microwave batch reactor in the pyrolysis of waste tyres, with the reactor volume being 1 liter.

The catalytic co-pyrolysis of waste tyres with different biomass wastes, such as soapstock and sawdust, was studied in a laboratory scale microwave reactor (5 g of sample) with HZSM-5 zeolite catalysts placed in situ [177,178].

3.7. Other reactor designs

The research group headed by Prof. Roy developed vacuum reactors for the pyrolysis of different solid wastes including waste tyres [134,135,179,180]. Thus, the process was successfully scaled up and operated in continuous regime with a tyre feed of up to 200 kg h⁻¹. More recently, Zhang et al. [52] studied the batch vacuum pyrolysis of waste tyres using Na₂CO₃ and NaOH as in situ catalysts in the 450 to 600 °C range.

The ablative reactor is a well-developed technology for biomass fast pyrolysis [181], and Helleur et al. [117] evaluated its applicability for waste tyres. Although stirred reactors have been commonly used in the pyrolysis of waste plastics [77], they have also been applied in a few cases to waste tyre pyrolysis. Thus, Ayanoglu and Yumrutas [182] studied pyrolysis of waste tyres in a stirred reactor operating in batch regime at 450 °C. In this study, two different catalysts were used in situ, CaO and natural zeolite. Li et al. [183] also studied the pyrolysis of waste tyres in a batch stirred reactor (150 g of sample) with a heating rate of 15 °C min⁻¹ in the 430 to 500 °C range. Thus, they studied the effect of using in situ different catalysts, as are ZSM-5, USY, β, SAPO-11, and ZSM-22. Abbas-Abadi and Haghghi [184] used similar experimental equipment in the batch pyrolysis of 100 g of tyres at 450 °C on different catalyst, i.e., FCC, Ga/FCC, HZSM-5 and mordenite. Tang and Huang [185,186] proposed the use of plasma technology for the valorization waste tyres by pyrolysis. The continuous (up to 0.5 g

1 min⁻¹ in the feed) experimental unit led to high gas yields with remarkable hydrogen
2 contents due to the high temperatures reached.
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4 Zeaiter et al. [187] studied tyre pyrolysis and in line catalytic cracking of the volatile
5 stream on different catalysts (H β , USY and TiO₂) in a batch (1 g) solar concentrator
6 reactor.
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11 **3.8. Contact method with the catalyst**

12 The contact between tyre pyrolysis volatile products and the catalyst can be performed
13 following two different strategies, as are the use of the catalyst in the same reactor, i.e.,
14 in situ catalytic pyrolysis, and the use of a second reactor for the in line catalytic
15 cracking of pyrolysis volatiles. **Figure 5 summarizes the in situ and ex situ catalytic**
16 **pyrolysis strategies.**
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27 The main interest of in situ catalytic pyrolysis is related to the simplicity of reactor
28 design and operation. However, the in line catalytic treatment of pyrolysis volatiles
29 have several advantages compared to the in situ one, as are: i) an independent
30 temperature optimization of pyrolysis and catalytic treatment steps can be implemented,
31 ii) the direct contact between the impurities contained in waste tyres and the catalyst is
32 avoided, as the impurities remain in the pyrolysis reactor, iii) a more efficient and
33 reproducible contact with the catalyst is achieved in an independent catalytic reactor, iv)
34 the deposition of carbonaceous residue on the catalyst and its deactivation is minimized,
35 and v) the recovery and regeneration of the catalyst is also eased.
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48 The in line catalytic cracking of tyre pyrolysis derived volatiles has been mainly studied
49 in fixed bed reactors, with this reactor being combined with different designs for the
50 pyrolysis step. Thus, the most studied configuration is made up of two fixed bed
51 reactors for the pyrolysis and catalytic cracking steps operating in batch regime
52 [81,85,188-191]. Kordoghli et al. [81,99,188] studied the pyrolysis of batches of 30 g of
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scrap tyres at 500 °C and the in line cracking of the stream leaving the first reactor on different catalysts, such as MgO, Al₂O₃, CaCO₃, and zeolite ZSM-5. The experimental unit was of great simplicity, as both beds were located within the same oven. The research group by Jitkarnka [93,95,96,189,192,193] has widely studied the catalytic pyrolysis of waste tyres in an experimental unit consisting of a batch fixed bed reactor operating at 500 °C for the pyrolysis step (30 g of tyre) and another one for the catalytic treatment at 350 °C. Thus, these authors tested several catalysts, such as HZSM-5, HMOR, HY, HBETA and pyrolysis char, and studied the effect of different metal loads (Ni, Pt or Cu). Shen et al. [194-196] studied the batch catalytic pyrolysis of waste tyres on HZSM-5 and HY zeolites in an experimental unit made up of two fixed bed reactors, with the pyrolysis step being performed at 500 °C and the catalytic cracking in the 350-500 °C range, and different catalyst/tyre ratios being also used. Williams and Brindle [85,190] studied the batch pyrolysis (200 g of tyre) at 500 °C and the in line cracking of pyrolysis volatiles on HY and HZSM-5 zeolites in the 430 to 600 °C range. Moreover, the same authors [82,151] studied the batch pyrolysis of waste tyres in a fluidized bed reactor followed by the catalytic cracking of the volatiles on HY and HZSM-5 zeolites in a fixed bed reactor.

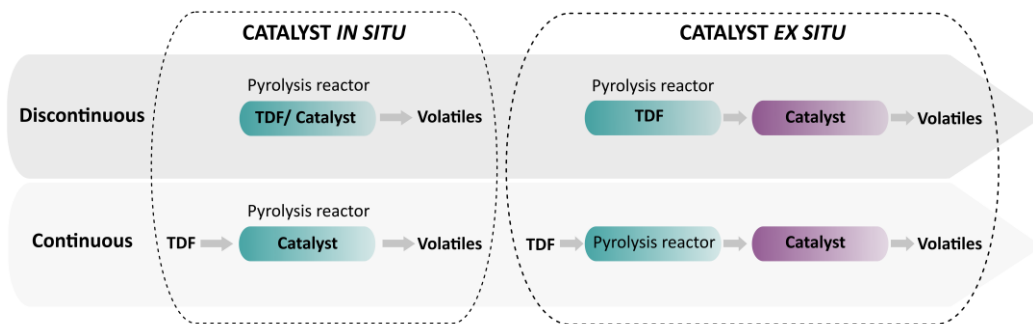


Figure 5. Scheme of the ex situ and in situ waste tyre catalytic pyrolysis processes.

Choi et al. [94] developed an original process consisting of two in line reactors operating in continuous regime (a feed of 5 g min⁻¹). The first one was an auger reactor

1 in which a partial degradation of waste tyres took place at 340 °C, whereas the second
2 one was a fluidized bed reactor operating at 520 °C with different catalysts, such as
3 dolomite and olivine. In a recent study, the same authors tested the influence different
4 bed additives in the fluidized bed reactor (CaO, Fe, calcined olivine, FeO) have on the
5 TPO sulfur content reduction [106].
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11 **4. Catalysts for tyre pyrolysis**

12 Many catalysts has been applied in the tyre pyrolysis process in order to improve the
13 quality of the TPO and gaseous products, increase the content of high value added
14 chemicals, such as aromatics and light olefins, and reduce sulfur containing compounds
15 [39]. Although microporous acid zeolites have been the most studied catalysts, other
16 ones such as mesoporous acid materials and basic catalysts have received attention in
17 the literature [197]. Thus, the most significant properties of these catalysts have been
18 summarized in this review for a better understanding of their role in the tyre pyrolysis
19 reaction mechanism and their influence on the product distribution obtained.
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33 **4.1. Acid catalysts**

34 Zeolites are microporous acid materials that allow shape-selective catalysis due to their
35 unique features: i) uniform pore diameter and ii) pores in the range of molecular
36 dimensions [198]. In fact, the compounds involved in tyre pyrolysis are of the same
37 order of magnitude of zeolite pores and cavities, lending to the zeolite the properties of
38 reactant shape selectivity, product shape selectivity and transition state selectivity.
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48 Thereby, its pore dimensions and steric limitations control the products that penetrate
49 inside the zeolite, allow their reaction there, as well their exit from the zeolite.
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51 Therefore, the restrictions of each zeolite to component diffusion have been identified in
52 the literature based on their shape selectivity [199,200], i.e., the zeolite pore sizes
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(small, medium or large pores) have been related to the products that may diffuse into the porous structure according to the compound kinetic diameter.

In addition to shape selectivity, acidity is one of the main properties of zeolite catalysts. Three aspects should be distinguished into the term of acidity: the nature (Brønsted or Lewis), the density and the strength of the acid sites. On the one hand, Brønsted acid sites are the ones that bind OH groups between Al and Si tetrahedra and Lewis sites are generally related to the presence of extra framework aluminium, whose density increases as Al^{3+} content in the zeolite is increased [201]. On the other hand, an isolated Al-OH surrounded by Si^{4+} atoms is identified as the acid site with the highest acid strength [198]. Therefore, Si/Al ratio can be used for adjusting zeolite acid density, as well as its acid strength, i.e., as Al^{3+} content is increased the acid density increases to the detriment of the acid strength and vice versa. Besides, the migration of Al^{3+} outside the lattice to form extra framework aluminium species, and consequently Lewis acid sites, is more probable when a high Al^{3+} content zeolite is used. The acid sites of the catalyst play a major role in the catalytic cracking mechanism via β -scission reactions, with cracking initiation taking place with the formation of carbenium ion by the addition of a hydride ion to an olefin on Brønsted acid sites or the abstraction of a hydride ion to a paraffin on Lewis acid sites [202]. In addition to the C-C bond cleavage, cracking mechanism involves isomerisation, hydrogen transfer, cyclization, aromatization or condensation reactions that are also activated by zeolite acid sites.

Thus, taking into account the different pore dimensions, structures and acidities of the zeolites, various zeolite types have been used for tyre pyrolysis, with HZSM-5 and HY being the most studied ones [39,197].

Figure 6 shows the structures of the main zeolites used in tyre pyrolysis. HZSM-5 is a 10 membered-ring zeolite and has a three-dimensional pore structure with pores in the

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range of 5.1x5.5 Å and 5.3x5.6 Å, whereas HY is a 12 membered-ring zeolite with a three-dimensional pore structure and pore channels of 7.4x7.4 Å [203]. Therefore, one of the differences between these zeolites lies in their shape selectivity caused by their different pore sizes, with the larger molecule diffusing into the HZSM-5 type catalyst being of a size equal to C₁₀ molecule, such as naphthalene [85]. However, the larger pores of the HY zeolite allow the diffusion of C₁₂ compounds, such as dimethylnaphthalene [199].

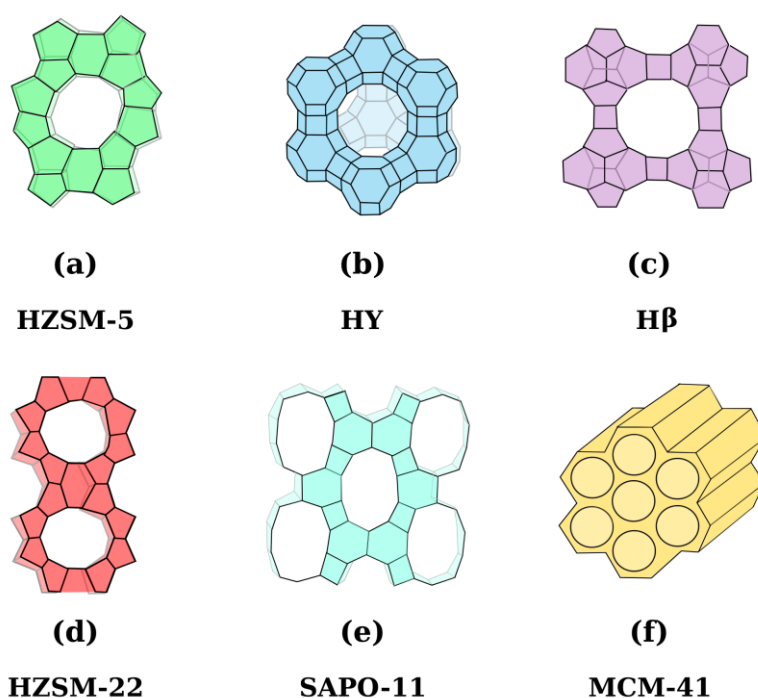


Figure 6. Structures of the main zeolites. HZSM-5 (a), HY (b), Hβ (c), HZSM-22 (d), SAPO-11 (e) and MCM-41 (f).

Besides, the shape-selectivity of the HZSM-5 zeolite favors monomolecular cracking [204], minimizing hydrogen transfer reactions and subsequent cyclization and aromatization reactions. Apart from its shape-selectivity, the higher aromatization capacity of the HY zeolite compared to the HZSM-5 zeolite is also attributed to its higher acid density [86,183,190], favoring BTX and PAH formation reactions.

1 Furthermore, the diffusion of PAH hydrocarbons formed inside the pore structure of the
2 zeolites is hindered by steric limitations, and they undergo condensation reactions to
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4 form coke deposits on the acid sites, causing catalyst deactivation [85].
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7 Apart from HY and HZSM-5, other zeolites have been studied in literature, such as H β ,
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9 HZSM-22, HMOR and SAPO [183,184,189,205]. H β has three-dimensional structure,
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11 with its pore sizes being 6.6x6.7 Å and 5.6x5.6 Å, which are halfway between those of
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13 HZSM-5 and HY [203]. Thereby, the H β zeolite shows an intermediate performance
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15 between HY and HZSM-5 catalysts in tyre pyrolysis [183]. Regarding the HMOR
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17 zeolite, it has a two-dimensional structure with pore channel sizes of 6.5x7 Å and
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19 5.7x2.6 Å [203], but, given the small size of the latter for most molecule diffusion, it is
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21 commonly considered as a one dimensional zeolite [189]. Although the large pores of
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23 this zeolite allow bimolecular cracking reactions, the aromatic yields obtained using this
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25 catalyst [184,189] are rather low, presumably due to its one dimensional structure that
26
27 eases product diffusion through microporous channels and minimizes secondary
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29 reactions of isomerisation, cyclization, hydrogen-transfer and aromatization. Li et al.
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31 [183] studied also SAPO-11 and ZSM-22 zeolites with intermediate pore sizes and
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33 Si/Al ratios of 4 and 58, respectively. This difference in catalyst acidity leads to higher
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35 gas and aromatic yields when the SAPO-11 catalyst is used, as its higher acidity
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37 enhances both primary and secondary cracking reactions.
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46 Nevertheless, considering the compounds formed in tyre pyrolysis, access to zeolite
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48 micropores is considerably restricted due to the limitations for the diffusion of these
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50 large molecules. Moreover, this low mass transfer rate may be responsible for aromatic
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52 condensation reactions to form coke deposits on the catalyst active sites. Thereby,
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54 increasing attention has been paid in the literature to ordered mesoporous materials
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56 (OMM), such as MCM-41 and SBA-15 [206]. Due to the bulky nature of bio-oil
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1 compounds and waxes, OMM have been widely applied in biomass and plastic
2 pyrolysis and, although they are not shape-selective catalysts and lead to a wide product
3 distribution, compound diffusion through the pore structure is enhanced and catalyst
4 deactivation is attenuated [77,78,207]. Given that tyre pyrolysis leads to a high aromatic
5 content in the volatile stream formed, OMM have been applied as metal support for
6 bifunctional catalyst [193,208], as aromatic compound hydrogenation occurs on metal
7 sites and subsequent cracking or ring opening on acid sites. The same authors studied
8 also bifunctional catalysts using zeolites as acid phase [97,205], and observed an
9 increase in the reactivity of aromatic compounds, as well as sulphur removal by the
10 catalyst metal sites.

11 Disordered large pore structure acid materials, such as Al_2O_3 [81,209,210], expanded
12 perlite [211] or Criteriom 424 [212], are inexpensive materials and they have been used
13 for tyre pyrolysis. However, these catalysts have weak and few acid sites compared to
14 zeolites or OMM, and have therefore a low activity for cracking reactions, as well as for
15 secondary isomerization, cyclization or aromatization reactions.

16 **4.2. Base catalysts**

17 Although base catalysts are not as active as acid ones for C-C bond cleavage, they show
18 activity for hydrogenation, isomerization, alkylation or for reactions involving
19 heteroatoms to promote double bond migration in unsaturated compounds [78,213].

20 Base active sites are also classified as Brønsted and Lewis base sites, as the former
21 accepts a proton from the reactant and the later donates an electron pair to the reactant
22 [214]. These base catalyst active sites are generated under high temperature treatments,
23 with metal oxides leading to the removal of the contaminants adsorbed under
24 atmospheric conditions, such as CO_2 or H_2O , and hydroxides and carbonates to
25 decomposition reactions [215].

1 Base catalysts have shown good performance for biomass catalytic pyrolysis leading to
2 decarbonylation and deoxygenation reactions and improving the quality of the bio-oil
3 obtained [78]. In addition, base catalysts show good activity for catalytic cracking of
4 plastics, such as polystyrene, as they promote cracking initiation via random scission (as
5 in thermal pyrolysis) or via the formation of carboanions by the elimination of hydrogen
6 atoms from the polystyrene adsorbed on base sites, accelerating plastic
7 depolymerisation [216]. Following a similar cracking initiation mechanism, tyre
8 pyrolysis on a base catalyst undergoes secondary reactions, such as isomerisation,
9 alkylation, decomposition or cleavage of carbon-heteroatom bonds [213].

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21 Amongst the base catalysts, alkali metal earth oxides (MgO and CaO) have been the
22 most used ones for catalytic tyre pyrolysis [81,209,213,217], as they enhance cracking
23 activity and improve the quality of the liquid obtained. Similarly, carbonates,
24 hydroxides or natural materials, such as dolomite, olivine or red mud
25 [52,84,94,141,218], have also been tested. It is to note that dolomite and olivine show
26 good activity for sulphur removal, leading to a liquid fraction with low sulphur content
27 [94]. Likewise, MgCl₂ has been proven to be active for desulphurization, and allows
28 obtaining tyre pyrolysis oil with low sulphur content [142].

29 **5. Effect of catalyst nature and process conditions on product distribution**

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This section analyses the most relevant results obtained in waste tyre catalytic pyrolysis.
The aim is to assess the influence of process parameters on the product distribution of
catalytic pyrolysis. Thus, three subsections have considered, the first one analyzes the
role played by the catalyst nature, whereas the following two sections deal with the
influence of the main process parameters, as are temperature and catalyst/tyre ratio.
Moreover, Tables 3 and 4 summarize the main results reported in the in situ and in line

1 waste tyre catalytic pyrolysis, respectively. It should be noted that in these tables the
2 mass of catalyst used was not included in the char yield values reported.
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5 **5.1. Influence of catalyst type**

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8 This section analyzes the influence of the catalyst nature on the product distribution
9 obtained in waste tyre pyrolysis. However, the studies performed in the literature have
10 been carried out under a wide range of experimental conditions of temperature,
11 residence time, heating rate, reactor design and catalyst/tyre ratio. These differences
12 hinder a direct comparison of the literature results, as they greatly condition a
13 comparison of catalysts' performance. Accordingly, some representative results for
14 different catalysts under the same conditions have been selected in order to obtain
15 relevant conclusions. In addition, the studies selected also include product yields
16 obtained without catalyst, as they allow for a better understanding of the role played by
17 each catalyst. Thus, Figure 7 summarizes the results obtained by different authors in the
18 catalytic pyrolysis of waste tyres. As observed, acid catalysts promote gas production
19 by TPO cracking reactions and improve tyre conversion, especially at low temperatures,
20 but base catalysts lead to an increase in TPO yield.
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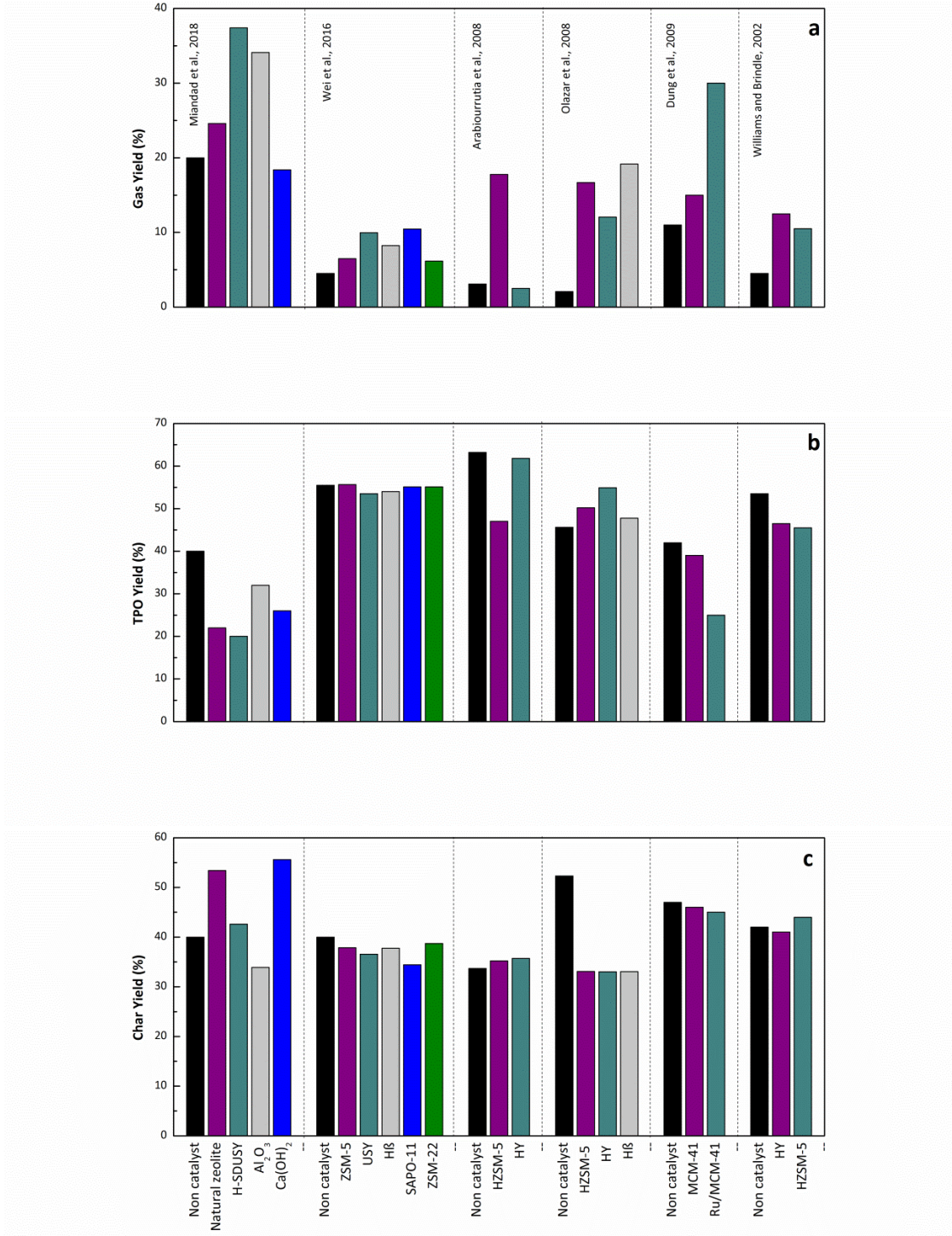


Figure 67 Influence of different catalysts in the yield of gases (7a), TPO (7b) and char (7c) in waste tyre pyrolysis. Miandad et al. 2018 [84], Wei et al. 2016 [183], Arabiourrutia et al. 2008 [87], Olazar et al. 2008 [219], Dung et al. 2009 [193] and Williams and Brindle 2002 [82].

1 Thus, Miandad et al. [84] studied the batch catalytic pyrolysis of waste tyres in a 1 kg
2 fixed bed reactor at 450 °C (heated at 10 °C min⁻¹) with a catalyst/tyre ratio of 0.1. The
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4 results obtained in thermal pyrolysis were compared with those obtained using natural
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6 and H-SDUSY zeolites, Ca(OH)₂ and Al₂O₃ catalysts. These authors observed a
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8 remarkable reduction of TPO yield with all the catalyst studied when compared with the
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10 results obtained in thermal pyrolysis. Furthermore, this decrease is associated with an
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12 increase in the yields of gas and solid products. This reduction was especially relevant
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14 using natural and H-SDUSY zeolites. Thus, the TPO yield decreased from 40 wt.% in
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16 thermal pyrolysis to 22 and 20 wt% when the mentioned zeolites were used.
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22 Williams and Brindle [82,151] analyzed the performance of HZSM-5 and HY catalysts
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24 in the in line cracking (in a fixed bed) of the volatiles obtained in the pyrolysis step
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26 performed in a fluidized bed reactor in the 450 to 600 °C range. For the experiments
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28 without catalyst, the zeolites were replaced with inert ceramic beads of similar size to
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30 the catalyst in the fixed bed reactor. Thus, the use of these zeolites led to an increase in
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32 the gas yield and a reduction in TPO. It is to note that the HY zeolite led to a higher gas
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34 yield than the HZSM-5, 12.5 and 10.5 wt.%, respectively, at 500 °C. In spite of the
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36 severe shape selectivity of the HZSM-5 zeolite, which may selectively promote lighter
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38 compound formation, the HY zeolite has a lower SiO₂/Al₂O₃ ratio, and therefore higher
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40 acidity, which explains the obtained results. It is to note that the catalysts effect on
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42 product distribution in fluidized bed reactors was not as remarkable as that observed by
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44 other authors in fixed bed reactors. This behavior was associated with the short
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46 residence time of pyrolysis volatiles in the fluidized bed reactor, which hinders their
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48 overcracking. In fact, the same authors also studied the performance of the same
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50 catalyst in a fixed bed reactor and reported a much remarkable effect [190].
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The in situ catalytic pyrolysis of tyres on HZSM-5, HY and H β zeolites was studied by Olazar et al. [219] in a fast heating microreactor at 450 °C. These catalysts improved both the TPO and, especially, the gas yield, as tyre conversion greatly improved in relation to the results obtained in thermal pyrolysis, with this result associated with the relatively low pyrolysis temperature used. Among these catalysts, HZSM-5 and H β zeolites led to higher gas yields than HY (16.7, 19.2 and 12.1 wt.%, respectively). These differences are related to the different porous structure and acid properties of the zeolites. It is to note that the presence of strong acid sites on HZSM-5 and H β zeolite catalysts is responsible for the higher conversion of liquid products into gases. Moreover, these authors studied the influence of HY and HZSM-5 zeolites in the situ catalytic pyrolysis in a conical spouted bed reactor at 425 and 500 °C [86,87]. In the same line, the HZSM-5 zeolite led to an increase in the gas yield from 2.0 wt.% obtained in the thermal pyrolysis to 17.8 wt.% in the catalytic one at 500 °C, whereas the TPO yield decreased from 63.2 to 47.0 wt.%. However, the product distribution obtained with the HY zeolite is similar to that reported without catalyst. These authors suggested that the HZSM-5 zeolite promotes the cracking of heavy fractions, whereas the HY zeolite catalyst favors alkylation and aromatization of C₁-C₄ fraction components to give heavier fraction components. This different performance of the catalysts is due to their different shape selectivity.

Table 3. Product distributions obtained by different authors in the in situ catalytic pyrolysis of waste tyres.

Reference	Reactor	Temperature (°C)	Catalyst	Catalyst/tyre ratio	Yields wt.%		
					Gas	TPO	Char
[220]	Fixed bed (150 g)	400	CaC ₂	0.5	34.5	33.5	32
[213]	Fixed bed	400	MgO	-	19.3	27	53.5
		400	CaCO ₃	-	31.9	29.2	38.9

[210]	Fixed bed	400	Al ₂ O ₃	-	21	23.2	55.8
		400	SiO ₂	-	15.5	28.2	56.3
		400	Al ₂ O ₃ +SiO ₂	-	5	14.8	80.2
[142]	Fixed bed (20 g)	407	MgCl ₂	0.114	16.2	38.2	45.6
		487	Thermal pyrolysis	-	24.8	19.8	55.4
[221]	Fixed bed (0.5 g)	450	HZSM-5	1	31	33	36
		450	Thermal pyrolysis	-	6	58	36
[211]	Fixed bed (10 g)	425	Expanded perlite	0.25	19.5	56	24.5
		425	Thermal pyrolysis	-	10	60	30
[218]	Fixed bed	500	Ca(OH) ₂	0.05	12	40	48
[52]	Fixed bed (100 g)	500	Na ₂ CO ₃		14.6	47.8	37.6
		500	NaOH		13.3	48.1	38.6
		500	Thermal pyrolysis	-	21.8	42.1	26.1
[219]	Microreactor (12 mg)	450	HZSM-5	5	16.7	50.2	33.1
		450	HY	5	12.1	54.9	33
		450	Hβ	5	19.1	47.8	33.1
		450	Thermal pyrolysis	-	2	45.7	52.3
[86]	Conical spouted bed (2 g)	500	HZSM.5	7.5	17.8	47.0	35.2
		500	Thermal pyrolysis	-	3.1	62.9	34.0
[222]	Conical spouted bed (3 g min ⁻¹)	450	Equilibrated FCC	10 g cat 3 g tyre-1 min-1	0.6	64.4	35
		425	Thermal pyrolysis	-	1.8	64.3	33.9
[183]	Stirred reactor (150 g)	500	ZSM-5	0.01	6.5	55.6	37.9
		500	USY	0.01	10	53.5	36.5
		500	β	0.01	8.2	54	37.8
		500	SAPO-11	0.01	10.5	55.1	34.4
		500	ZSM-11	0.01	6.2	55.1	38.7
		500	Thermal pyrolysis	-	4.5	55.5	40.0
[9]	Rotary oven (200 g min ⁻¹)	800	Blast-furnace slags	1	10.25	58.3	31.4

[187]	Fixed bed (1 g)	550	H β	0.3	32.5	34	33.5
		550	HUSY	0.3	32	33	35
		550	TiO ₂	0.3	30.5	26.5	43
		550	Thermal pyrolysis	-	28.5	28.5	43
[84]	Fixed bed (1 kg)	450	Natural zeolite	0.1	24.6	22	53.4
		450	H-SDUSY	0.1	37.4	20	42.6
		450	Al ₂ O ₃	0.1	34.1	32	33.9
		450	Ca(OH) ₂	0.1	18.4	26	55.6
		450	Thermal pyrolysis	-	20	40	40

Zhang et al. [52] studied the influence of basic catalysts, such as Na₂CO₃ and NaOH, in a fixed bed batch reactor operating under vacuum conditions. At 500 °C, the NaOH catalyst was able to improve the TPO yield from 42.1 wt.% (obtained in thermal pyrolysis) to 48.° wt.%. However, the yield obtained with Na₂CO₃ is of the same order of that obtained without catalysts. Accordingly, it was concluded that only NaOH has a positive effect promoting tyre decomposition.

Kordoghli et al. [188] compared the performance of several catalysts of different nature (MgO, Al₂O₃, CaCO₃, and zeolite ZSM-5) in the batch pyrolysis of waste tyre. Amongst them, only MgO and Al₂O₃ showed a remarkable effect on product distribution with respect to thermal pyrolysis. Therefore, Al₂O₃ leads to an increase in gaseous products, whereas MgO improved TPO production.

The research group by Jitkarnka et al. [95,97,205] studied the performance of different catalysts in the in line cracking of waste tyres in a laboratory scale batch unit. These authors proposed Fe or Cu doped zeolites for the improvement of oil composition and reduction of sulfur content in the TPO. Moreover, other original aspect studied by this group was the role played by the use of catalysts in the char properties. These authors also proposed the use of tyre derived char (both raw char and acid treated) as catalyst

1 for waste tyre valorization [93]. Although the char was originally proposed for the
2 catalytic tar abatement in biomass gasification processes [223], it has positive effect on
3 waste tyre pyrolysis. Thus, Jitkarnka et al. reported an improvement in oil quality by
4 favoring the production of the light oil fraction.
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10 More recently, the catalytic effect of tyre derived char was evaluated by Wang et al.
11 [91] in a two fixed bed reactor laboratory unit. Tyre char showed a remarkable catalytic
12 activity and high selectivity towards the production of light compounds and valuable
13 single-ring aromatics.
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21 The in line catalytic cracking of tyre pyrolysis volatiles on USY and ZSM-5 zeolites in
22 a two fixed bed batch reactor system was studied by Shen et al. [194,195]. The main
23 effect of both zeolites is an increase in the production of gaseous products in the
24 detriment of a decrease in that of TPO. Thus, the TPO yield of 52.0 wt.% obtained
25 without catalyst was reduced to 30.4 and 32.1 wt.% with USY and ZSM-5 zeolites, and
26 that of the gas increased from 11.9 to 33.5 and 31.8 wt.%, respectively. Thus, they
27 observed that the USY zeolite catalyst has a higher cracking activity than the ZSM-5
28 catalyst, which led to lower TPO yields. Operating in the pyrolysis step at 500 °C in a
29 fixed bed without catalyst, the yields of gaseous products and TPO were of 11.9 and
30 60.0 wt.%, respectively. Moreover when the catalytic cracking step was also performed
31 at 500 °C, the gas and TPO yields were 35.5 and 28.4 wt.% for USY and 31.8 and 32.1
32 wt.% for the ZSM-5 zeolite, respectively. This difference is due to two factors, as are: i)
33 a lower Si/Al ratio leads higher acidity and activity (Si/Al ratio was 5 for USY and 40
34 for the ZSM-5); and ii) a large pore size enables hydrocarbons of larger size to enter the
35 pore system.
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Dung et al. [193] studied the pyrolysis and in line catalytic cracking of waste tyres on MCM-41 and Ru/MCM-41 catalysts in a unit made up of two fixed bed reactors. Both catalysts greatly increase the yield of the gaseous product, especially light olefins, which was the target product in their study. In fact, the gas yield increased from 11 wt.% in thermal pyrolysis to 15 and 30 wt.% with MCM-41 and Ru/MCM-41 catalysts, respectively. These authors remarked the interest of Ru incorporation, as it improved light olefin yield and, at the same time, attenuated the undesirable PAH formation.

Wei et al. [183] carried out a complete comparative study using ZSM-5, USY, H β , SAPO-11 and ZSM-22 acid catalysts in situ in a batch stirred reactor at 500 °C. All the catalysts tested improved tyre conversion with a reduction in the solid product yield, but an increase in the gas yield compared to thermal pyrolysis. SAPO-11 and HY catalysts were those that led to higher gas yields, and these results were associated with higher surface areas and stronger acidities of the catalysts, which accelerate the conversion of scrap tyres and produce light compounds.

Based on the above-mentioned results, some general conclusion on the role played by different catalysts may be drawn. Thus, the use of acid catalysts, such as zeolites, SAPOs and ordered mesoporous structured catalysts, promote the cracking of TPO and increase gaseous product yields. The extent of these cracking reactions is conditioned by operating conditions and the properties of the catalysts, especially the combination between acidity (total acidity and acid strength) and porous structure (shape selectivity and steric hindrance). The interest in using base catalysts in tyre pyrolysis lies in the increase of TPO yield. In fact, several authors have reported a positive effect of basic catalysts, such as MgO, Na₂CO₃ or NaOH. Accordingly, catalyst selection and tuning of operating conditions should be jointly considered in order to increase the yield of products of interest.

Table 4. Product distributions obtained by different authors in the in line catalytic pyrolysis of waste tyres.

Reference	Reactor	Temperature (°C)	Catalyst	Catalyst/tyre ratio	Yields wt.%		
					Gas	Liquid	Char
[190]	Fixed bed / fixed bed	500/430	ZSM-5	1	15.10	42.9	38
		500/430	HY	1	16.80	38.7	37.3
[82]	Fluidized bed / fixed bed (3.5 g min ⁻¹)	500/500	ZSM-5	0.5	9.50	48	42.5
		500/500	HY	0.5	9.00	50	41
		500	Thermal pyrolysis	-	5	54	41
[191]	Fixed bed / fixed bed (20 g)	500/600	USY	0.5	35.50	20.1	36
		500	Thermal pyrolysis	-	11.9	52.0	36.1
[194]	Fixed bed / fixed bed (20 g)	500/600	HZSM-5	1	26	32.1	36
		500	Thermal pyrolysis	-	11.9	52.0	36.1
[193]	Fixed bed / fixed bed (30 g)	500/350	MCM-41	0.25	15.00	38	47
		500/350	Ru/MCM-41	0.25	30.00	25.5	44.5
		500	Thermal pyrolysis	-	11	47	42
[83]	Fixed bed / fixed bed (30 g)	500/350	HMOR	0.33	17.60	35.2	47.8
			HMOR + ITQ-21 (2 wt.%)	0.25	13.80	41	45.2
			HMOR + ITQ-24 (2 wt.%)	0.25	12.00	42.4	45.6
		500	Thermal pyrolysis	-	10.3	44	45.6
[224]	Fixed bed / fixed bed (30 g)	500/350	SBA-1	0.25	11.00	42	47
			Ru (1 wt.%) / SBA-1	0.25	20.00	35	44
[225]	Fixed bed / fixed bed (30 g)	500/350	Al-MCM-48	0.25	8.50	43	42.5
		500	Thermal pyrolysis	-	9	47	44

[208]	Fixed bed / fixed bed (30 g)	500/350	MCM-48	0.25	23.00	28.5	48.5
		500/350	0.7%Ru/MCM-48	0.25	26.00	27.5	46.5
		500	Thermal pyrolysis	-	13	40	47
[205]	Fixed bed / fixed bed (30 g)	500/350	H β	0.25	8.00	44	41.6
			HY	0.25	10.00	42.5	43
			HMOR	0.25	11.60	43.9	41.5
			Cu/H β	0.25	12.70	38.5	41.5
			Cu/HY	0.25	13.20	40.3	41.5
		Cu/HMOR	0.25	12.50	42.5	41.8	
		500	Thermal pyrolysis	-	11.6	46.0	42.4
[189]	Fixed bed / fixed bed (30 g)	500/350	KL	0.25	12.20	43.5	41.5
			HMOR	0.25	11.90	43.9	41.6
			H β	0.25	9.60	43.4	41.6
			HZSM-5	0.25	13.20	43.1	41.7
			HY	0.25	10.80	42.6	42.3
				500	Thermal pyrolysis	-	11.6
[97]	Fixed bed / fixed bed (30 g)	500/350	5%Fe/KL	0.25	12.10	42.9	42.5
			5%Fe/HMOR	0.25	13.30	42	42.4
			5%Fe/H β	0.25	11.40	43.6	41.7
			5%Fe/HZSM-5	0.25	16.20	39	41.8
				500	Thermal pyrolysis	-	11.6
[95]	Fixed bed / fixed bed (30 g)	500/350	HY	0.25	10.70	41.2	43.1
			MCM-41	0.25	8.20	41.5	43.5
			HY/MCM-41	0.25	9.40	42.5	43
				500	Thermal pyrolysis	-	12
[93]	Fixed bed / fixed bed (30 g)	500/350	Untreated char	0.25	13.00	41	45
			HNO ₃ treated char	0.25	14.50	38.4	45.1
				500	Thermal pyrolysis	-	12
[219]	Fixed bed/fixed bed	450/400	HZSM-5	0.06	21.10	26.6	52.3
		450	Thermal pyrolysis	-	2	45.7	52.3
[226]	Fixed bed/fixed bed	500/500	MgO	0.03	32.90	27.1	36.8
			CaO	0.03	35.20	27.5	36.1
				500	Thermal pyrolysis	-	24
[81]	Fixed bed/fixed bed	550/550	Al ₂ O ₃	0.03	30.00	32	38
			CaCO ₃	0.03	23.50	39.5	37
			ZSM-5	0.03	25.80	30	44.2
			MgO	0.03	17.00	42.5	40.5
				550	Thermal pyrolysis	-	18

[188]	Fixed bed/fixed bed	500/500	Al ₂ O ₃	0.03	31.00	26	43
			CaCO ₃	0.03	22.00	36.5	41.5
			MgO	0.03	16.80	38.8	44.4
			ZSM-5	0.03	25.20	34.2	40.6
[94]	Auger reactor/fluidized bed (5 g min ⁻¹)	340/520	Natural dolomite	3200 g cat	9.80	48.2	32.9
			Calcined dolomite	3200 g cat	12.30	46	33.1
			Natural olivine	2400 g cat	9.50	47.3	33.4
			Calcined olivine	3200 g cat	11.40	46.5	33.3
		340/520	Thermal pyrolysis	-	2.7	44.1	33.6

5.2. Influence of temperature

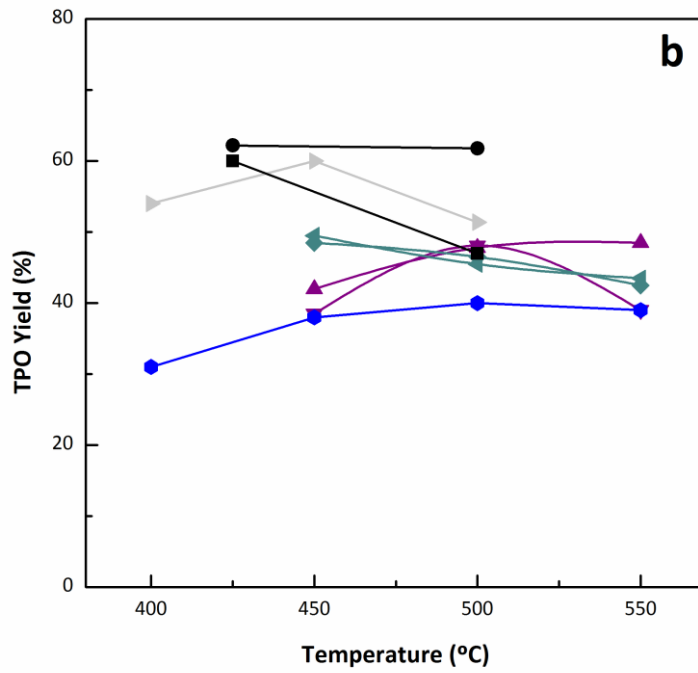
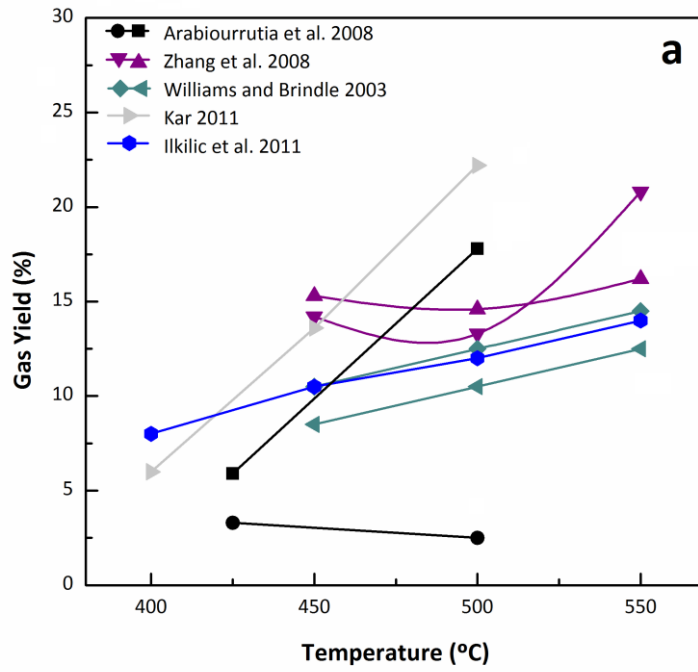
Temperature is the main variable governing tyre pyrolysis, and its final effect is also conditioned by other parameters involved in the process, such as pressure, heating rate and superficial velocity of the carrier gas [3]. In the thermal pyrolysis, the optimum temperature range for maximizing the TPO yield is between 450 and 550 °C [3,8,10,115,123]. At lower temperatures, the conversion/devolatilization of the rubber compounds (SBR, BR or NR) is not fully completed, as they remain in the char (mainly composed of carbon black and inorganic species used in the tyre manufacturing) and give it a heterogeneous sticky-gumming nature [3,227]. On the contrary, higher temperatures enhance secondary cracking of pyrolysis vapors, thus favoring the gas formation at the expense of liquid hydrocarbons [5,8,57,228]. It is to note that, apart from temperature, the extent of these reactions will be highly influenced by the

1 residence time of primary pyrolysis products in the reactor. Regarding the solid fraction
2 or char, its yield usually remains steady when temperature is increased above that
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4 corresponding to full rubber devolatilization (above 500 °C). However, when vigorous
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6 gas-solid contact technologies (fluidized or spouted bed reactors) are used, some authors
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8 have also observed a slight increase in char yield by increasing temperature, as the
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10 volatile products released may be adsorbed on the surface of the char leading to new
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12 carbonaceous materials [115,229].
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17 The addition of catalysts to the pyrolysis system enhances reaction kinetics through the
18 cracking of high molecular weight compounds into light hydrocarbon and, at the same
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20 time, may potentially improve product quality [230]. Apart from the type of catalyst, the
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22 catalyst bed temperature also plays a significant role in the product distribution, given
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24 that the activation energy for pyrolysis reactions is remarkably lowered below that for
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26 thermal pyrolysis [82]. In order to assess the influence of temperature on the catalytic
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28 pyrolysis, Figure 8 shows the gas (a), TPO (b) and char (c) yields obtained by different
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30 authors operating *in situ* with different types of catalysts at different temperatures. As
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32 observed in Figures 8a and 8b, there is a clear general trend that an increase in the
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34 catalyst bed temperature considerably increases gas production at the expense of oil
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36 yield. Moreover, when these results are compared with those obtained without catalyst
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38 in the same studies (not shown in Figure 8), the gas yields in catalytic pyrolysis are
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40 higher and those of TPO lower when the process is performed at the same temperature,
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42 which is evidence that the catalyst promotes TPO secondary cracking reactions. The
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44 trend observed for the solid fraction (Figure 8c) is the same as in thermal pyrolysis, i.e.,
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46 its yield decreases by increasing temperature until rubber devolatilization is completed,
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48 and it then remains steady or increases slightly due to the occurrence of secondary
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50 reactions promoting TPO and char formation reactions. In this case, the yields in
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1 catalytic and thermal pyrolysis are almost the same, which means that the effect of the
2 catalyst is more remarkable in secondary cracking reactions involving primary vapors.
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4 According to Aguado et al. [231], the catalyst does not affect the primary reactions
5 because the reactant is a solid, but it has an influence on the evolution of volatile
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7 compounds, which depending on their molecular size or nature are liable to undergo
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9 transformations on the active sites of the catalyst.
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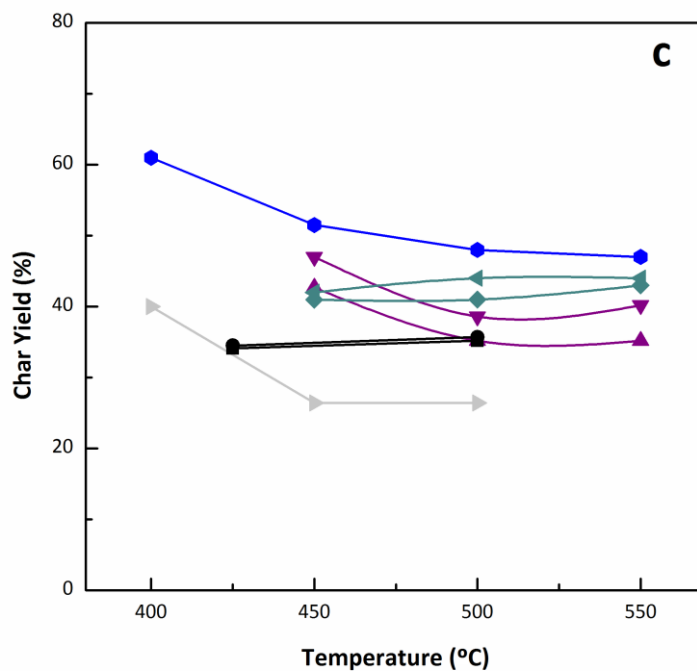


Figure 8. Effect of temperature on the gas (a), TPO (b) and char (c) yields in the in situ catalytic tyre pyrolysis. Arabiourrutia et. al. 2008 [87] ■HZSM-5/●HY, Zhang et al. 2008 [52] ▲Na₂CO₃/▼NaOH, Williams and Brindle 2003 [85] ◄HZSM-5/◆HY, Kar 2011[211] ►Perlite, Ilkilic and Aydin 2011 [218] ●Ca(OH)₂.

Moreover, some authors have also studied the effect of temperature in the *in-line* catalytic cracking system with two different reactors. As mentioned above, thermal pyrolysis takes place in the first one and the catalytic treatment of the volatiles in the second one. Figure 9 displays the gas (a) and TPO (b) yields obtained at different temperatures at the outlet of the catalytic reactor. In this case, the char yield is not included in Figure 9, given that its yield remains steady as temperature in the pyrolysis reactor is not modified. As observed, in all cases the yield of gas increased considerably at the expense of oil yield when temperature in the catalytic reactor was increased.

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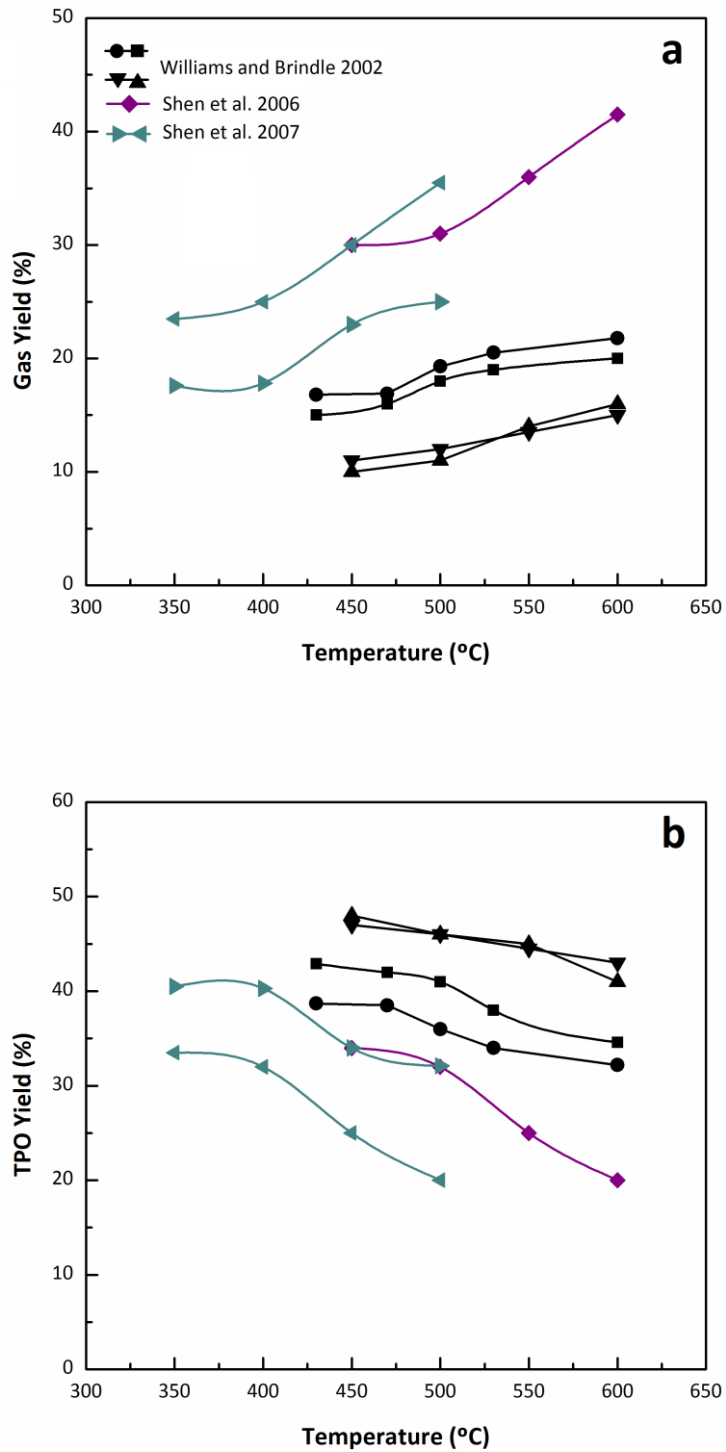


Figure 9. Effect of temperature on the yields of gas (a) and TPO (b) in the in line catalytic cracking of waste tyre pyrolysis. Williams and Brindle 2002 [190] ■HZSM-

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5/●HY, Williams and Brindle 2002 [82] ▲HZSM-5/▼HY, Shen et al., 2006 [191]
◆USY, Shen et al 2007 [194] ►HY/◀HZSM-5.

In view of the results displayed in Figures 8 and 9, it can be concluded that the effect of temperature on the catalytic pyrolysis is even more pronounced than in the non-catalytic one, especially when acid catalysts like zeolites are used. The shape selectivity characteristic of the zeolites has a considerable influence on the catalyst performance, and gas formation is therefore promoted [86,87]. For example, Arabiourrutia et al. [87] studied the thermal and *in situ* catalytic pyrolysis in a conical spouted bed reactor and concluded that the HZSM-5 improved the cracking capacity of the volatiles in the 425-500 °C range and allowed attaining higher gas yields and lower oil yields than those obtained with the HY catalyst. Thus, an increase in temperature favors HZSM-5 zeolite capacity for cracking heavy fractions to yield gases, but an intensification of condensation reactions is caused when the HY zeolite is used.

Williams and Bridle [82,85,151,190] also studied the effect of temperature on catalytic pyrolysis using HY and HZSM-5 catalysts, although the runs were conducted in a two stage pyrolysis–catalysis system. The tyres were pyrolysed in a fluidized [82,151] or fixed bed reactor [85,190] and the evolved pyrolysis gases were passed through a secondary fixed bed reactor containing the zeolite catalysts. They studied first the effect of temperature in the second catalytic reactor (between 450 and 600 °C,) with the pyrolysis step being performed at 500 °C. They observed that the influence of temperature on the product yield was more pronounced in the fixed bed reactor [190] than in the fluidized bed reactor [82]. Thus, in the fixed bed-fixed bed system (Y-zeolite catalyst in the second one), the total gas yield rose from 16.3 to 21.8 wt% and that of oil fell from 48.7 to 39.0 wt% by increasing the catalytic bed temperature, whereas in the fluidized bed-fixed bed system, the gas yield increased from 10.5 to 17.5 wt. % and that

1 of oil decreased from 48.5 to 43 wt. %. These differences are explained by the longer
2 residence time of the volatiles in the catalyst fixed-bed when the tyres are firstly
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of oil decreased from 48.5 to 43 wt. %. These differences are explained by the longer residence time of the volatiles in the catalyst fixed-bed when the tyres are firstly pyrolyzed in another fixed bed reactor. In fact, the gas velocities required for bed fluidization are higher than those in fixed beds, and therefore times for catalytic reaction are shorter. Furthermore, they observed similar gas and oil yields for both catalysts, although gas formation was slightly higher with the HZSM-5. In another work, these authors studied the effect of the first reactor temperature (450-600 °C) on product distribution, with the catalyst bed being at 500 °C [151]. In this case, the highest gas yield was obtained with the HY zeolite, with the maximum value being attained at 600 °C (17.5 wt. %), while the gas yield with the HZSM-5 ranged from 8.5 to 15 wt.%. The TPO yields for both catalysts were similar, but the oil yield was 5 to 10 wt. % higher compared to the yields obtained when an inert material was placed in the *in-line* reactor. Williams and Brindle [190] also studied the effect of temperature on the formation of the carbonaceous coke deposited on the catalyst. They observed that coke deposition increased marginally with temperature, from 7.2 to 8 wt. % with the HY zeolite and from 4 to 7.6 wt. % with the HZSM-5.

Shen et al. [194] also studied the effect of temperature (between 350 and 500 °C) in the second catalytic reactor (filled with USY and HZSM-5 type zeolites) in a two-stage pyrolysis system, with the pyrolysis step being performed at 500 °C in all the experiments. An increase in temperature in the catalytic step from 350 to 500 °C greatly increases the cracking capacity of both catalysts. In the case of USY zeolite, the gas yield increased from 23.7 to 35.5 wt.% in the mentioned range, with the gas yields corresponding to ZSM-5 being lower due its lower acidity.

The influence of temperature in the in situ batch pyrolysis of waste tyres on expanded perlite in the 350 to 500 °C range was studied by Kar [211]. A remarkable increase in

1 the tyre conversion was observed in the studied range. In fact, the solid product yield
2 decreased from 50.7 wt.% at 350 °C to 26.4 wt.% at 500 °C, whereas the gas steadily
3 increased from 2.99 to 20.22 wt.%. However, the TPO yield peaked at 425 °C, with the
4 maximum value being of 60.0 wt.%.
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10 The results reported in the literature reveal a great effect of temperature on waste tyre
11 catalytic pyrolysis. It should be noted that this effect is in general more noticeable than
12 that observed in thermal pyrolysis. The most commonly used catalysts in waste tyre
13 valorization by pyrolysis are of acid nature. An increase in temperature has shown a
14 marked increase in the cracking capacity of these catalysts, which greatly enhance the
15 production of gaseous products at the expenses of TPO. In addition, temperature
16 promotes other secondary reactions when acid catalysts are used, such as condensation
17 reactions to yield aromatic compounds, but also increase coke deposition. Therefore, a
18 correct value of temperature is essential in order to increase the yield of valuable
19 chemicals, such as light olefins and BTX, and avoid the formation of undesirable
20 product, such as CH₄ and PAHs.
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37 **5.3. Effect of Catalyst/Tyre ratio**

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41 The catalyst to reactant ratio greatly depends on the reactor design, catalyst-feed contact
42 method and the activity of the catalyst used. In order to assess the effect of this
43 parameter on the tyre pyrolysis, two terms are commonly used in the literature,
44 depending whether operation is performed in batch or continuous mode. In a batch
45 processing, *catalyst/feed* ratio defines the amount of catalyst to be used for a specific
46 amount of feedstock introduced in the reactor. Furthermore, *space-time* is used in
47 continuous runs and refers to the period of time the reactants take to pass through an
48 incremental catalyst volume or mass. In other words, it provides a measure of the
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1 capacity of the catalyst to convert a reactant, and may be described as the amount of
2 catalyst used per feedstock flow rate given on a volumetric or a weight basis. In
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4 continuous reactors, *space velocity* (the inverse of *space time*) is also commonly used,
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6 which reflects the rate at which a reactant is converted per unit time and catalyst mass or
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8 volume.
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12 Most of the works in catalytic pyrolysis comparing the effect of catalyst to tyre ratio
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14 have been performed in discontinuous mode, following either *in situ* or *in line*
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16 strategies. Figure 10 summarizes the influence catalyst/tyre ratio has on the gas (a) and
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18 TPO (b) yields attained by different authors in the *in situ* catalytic pyrolysis of waste
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20 tyres. Furthermore, Figure 11 analyzes the influence of the same parameter, but with the
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22 catalyst placed *in line*. As observed in Figures 10 and 11, this parameter has a clear
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24 influence on the extent of the catalytic reactions. An increase in the catalyst/tyre feed
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26 ratio leads to a decrease in the yield of oil and an increase in that of the gas. Indeed, an
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28 increase in the catalyst/tyre ratio means an increase in the catalyst active sites available
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30 for pyrolyzing the vapors, and more volatiles are therefore cracked into gases.
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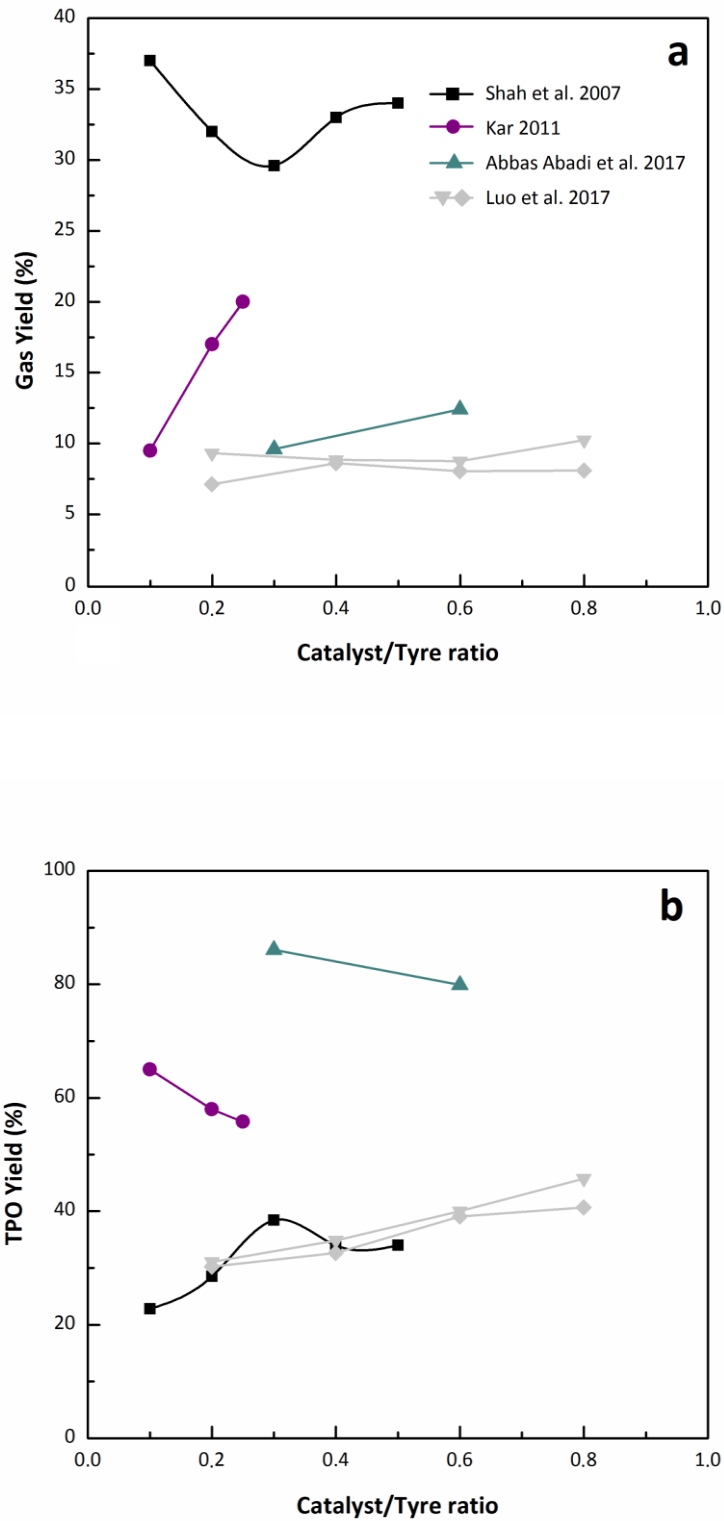
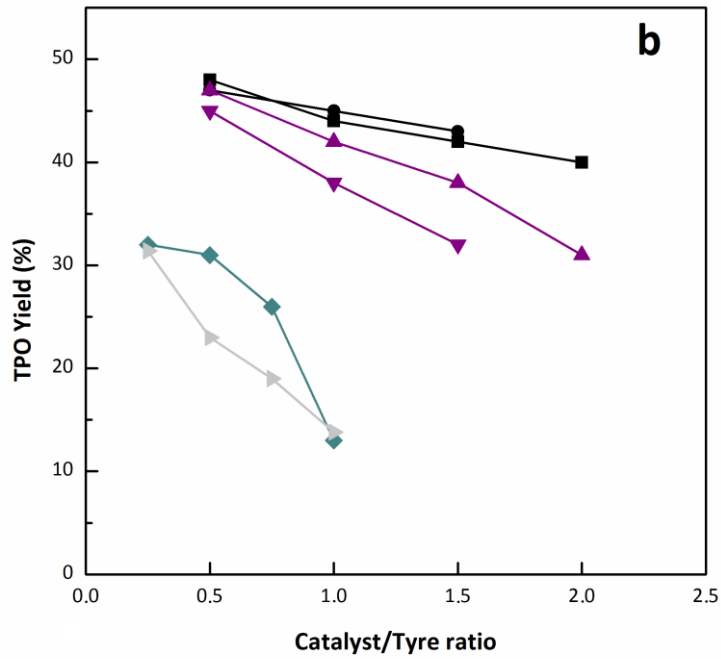
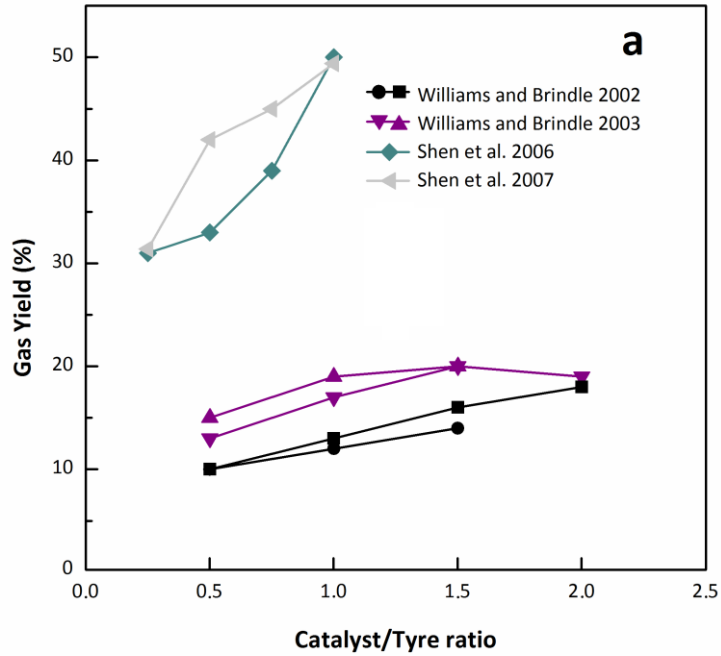


Figure 10. Influence of the catalyst/tyre ratio on the gas (a) and TPO (b) yields in the in situ catalytic pyrolysis of waste tyres. Shah et al. 2007 [220] ■HZSM-5, Kar

2011 [211] ●Perlite, Abbas Abadi et al., 2017 [184] ▲FCC, Luo et al., 2017 [9]

▼Blast furnace slag 800°C/◆Blast furnace slag 600°C.



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Figure 11 Influence of the catalyst/tyre ratio on the gas (a) and TPO (b) yields in the in line catalytic pyrolysis of waste tyres. Williams and Brindle 2002 [82] ■HZSM-5/●HY, Williams and Brindle 2003 [85] ▲HY /▼ HZSM-5, Shen et al. 2006 [191] ◆USY and Shen et al. 2007 [194] ►USY.

An increase in C/T ratio not only enhances cracking reactions, but also promotes the reactions involved in the formation of coke. An increase in coke yield is closely related to aromatization and dehydrogenation reactions on the catalyst surface. All the compounds formed in tyre pyrolysis, i.e., aromatic hydrocarbons, naphthenes, alkenes and alkanes, are involved, to a greater or lesser extent, in the formation of coke. Aromatic species and alkenes are prone to be involved in pathways leading to coke formation, as they take part in hydrogen transfer and cyclisation reactions. Accordingly, the extent of these reactions increases as C/T ratio is higher, and more coke is therefore deposited on the catalyst.

Shen et al., [195] showed the total gas yield increased from 16.5 to 49.4 wt% and oil yield decreased from 45.9 to 13.8 wt% as the catalyst/tyre ratio is increased from 0 to 1, with the catalyst being a USY zeolite. Furthermore, coke formation increased from 5.4 to 16.7 wt%, when the catalyst/tyre ratio was increased from 0.25 to 1. Similarly, Williams and Brindle [85] observed a decrease in oil yield by 24 wt.% (from 55.8 to 32 wt.%) and an increase in gas yield by 14 (from 6 to 20 wt.%) when the HY catalyst to tyre ratio was increased from 0 to 1.5. They also observed that the coke deposited on the catalyst increased from 4 to 10.1 wt. %.

Shah et al. [220] performed the waste tyre pyrolysis in a batch reactor at 350 °C on a calcium carbide (CaC₂) catalyst. They explored the effect of catalyst/tyre ratio in the 0.1-0.5 range, and observed that the gas yield decreased from 37 to 29 wt. % when the

1 C/T ratio was increased from 0.1 to 0.3, and it then increased to 34 % for a C/T value of
2 0.5. Concerning the liquid yield, it increased significantly when the C/T value was
3 increased to 0.3, and then decreased slightly.
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8 In a more recent work, Abbas-Abadi and Haghghi [184] studied the effect the amount
9 of spent FCC catalyst has on the SBR degradation, and observed that coke and non-
10 condensable yields increased as catalyst content was increased from 1.6% to 7.7% and
11 from 5.2% to 12.4%, respectively. Moreover, an increase in the C/feed ratio led to a
12 decrease in the TPO yield from 93.2 to 79.9 wt.%, but to a remarkable increase in the
13 aromatic content.
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23 Kar [211] studied the batch pyrolysis of tyres in a fixed bed reactor on expanded perlite
24 for a C/T ratio between 0 and 0.2. An increase in the catalyst mass in the bed improved
25 tyre conversion by reducing char yield. Moreover, the gas yield remained almost
26 constant up to a ratio of 0.1, for which they attained the maximum TPO yield (65.1
27 wt.%). A further increase in C/T ratio favored gas formation and caused TPO yield
28 reduction.
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38 The influence of $\text{Ca}(\text{OH})_2$ /tyre ratio in the batch pyrolysis in a fixed bed reactor at 450
39 °C was analyzed by İlkılıç and Aydın [218]. An increase in C/T ratio enhanced TPO
40 desulfurization, i.e., the sulfur content in the TPO was reduced from 1.4 wt.% without
41 catalyst to 0.8 with a C/T ratio of 0.15.
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49 The results obtained in the literature clearly show a positive effect of increasing C/T
50 ratio on the catalytic conversion. Thus, an increase in C/T ratio (acid catalysts)
51 promotes the cracking of TPO to yield gaseous products. Moreover, the formation of
52 aromatics and their evolution towards coke formation by means of cyclization and
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1 aromatization reactions is also favored by increasing the C/T ratio [232]. The same
2 qualitative effect has been reported in the catalytic cracking of waste plastics [233,234].
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5 **6. Catalysts role in the characteristics of the pyrolysis products**

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8 The characteristics of the pyrolysis products, especially those of the gases and the oil,
9 greatly depend on the catalyst type (acid, basic or metallic one) and properties (porosity,
10 acid strength and acid sites density), and on the pyrolysis operating conditions
11 (temperature, space time and heating rate, amongst others). Generally speaking, the gas
12 consists of a mixture of paraffinic and olefinic compounds, together with smaller
13 amounts of other hydrocarbons, and may be a source of valuable petrochemicals, such
14 as light olefins, or be used for supplying the heat required in the process, which would
15 render it energetically self-sufficient. The char or solid residue is a carbon-rich material,
16 which contains the initial carbon black and inorganic compounds (such as Zn, Si and
17 Ca) used in the tyre manufacture, and also other carbon based solids generated by
18 repolymerization reactions involving BR and SBR [40]. The most straightforward
19 application is the direct re-utilization of the char as carbon black, although this option
20 faces important limitations due to the characteristics of the residual carbon black (high
21 ash and sulfur content) [8]. Additionally, it may also be activated via physicochemical
22 routes to obtain activated carbon [74,75,117,235-237]. The liquid is usually referred as
23 tyre pyrolysis oil or TPO and contains valuable chemicals, such as aromatics, isoprene,
24 limonene and BTX, with render it a high heating value (40-44 MJ kg⁻¹) and
25 physicochemical properties comparable to those of fossil fuels [40,58,103,114]. The
26 concentration of different chemical families changed by increasing temperature. Thus,
27 production of aromatics was promoted at high temperatures by secondary
28 recombination reactions, whereas limonene and aliphatics were the major compounds in
29 the 425-475 °C range. The properties of the TPOs are evidence of their potential to
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1 substitute conventional fuels. However, some of them need to be improved by reducing
2 the contents of sulfur (which is in the 1-2.5 wt. % range in the thermal TPO), nitrogen
3 and polycyclic aromatic hydrocarbons, for which catalytic pyrolysis is regarded as one
4 of the most promising processes. In fact, the oil fraction is much more interesting than
5 the gas and char products, since it contains the most valuable petrochemicals [238].
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11 The aim of this section is to analyze the effect catalysts have on the TPO composition,
12 but without ignoring the characteristics of the gas stream. As previously stated, char
13 properties do not change significantly with the catalysts used in the pyrolysis, and it has
14 not therefore been included in this section.
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23 **6.1. TPO**

24 Several studies have shown that the oil contains variable concentrations of valuable
25 aromatic and aliphatic compounds, such as dl-limonene, benzene, toluene, and xylenes,
26 which may be used directly as substitutes for conventional fuels or petrochemical
27 feedstocks as a potential source of light aromatics [3,39,58,239]. Single-ring aromatic
28 compounds obtained in the pyrolysis of waste tyres are known for their high
29 commercial value. Catalytic pyrolysis of waste tyres on zeolite based catalysts was
30 proven to be a suitable method for the objective of maximizing the selectivity of single-
31 ring aromatic compounds [39,40,90,183].
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46 **6.1.1. Zeolites**

47 San Miguel et al. [240] incorporated *in situ* zeolites in the sample container of a
48 thermobalance and reported that these catalysts showed a marked selectivity towards the
49 formation of BTX, while causing an important reduction in olefinic hydrocarbons. This
50 indicates that Diels-Alder dehydrogenation of alkanes to alkenes occurs, followed by
51 cyclization and aromatization. This aromatization capacity is more marked in zeolitic
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1 materials with stronger acid properties and reduced steric restrictions, which is an
2 indication that these properties accelerate cyclization and aromatization reactions.
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4 Moreover, Olazar et al. [219] concluded that zeolites promote the cracking of non-
5 aromatic C₁₀⁻ fraction and dealkylation of both the aromatic C₁₀⁻ fraction and tar
6 molecules accessible to the porous structure of the catalyst. Likewise, zeolites with
7 suitable micropore structure and acidity lead to aromatics by olefin condensation and
8 hydrogen transfer mechanisms. Several researchers found that zeolites, especially
9 HZSM-5 and HY, significantly increase the concentrations of BTX, with the latter
10 having stronger acid sites and larger pores, and therefore leading to higher selective to
11 monoaromatic hydrocarbons [82,85,87,183,190,191,194,195,219]. In fact, large pore
12 sizes would enable large molecular size hydrocarbons to enter the porous system, and
13 therefore more pyrolysis vapors would experience catalytic cracking leading to the
14 formation of aromatic hydrocarbons [194]. However, the shape selectivity of the HY
15 zeolite also leads to the formation of heavier structures that make up the tar and
16 aromatic C₁₀⁻, which are favored by its higher hydrogen transfer capacity [219]. The
17 Si/Al ratio of the zeolites is another factor influencing the aromatic content in the TPO.
18 According to Shen et al. [194], the lower Si/Al ratio in HY zeolites resulted in higher
19 activity and an increase in aromatic hydrocarbons, but also more coke formation.
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Aguado et al., [231] proposed a kinetic scheme where HY zeolites selectively enhanced the reactions of condensation and alkylation of limonene and gasoline to aromatics, while the one based on a HZSM-5 zeolite selectively promoted the cracking of tar to lighter fractions (gas and C₁₀⁻ aromatics) and of limonene to isoprene and C₅-C₁₀ hydrocarbons. Olazar et al. [86], who previously investigated the use of HY and HZSM-5 zeolite catalysts in a conical spouted bed reactor, also observed this kinetic behavior. They reported an increase in the concentration of single-ring aromatic compounds in the

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oil from 20.17 wt.% in the absence of the catalysts to 32.49 wt.% with the HZSM-5 catalyst and to 40.49 wt.% with the HY catalyst. In addition, the presence of the catalyst in the pyrolysis reactor system led to higher benzene, toluene and xylene concentrations compared to thermal pyrolysis. They also reported that the concentration of polyaromatic hydrocarbons markedly increased with the HY catalyst, whereas it was less pronounced with the ZSM-5 catalyst. For example, naphthalene increased from 0.24 to 4.95 wt.%, and methyl-, dimethyl- and trimethyl naphthalenes increased from 0.22 to 11.9 wt.% with the HY catalyst. Williams and Brindle [85] produced an oil containing 24 wt.% toluene, 5 wt.% benzene, 20 wt.% m/p-xylenes and 7 wt.% o-xylene with the HY zeolite, whereas the overall yields of benzene, toluene and m-, p- and o-xylenes in the oil was 29.6 wt.% with the HZSM-5 catalyst. Shen et al. [194] analyzed the light fraction (<220 °C) of the oil produced after catalysis and determined concentrations of toluene of 11.6 wt.%, benzene 1.6 wt.% and xylenes 16.7 wt.% on the Y catalyst, whereas those using a HZSM-5 were 5.68, 0.99 and 12.95 wt. %, respectively. Ding et al. [90] also observed that the aromatization ability of the HZSM-5 was lower than that of HY in the catalytic pyrolysis of waste tyres, although they found that the selectivity of HZSM-5 to give BTXE was higher than that of HY.

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Apart from HY and HZSM-5, other types of zeolites have also been used in the waste tyre catalytic pyrolysis in order to improve the quality of the oil. For example, Muenpol et al. [189] tested 3 types of zeolites (H β , HMOR and the basic one KL), apart from HZSM-5 and HY. They concluded that the H β had higher selectivity to valuable monoaromatics (benzene, toluene, ethylbenzene, xylenes, styrene, cyclohexane, and cumene) (10.8 % in the oil) than HY (7.33 %), although the latter had higher sulfur removal ability (19.4 % removal) than H β (5.98 % removal) and led to lower coke content. This observation indicates that the impact of the acid strength is more pronounced for

1 producing valuable petrochemicals, but a higher acid density is needed for higher sulfur
2 removal ability. Besides, these authors observed that the pore channel structure affected
3 the contact time of molecules, as it may allow for their stay inside the pore. Thus, a
4 higher contact time in a 3D pore channel (H β) means a higher cracking ability and
5 petrochemical production (10.8 % in tyre-derived oil) than in a 1D pore channel
6 (HMOR), which accounted for only a total of 2.32 %. Finally, KL had the lowest
7 cracking activity, as it allowed attaining the lowest concentration of valuable chemicals,
8 but its sulfur-removing ability reached up to 12.8 %. Li et al. [183] also studied the
9 effect of H β , HZSM-22 and SAPO-11, as well as ZSM-5 and USY zeolites. In this case,
10 they observed that the lower acidity and smaller pore size of the HZSM-22 resulted in
11 lower activity, i.e., the lowest content of single-ring aromatics and (39 %) and the
12 highest aliphatic content (57 %) in the oil. In addition, H β and SAPO-11 catalysts gave
13 the highest contents of alkyl-benzenes, i.e., 39.8 wt% and 42.5 wt%, respectively, due to
14 their stronger acidity and larger pores, whereas USY and ZSM-5 led to similar
15 aromatic contents. Abbas-Abadi et al. [184] studied the effects of different catalysts,
16 i.e., spent FCC, gallium promoted spent FCC (Ga/FCC), HZSM-5, and mordenite, on
17 the SBR degradation using a stirred semi-batch reactor. The main products obtained
18 were light hydrocarbons within the gasoline range, though Ga/FCC and spent FCC
19 tended to produce more oil fraction, with aromatic compounds as the main product
20 (62.1 and 52.3 wt. %, respectively). Amutio et al. [222] used a commercial FCC catalyst
21 to perform the valorisation of waste tyres by *in situ* catalytic pyrolysis in a conical
22 spouted bed reactor. High diesel (50.5 wt %) yield was obtained, together with low gas
23 (0.6 wt %) and gasoline (13.9 wt %) fractions. The liquid obtained was highly aromatic,
24 although the low shape selectivity favored the generation of aromatic C₁₁⁺ in the liquid
25 fraction, by means of BTX alkylation and condensation of olefins and aromatics.
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Moreover, the incorporation of transition metals into the zeolite framework has also been studied in waste tyre pyrolysis, and encouraging results were obtained [88,96,97,205]. Due to the metal and zeolite properties, the metal-loaded zeolites may exhibit multi-functions in catalysis, including hydrogenation, dehydrogenation, ring-opening, cracking, and aromatization, thus leading to higher formation of valuable petrochemicals, including BTX. Furthermore, metal/zeolite catalysts contribute to decreasing sulfur content in the waste tyre-derived oil. Yuwapornpanit and Jitkarnka [205] revealed that benzene and ethylbenzene were common petrochemicals produced in high concentration by Cu-loaded catalysts (Cu/HY, Cu/H β and Cu/HMOR). In addition, they found that Cu-support interaction greatly affected sulfur removal from oils, especially Cu/H β , which allowed reducing S content in the oil to 0.7 wt, % (sulfur containing compounds were converted into thermodynamically stable forms on Cu). Namchot and Jitkarnka [95] and Muenpol and Jitkarnka [97] analyzed the impact Ni and Fe supported on zeolites have on hydrocarbon compounds and petrochemicals, respectively. Both studies showed that Ni and Fe doped catalysts enhanced aromatic formation and sulfur removal from oil. Vichaphund et al. [88] compared the performance of HZSM-5 with Ni/HZSM-5 and HZSM-5 derived from fly ash in the catalytic treatment of pyrolytic vapors of rubber wastes. They concluded that aromatic selectivity was higher when using the HZSM-5, but Ni/HZSM-5 catalyst yielded a lower naphthalene selectivity. This might be due to the transformation of naphthalenes (diaromatics) to valuable aromatics via two reaction steps: i) firstly, naphthalene species react on the Ni site by hydrogenation to form tetralinic species and; ii) then, the tetralinic species crack on the acid site to form BTX. This trend is also supported by the higher selectivity to BTX observed by Namchot and Jitkarnka [96]. Their results indicate that the addition of nickel on HZSM-5 promoted the transformation of multi-

1 ring aromatics to mono-aromatics and aromatization of naphthenes and olefins to mono-
2 aromatics.
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5 Although zeolites have been widely used to increase BTX content, a significant amount
6 of poly and polar aromatics still remain in the TPO [95,208]. As previously mentioned,
7 the formation of aromatics increased when catalyst acidity and acid density were
8 increased, but aromatic molecules larger than the micropore size of the zeolites cannot
9 be cracked into smaller aromatics or light hydrocarbons. Hence, mesoporous materials
10 with larger pore size and lower acidity, such as MCM-41 have been used for reducing
11 the formation of poly- and polar-aromatics, but they also promoted the formation of
12 saturated hydrocarbons [193]. In addition, a mesoporous material (SBA-1) was used as
13 a catalyst for waste tyre pyrolysis, but due to its excessive weak acidity did not reduce
14 the concentration of di-, poly- and polar-aromatic compounds in the oil [224]. However,
15 the addition of Ruthenium to SBA-1 drastically decreased the concentration of poly and
16 polar aromatics, but their concentration in the oil was still higher than 5 %.
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35 In order to combine the advantages and overcome the shortcomings of both
36 microporous zeolites and mesoporous molecular sieves, composite materials have been
37 developed. The good characteristics of composites are large pore size and wide surface
38 acidity distribution. For example, Namchot and Jintkarka [95] studied the catalytic
39 pyrolysis of wastes tyre using a core-shell composite of HY and MCM-41 as catalyst in
40 a bench-scale reactor. The oil produced from the composite catalyst contained a higher
41 amount of gasoline and valuable aromatics, especially ethyl-benzene (4.2 wt. % in
42 maltene) and toluene (1 wt. % in maltene), than the pure HY (3.4 and 0.2 wt. %,
43 respectively) and MCM-41 catalysts (2.2 and 0.3 wt. %, respectively). These results are
44 evidence of a bimodal pore size distribution, and a good balance of acidity between
45 micropore and mesopore layers in the core-shell composite leading to a higher cracking
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activity and selectivity to valuable petrochemicals than pure HY and MCM-41 catalysts. Furthermore, the core-shell catalysts also led to higher sulfur removal in the oil (13.5 %) than HY and MCM-41 catalysts (both 8.3 % removal).

6.1.2. Base, natural and other catalysts

Other acid/base additives or natural catalysts have been also used in tyre pyrolysis, although the results have not been as satisfactory as those obtained with zeolites or composite materials [81,84,92,93,141,210,213]. Thus, Miandad et al. [84] examined the effect various catalysts have on waste tyre pyrolysis oil, as are natural zeolite, synthesized zeolite (H-SDUSY), activated alumina (Al_2O_3), and activated calcium hydroxide ($\text{Ca}(\text{OH})_2$), which they used in a small pilot scale pyrolysis reactor. The concentration of aromatic compounds in the liquid oil decreased to 60.9% on the $\text{Ca}(\text{OH})_2$, 71.0% on the natural zeolite and 84.6% on the Al_2O_3 , with the liquid oil produced with the synthetic zeolite catalyst having 93.7% of aromatic compounds. Besides, Al_2O_3 and natural zeolite and, to a lesser extent CaOH_2 , formed multiple ring aromatic hydrocarbons in the liquid oil. Shah et al. [210] studied the influence SiO_2 , Al_2O_3 and their mixture ($\text{Al}_2\text{O}_3/\text{SiO}_2$) have on the pyrolysis of used tyre rubber. They found that the oil derived from the catalytic pyrolysis on Al_2O_3 contains a higher concentration of polar compounds (40%) and a lower concentration of aliphatic hydrocarbons, whereas the amount of aromatic hydrocarbons does seem to be influenced. Besides, these authors also tested basic catalysts (MgO and CaCO_3) and found that both catalysts produced about 25 wt. % of aliphatic hydrocarbons in the liquid fraction, whereas MgO led to an increase in the amount of aromatic hydrocarbons (55%wt) [213]. In order to enhance secondary cracking reactions of pyrolysis vapors, Leng et al. [92] mixed a ZnO catalyst with raw tyres, and placed the mixture in a separate layer in a reactor containing a HZSM-5 catalyst. Their results evidence that this

1 strategy improves the performance for selectively producing BTX (26.20 %) over that
2 of using ZnO and HZSM-5 separately. Seng-eiad and Jitkarnka [93] investigated the
3 potential of untreated and HNO₃-treated chars derived from waste tyre pyrolysis. They
4 observed that the HNO₃-treated char increased the gas production due to its enhanced
5 acidity, surface area and pore size (after the acid treatment process), and promoted
6 cracking activity. However, the untreated char contained a higher content of mineral
7 species than the treated one, which promoted valuable petrochemical production.
8 Additionally, the untreated and treated chars did not only remove large-size aromatics
9 and heavy fractions in TPOs, but also sulfur compounds.
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22 One of the main objectives of basic catalysts lies in reducing the sulfur content in the
23 TPO [218,241]. Thus, when a CaO catalyst is added, the possible desulfurization
24 reactions that may occur in the pyrolysis of tyres are as follows:
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37 İlkılıç and Aydın [218] used a Ca(OH)₂ basic catalyst and observed that the sulfur
38 amount in the liquid fuel sharply decreased from 1.4 to 0.9 wt. % when 5% catalyst
39 (based on the tyre amount) was used. However, the sulfur reduction was not linear with
40 the amount of catalyst, and when 10% and 15% of catalyst amounts were used, almost
41 similar results were observed (0.85 and 0.82 wt. %, respectively). Similarly, Ayanoglu
42 and Yumrutaş [241] used CaO mixed with the TPO obtained in the thermal pyrolysis.
43 The initial TPO had a S content of 1.42 wt. %, but the gasoline-like fuel obtained after
44 the catalytic process had no sulfur and the diesel-like fuel contained only 0.8 wt. %
45 sulfur.
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As observed in this section, most of the studies in the literature use acidic catalysts in order to increase the yield of single-ring aromatics, which are of potential value and therefore interesting from an economic point of view. However, this improvement in the benzene–toluene–xylenes content is commonly at the expense of limonene yield, which is also a high value added product [51]. Limonene is a cyclic terpene (C₁₀H₁₆), whose main source is the polyisoprene (NR) contained in the tyre, and is useful in the formulation of industrial products (solvents, resins, adhesives) [51,58]. The most promising routes for producing dipentene require basic additives [51]. Zhang et al. [52] showed that dipentene yield could be improved significantly with NaOH under vacuum conditions. Although dipentene concentration in the TPO is similar as in uncatalyzed runs, more oil is obtained when using NaOH, a higher amount of dipentene is therefore formed. Likewise, Kar [211] used expanded perlite (79 % Al₂O₃ and 13 % of SiO₂, amongst others) as catalyst, and obtained similar dipentene yields. Additionally, Choi et al. [94,113,114] operated in a two-stage system consisting of an auger reactor and a fluidized bed, with sand, dolomite, olivine, CaO and FeO as bed materials. This two-reactor strategy allowed increasing limonene content with the highest value of CaO additive they used (7.8 wt. %), whereas dolomite and olivine (calcined or uncalcined) did not bring about any observable increase in the yield of DL-limonene compared to uncatalyzed reactions. Furthermore, when natural and calcined dolomite were used, the yield of aromatics increased slightly to 20-25 wt. % (the values without catalyst were in the 18-22 wt. % range) and the sulfur content was reduced with all catalysts analyzed from 1 % to approximately 0.5 wt. %.

6.2. Gaseous fraction products

The gaseous fraction in the thermal pyrolysis is mainly composed of paraffins and olefins with carbon numbers ranging from 1 to 5. The gaseous fraction is mainly

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composed of the following compounds: hydrogen (H₂) carbon monoxide (CO), carbon dioxide (CO₂), methane (CH₄), ethane (C₂H₆), ethane (C₂H₄), propane (C₃H₈), propene (C₃H₆), butane (C₄H₁₀), butenes (C₄H₈), butadiene (C₄H₆), isoprene (C₅H₈), pentene (C₅H₁₀) and low concentrations of certain sulfur (H₂S, SO₂, COS, CS₂) and nitrogen (NH₃) compounds [3,8,76,173,176]. H₂S is produced from the volatilization of the sulfur used in the vulcanization, and its concentration in the gas fraction is generally low. C₄-C₅ hydrocarbons are directly formed from natural or synthetic rubber depolymerisation, whereas lighter compounds are usually formed from secondary cracking reactions. The use of catalysts promote these secondary cracking reactions, thus producing more light hydrocarbons (in the C₁-C₃ range) at the expense of larger molecules in the TPO [52,81,82,86,87,219]. Besides, the use of some catalysts also enhanced the formation of C₄-C₅ hydrocarbons in the gaseous stream [95,97,189,208]. According to Namchot and Jitkarnka [95], the mixture of C₄ and C₅ hydrocarbons, with some of them being the monomers of tyre rubber (butadiene and isoprene), is directly formed by breaking the C-C bond of the molecules that make up SBR and NR, and zeolites and mesoporous materials improve the cracking ability of these chains. A high content of these hydrocarbons leads to an increase in the calorific value, which makes more interesting the gas for covering pyrolysis energy requirements, even though it is also suitable for fuel applications after appropriate gas conditioning [114,188,209].

Arabiourrutia et al. [87] observed that the yields of ethene, propene, 1,3-butadiene, 2-butene increased considerably using HZSM-5 and HY zeolites. They also observed a higher selectivity to propene and butadiene with the HZSM-5 (due to the shape selectivity of this zeolite, which favors monomolecular cracking) [219], while HY has higher activity for butadiene transformation due to its higher hydrogen-transfer capacity. These results are reasonable in view of the well-known capacity of the HZSM-

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5 zeolite for monomolecular cracking reactions and because ethene is the final product of the oligomerization-cracking reactions of heavier olefins [86,219].

Although attention has been mainly devoted to the improvement of TPO characteristics, there are studies focusing on the upgrading of the properties of the gaseous stream, as are those dealing with the increase in light olefin formation using different types of catalysts [193,208,242]. As is well known, olefins, especially light olefins, are essential organic chemical raw materials. Currently, light olefins are mainly produced from oil in steam crackers and refinery fluid catalytic cracking units [243]. In order to increase olefin production, Witpathomwong et al. [208] used synthesized Ru/MCM-48 catalysts and observed that the mesoporous structure of the MCM-48 provides higher selectivity to propylene than to ethylene. When Ru metal was incorporated, the yields of ethylene and propylene were slightly improved, and a higher gas production was attained. Similarly, He et al. [242] combined a nano-HZSM-5 of short micropore channels with a mesoporous γ -Al₂O₃ to obtain a nano-HZSM-5/ γ -Al₂O₃ composite catalyst in order to increase light olefin production. They concluded this catalyst selectively produced 29.9% olefins, especially C₄ olefins.

The presence of CO and CO₂ in the tyre pyrolysis gases was attributed to the thermal degradation of oxygenated additives, such as extender oils or stearic acid, and charges like CaCO₃ [74]. Their yields commonly increase when a catalyst is used [87], but due to the higher increase of other light hydrocarbons, their concentrations are lower in the produced gas [86,190,219]. In fact, Olazar et al. [86,219] observed that the presence of HZSM-5 and HY catalysts reduce the concentration of CO and CO₂, due to the low activity of these catalysts for decarbonylation and decarboxylation reactions.

Conclusions

1 A detailed review has been carried of the literature on waste tyre catalytic pyrolysis
2 from the pioneering studies in the 1980s to the most recent ones. Fundamentals aspects
3 of this process are addressed. Thus, the different catalysts used in the literature, their
4 role in product yields and their composition and the reaction mechanism are discussed
5 in detail. In addition, technological aspects of the process are also considered with a
6 thorough review of the main pyrolysis technologies, which allows drawing the
7 conclusions detailed below.
8

9 The main interest of waste tyre valorization by pyrolysis lies in the potential
10 applications of the products obtained, i.e., gas, TPO and char, whose yields and
11 composition strongly depend on pyrolysis conditions. The main product obtained in the
12 thermal pyrolysis is the liquid fraction, usually named tyre pyrolysis oil or TPO.
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14 However, the use of highly acid catalysts may promote TPO cracking and greatly
15 reduce its yield. This liquid has a complex composition including hydrocarbons of
16 different nature (aromatics, paraffins, olefins and naphthenes) and sulfur compounds,
17 which limits its direct use as fuel. Moreover, this oil is characterized by its remarkable
18 heating value, usually in the 41-44 MJ kg⁻¹ range, with a wide boiling point range. It is
19 to note that the interest of catalytic pyrolysis is usually related to the improvement of
20 this fraction features or its yield. Thus, great attention has been paid to the production of
21 interesting chemicals, such as aromatics. In addition, the reduction of sulfur content in
22 the TPO and the cracking of the oil heavy fraction is also commonly pursued in waste
23 tyres catalytic pyrolysis. Pyrolysis gases can be used as fuel, although specific catalysts
24 may promote the production of light olefins. Finally, the char or solid product is a
25 carbonaceous material with interesting applications as a source of activated carbons or
26 recycled carbon black. It should be noted that the use of catalysts has a limited impact
27 on the char yield and features. Accordingly, the literature dealing with catalytic
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pyrolysis paid limited attention to the solid fraction. However, it should be pointed out that this product has a great impact on the overall economy and profitability of the process.

Regarding the technological aspects of the process, a wide range of reactor configurations have been reported for the catalytic pyrolysis of waste tyres, with catalysts being placed either in situ or in line in a second reactor. The vast majority of the studies in the literature are of preliminary nature. Thus, laboratory scale fixed bed batch reactors are the most common ones. Moreover, some studies were performed in different bench scale units, including fluidized beds, spouted beds and rotary reactors. Finally, the results reported at pilot plant scale operating under fast pyrolysis in continuous regime are scarce, although they are those with better perspectives for their implantation. Therefore, the limited technical development of this process is a challenge to be overcome for the full scale development of the process.

Catalysts of different nature have been applied in the valorization of waste tyres, with zeolites being the most widely used. The acidity and shape selectivity of these catalysts promote the cracking of TPO and increase the production of gaseous products. Thus, the interest in the use of different zeolites, such as ZSM-5, Y and β , has been associated with the production of valuable chemicals, such as aromatics and light olefins.

Furthermore, base catalysts, such as MgO, Na₂CO₃ and NaOH, led to a positive effect on TPO yield. Therefore, the higher selectivity towards valuable fractions and/or chemicals observed with suitable catalysts reinforces the commercial interest and perspectives of waste tyre valorization by catalytic pyrolysis. It should be also noted that the lack of experience in full scale units involves a serious challenge. Thus, fundamental aspects to understand and evaluate the catalytic performance at full scale, as are those related to catalyst deactivation and regeneration, have hardly been

1 approached. It is to note that detailed knowledge on catalyst deactivation is required for
2 the optimum reactor design and implementation of advanced reaction-regeneration
3 strategies. In fact, these studies are required to assess material and operating costs in
4 catalytic pyrolysis in relation to the non-catalytic process in order to strike a balance
5 between the improvement in the value of the product and the increase in the processing
6 cost.
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13 In spite of the limited success of industrial projects involving tyre pyrolysis and the
14 incipient steps taken in catalytic pyrolysis, the need for sustainable and environmentally
15 friendly valorization processes is a key factor that surely will boost the development of
16 thermochemical valorization processes.
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40 **Nomenclature**

41
42 BR Butadiene rubber
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44 BTX Benzene, toluene and xylene
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46 CSBR Conical spouted bed reactor
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48 C/T Catalyst to tyre ratio
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51 FCC Fluid catalytic cracking
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54 NR Natural rubber
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57 OMM Ordered mesoporous materials
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60 PAH Polycyclic aromatic hydrocarbons
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1 SAPO Silica-alumina-phosphate

2 SBR Styrene butadiene rubber

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5 TDF Tyre drived fuel

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7 TPO Tyre pyrolosis oil

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10 VOC Volatile organic compounds

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12 WT Waste tyre

13 14 **References**

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