



## Valorisation of Waste Tires by Pyrolysis over a FCC Catalyst in a Conical Spouted Bed Reactor

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A commercial FCC catalyst based on a zeolite active phase has been used to perform the valorisation of waste tires by in situ catalytic pyrolysis. The process has been carried out in a conical spouted bed reactor provided by a continuous feeding system. The catalyst has been subjected to a steaming treatment in order to maximize diesel fraction. High diesel (50.5 wt %) and char (35 wt %) yields are obtained, together with low gas (0.6 wt %) and gasoline (13.9 wt %) fractions. The obtained liquid is highly aromatic, which is formed at the expense of the non-aromatic gasoline fraction.

### 1. Introduction

Waste tires management is a major environmental problem due to the large amount generated worldwide (over 26 Mt in 2011 (IRSG, 2012)) and the regulations that forbid their landfill. New routes for waste tires recycling have been developed, such as their use in asphalt surfacing and in the manufacturing of waterproofing systems and composites for construction (Yilmaz et al., 2009). However, pyrolysis is one of the most feasible technologies for waste tire valorisation, as it enables the subsequent individual valorisation of gaseous, liquid, and carbon black fractions and it has a higher efficiency for energy and a lower environmental impact than incineration (Sharma et al., 2000).

Several reactor configurations have been used to perform waste tires pyrolysis, such as fixed beds (Islam et al., 2008), rotary kilns (Aylon et al., 2008), circulating fluid beds (Dai et al., 2001), bubbling fluid beds (Kaminski et al., 2009) and vacuum moving beds (Roy et al., 1999). A conical spouted bed reactor (CSBR) has been used in this study for tire pyrolysis. This reactor is an alternative technology to classical fluid beds for handling sticky and irregular materials such as scrap tires (Olazar et al., 2008), due to the cyclic particle movement that avoids bed defluidization by agglomeration of particles and leads to high mass and heat transfer rates between phases; the short residence time of volatiles, which minimizes secondary reactions and allows high yields of sensitive products; and its capacity for treating scrap tires with a wide particle size distribution or with acid catalysts, without bed segregation problems.

The pyrolysis of tires produces a liquid yield typically in the 50-60 wt % range, which could be used as fuel or as refinery feedstock (Karthikeyan et al., 2012). However, in order to increase the production of high value individual compounds, the use of catalysts is required. In this sense, acid catalyst, such as HZSM-5 or HY zeolites, enhance cracking reactions that lead to higher yields of light olefins and BTX, or diesel fraction (Arabiourrutia et al., 2008; Olazar et al., 2008). However, this catalytic process may not be viable due to the high cost of manufacturing the catalysts mentioned above. Therefore, the use of equilibrated fluid catalytic cracking (FCC) catalysts in the pyrolysis process would be economically

advantageous, as the FCC process generates huge quantities of spent catalyst that is still active for other processes.

In this work, the in situ use of a FCC catalyst in the pyrolysis of waste tires in a conical spouted bed reactor has been studied with the aim of obtaining a higher yield of diesel fraction that could be further used a fuel.

## 2. Experimental

### 2.1 Raw material and catalyst

The tire material was supplied by JENECAN S.L. (Bilbao, Spain), laminated and completely free of steel, carcass and textiles. This material is a typical formulation used for cars and consists of natural rubber and styrene-butadiene rubber in the same proportion, carbon black and additives such as zinc oxide, phenolic resin, and to a lesser degree, aromatic oil. The tire material has been ground to a particle size below 1 mm after been frozen in liquid nitrogen. The high heating value (determined in an isoperibolic calorimetric bomb, Parr 1356) is 38.5 MJ kg<sup>-1</sup>.

A commercial FCC catalyst based on a zeolite active phase has been used in the catalytic pyrolysis of waste tires. The catalyst has been subjected to a steaming treatment at 816 °C for 8 h, as suggested by Degnan et al. (2000), in order to decrease the acid site density and the number of strong acid sites in the structure (Occelli et al., 2001). This treatment improves the production of diesel-oil fraction, as has been previously observed in the catalytic pyrolysis of HDPE (Olazar et al., 2009).

The porous structure of the catalyst has been characterized by N<sub>2</sub> adsorption–desorption (Micromeritics ASAP 2010) and total acidity and the acid strength distribution of the catalyst have also been determined in a calorimeter (Setaram TGDCS111), Table 1.

Table 1: Properties of the equilibrated FCC catalyst.

BET surface area (m <sup>2</sup> g <sup>-1</sup> )	187
Micropore volume (cm <sup>3</sup> g <sup>-1</sup> )	0.06
Mesopore volume (cm <sup>3</sup> g <sup>-1</sup> )	0.10
Predominant pore diameter (Å)	473
Acid strength (kJ mmol NH <sub>3</sub> <sup>-1</sup> )	88
Total acidity (mmol NH <sub>3</sub> g cat <sup>-1</sup> )	0.04

### 2.2 Pyrolysis plant and experimental procedure

The experimental equipment used to perform the catalytic pyrolysis runs is shown in Figure 1. The pyrolysis plant, which is provided by a conical spouted bed reactor, has been based on previous hydrodynamic studies and on its application in the pyrolysis of different materials, such as plastics, biomass or tires. (Olazar et al., 2009; Amutio et al., 2012; Lopez et al., 2009, 2010).

The plant has a system for feeding scrap tires, which is pneumatically actuated and is able to feed up to 300 g h<sup>-1</sup> of tire. The nitrogen flow is controlled by a mass flow meter that allows for feeding up to 30 L min<sup>-1</sup>. Prior to entering the reactor, it is heated to the reaction temperature by means of a preheater.

The reactor is the main element of the unit and is a spouted bed of conical geometry with a cylindrical upper section. The total height of the reactor is 34 cm, the height of the conical section 20.5 cm, and the angle of the conical section 28°. The diameter of the cylindrical section is 12.3 cm, the bottom diameter 2 cm and the gas inlet diameter 1 cm. The conical spouted bed reactor allows continuous operation by selectively removing the carbon black from the bed, which avoids its accumulation throughout the pyrolysis process (Lopez, 2009).

The volatile products leave the reactor together with the inert gas and pass through a high-efficiency cyclone followed by a 25 mm sintered filter, both placed at the reactor outlet. The gases leaving this filter circulate through a volatile condensation system consisting of a condenser and two coalescence filters. The condenser is a double shell tube cooled by tap water. The coalescence filters ensure total condensation of volatile hydrocarbons.

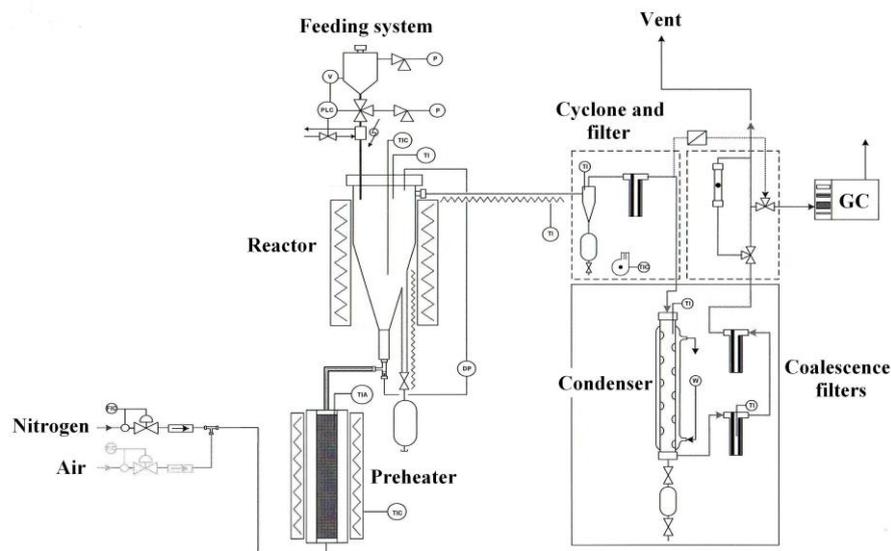


Figure 1: Scheme of the pyrolysis unit

Pyrolysis runs have been carried out at 450 °C with the steamed FCC catalyst. The bed was initially made up of 30 g of catalyst (particle size between 20 and 90  $\mu\text{m}$ ), and in order to ensure stable spouting, the nitrogen flow rate has been set at 1.2 times the minimum spouting velocity, 0.7 L  $\text{min}^{-1}$  (measured at normal conditions).

The scrap tire has been continuously fed with a rate of 3 g  $\text{min}^{-1}$ . In each run 100 g of tires were fed and product analysis has been carried out on line by means of a Varian 3900 chromatograph for the volatile compounds and a Varian 4900 micro GC for the permanent gases. The volatile compounds are introduced in the chromatograph by means of a thermostated line connected to the reactor outlet that is maintained at 280 °C in order to avoid condensation problems. Once a run has been completed, the char (carbon black) collected by the lateral outlet and cyclone and filter has been weighted and the mass balance has been closed based on the yield of carbon black and the yield of volatiles.

### 3. Results

The products obtained in the catalytic pyrolysis process of waste tires have been grouped into four fractions: C<sub>1</sub>-C<sub>4</sub> gas fraction, C<sub>5</sub>-C<sub>10</sub> gasoline fraction, C<sub>11+</sub> diesel fraction and char, whose yields are summarized in Table 2.

Table 2: Yields of the fractions obtained in the pyrolysis of waste tires at 450 °C over a FCC catalyst.

Fraction	Yield (wt %)
C <sub>1</sub> -C <sub>4</sub>	0.6
C <sub>5</sub> -C <sub>10</sub>	13.9
C <sub>11+</sub>	50.5
Char	35

As observed, the main product fraction is C<sub>11+</sub> or diesel fraction, followed by char fraction or residual carbon black. The latter is a carbonaceous product (more than 85 wt % of carbon), with a heating value around 30 MJ  $\text{kg}^{-1}$  and low surface area (around 36  $\text{m}^2 \text{g}^{-1}$ ) (Lopez et al., 2009, 2010), that can be used in tire formulation or converted into activated carbons by several processes (Mui et al., 2007).

Gas and C<sub>5</sub>-C<sub>9</sub> gasoline fractions' yields are low due to the severe steaming process treatment, which is known to increase diesel production.

Table 3 shows the composition of the gas, gasoline and diesel fractions, according to their chemical bonds, as well as the yields of the most important individual compounds in each group.

Table 3: Composition of the fractions obtained in the catalytic pyrolysis of waste tires.

<b>Compound</b>	<b>Yield (wt %)</b>
<b>C<sub>1</sub>-C<sub>4</sub></b>	<b>0.6</b>
<i>Propylene</i>	0.11
<i>1-butene</i>	0.15
<b>C<sub>5</sub>-C<sub>10</sub></b>	<b>13.9</b>
Paraffins	0.0
Isoparaffins	0.2
<i>2-methyl-nonane</i>	0.14
Aromatics	9.75
<i>ethyl benzene</i>	0.88
<i>1-methyl-4-(1-methylethyl) benzene</i>	1.96
<i>1-ethenyl-3-methylbenzene</i>	0.79
<i>(1-methyl-2-propenyl) benzene</i>	0.84
Naphthenes	0.6
<i>1-ethyl-5-cyclopentane</i>	0.08
<i>ethenyl cyclohexane</i>	0.11
Olefins	2.6
<i>2-pentene</i>	0.11
<i>1-methyl-4-(1-methylethyl)-1,3-cyclohexadiene</i>	0.31
<i>5-methyl-3-(1-methylethenyl) cyclohexane</i>	0.15
<b>C<sub>11</sub>+</b>	<b>50.5</b>
Paraffins	1.0
<i>Pentadecane</i>	0.35
<i>Heptadecane</i>	0.35
Isoparaffins	0.0
Aromatics	45.2
<i>2,3-dihydro-5-methyl-1H-indene</i>	0.75
<i>Naphthalene</i>	1.18
<i>1,3-dimethyl-2,3-dihydro-1H-indene</i>	0.71
<i>2-ethyl-2,3-dihydro-1H-indene</i>	1.01
<i>4,7-dimethyl-2,3-dihydro-1H-indene</i>	0.81
<i>2-methylnaphthalene</i>	2.82
<i>1-ethyl-1,2,3,4-tetrahydronaphthalene</i>	1.01
<i>1-methylnaphthalene</i>	2.36
<i>2-ethylnaphthalene</i>	1.06
<i>1,2,3,4-tetrahydro-1,6-dimethylnaphthalene</i>	1.35
<i>1,5-dimethylnaphthalene</i>	1.47
<i>1,7-dimethylnaphthalene</i>	1.43
<i>2,4-cyclohexadien-1-ilbenzene</i>	0.79
<i>1-(2-propenyl)naphthalene</i>	0.74
<i>2-(2-propenyl)naphthalene</i>	0.74
Naphthenes	0.0
Olefins	0.0
<b>Char</b>	<b>35</b>

Gas fraction is mainly made up of olefins, such as propylene or 1-butene, with lower amounts of alkanes. Gasoline C<sub>5</sub>-C<sub>10</sub> fraction is highly aromatic, with the most important compounds being those with a high carbon number (C<sub>9</sub> and C<sub>10</sub>). Furthermore, C<sub>11+</sub> or diesel fraction is composed of aromatics with a wide distribution range, being the main compounds indene and naphthalene derivatives.

In order to study the effect of the FCC catalyst addition in tires pyrolysis, the results obtained in this runs have been compared to those obtained previously in non-catalytic pyrolysis (Lopez et al., 2009, 2010), Figure 2. Liquid fractions (C<sub>5</sub>-C<sub>10</sub> and C<sub>11+</sub>) have in turn been divided according to their type of bond into aromatics and non-aromatics.

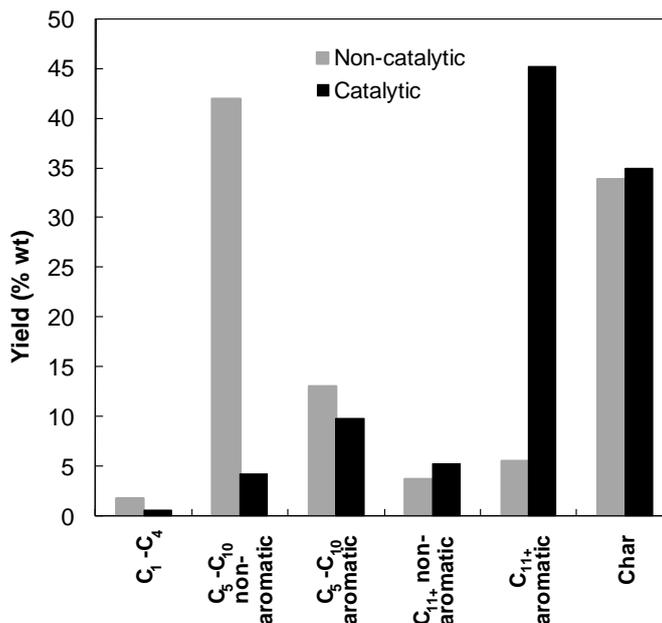


Figure 2: Influence of the addition of the FCC catalyst in the pyrolysis of waste tires.

It is noteworthy that the addition of the FCC catalyst produces a high yield of C<sub>11+</sub> diesel fraction, at the expense of a decrease in the yield of C<sub>5</sub>-C<sub>10</sub> gasoline. Furthermore, the liquid obtained in the non-catalytic pyrolysis is mostly non-aromatic; whereas that obtained with the FCC catalyst is a highly aromatic liquid that will have to be subjected to further treatments before its use as fuel. This trend was previously observed in the catalytic pyrolysis of tires with other types of zeolites, where the HZSM-5 produced a higher gas yield, mainly made up of olefins, and exhibited a high selectivity towards BTX compounds, whereas HY zeolite produced a C<sub>11+</sub> aromatic fraction (Arabiourrutia et al., 2008; Olazar et al., 2008). The FCC catalyst, as the HY, has low shape selectivity that favours the generation of aromatic C<sub>11+</sub> in the liquid fraction, by means of BTX alkylation and condensation of olefins and aromatics fraction (Arabiourrutia et al., 2008; Olazar et al., 2008).

#### 4. Conclusions

The conical spouted bed reactor is a suitable technology for in situ catalytic pyrolysis of waste tires, without problems of stability, segregation, or bed agglomeration. FCC catalyst has a significant effect on product distribution and composition, increasing the yield of diesel fraction, from 9 wt % at non-catalytic pyrolysis to 50 wt %. A highly aromatic C<sub>11+</sub> liquid is obtained, at the expense of gasoline non-aromatic fraction, due to the alkylation and condensation reactions that favour the formation of naphthalene derivative compounds. Therefore, so as to meet commercial fuel standards, the liquid should be subjected to hydrotreatment processes.

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