Role of the Catalyst in the Pyrolysis of Polyolefin Mixtures and Used Tires

Humberto Palza, Cristian Aravena, and Madeleine Colet*

Departamento de Ingeniería Química y Biotecnología, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Beauchef 851, Santiago, Chile

ABSTRACT: The role of polymeric structures and the presence of a catalyst in the pyrolysis of polyolefin mixtures and used tires was studied in a fixed bed reactor at 450 °C. Our results showed that while thermal pyrolysis of high density polyethylene (HDPE) produced 23.3%wt of condensable products, a mixture of polyolefins (HDPE, LDPE, and PP) showed an increase of more than 23%wt in this fraction. In both cases, a wide carbon number distribution was obtained for the condensable products, confirming that there was not any selectivity. By using HZSM-5 zeolites, the pyrolysis of pure HDPE was dramatically changed with both more gaseous products and a major selectivity toward C10−C16 hydrocarbons in the condensable fraction. It is noteworthy that, although the PP present in the mixture increases the production of lighter hydrocarbons as compared with pure HDPE, no major differences in product distribution were observed between HDPE and polyolefin mixture in catalytic pyrolysis. However, the zeolites used improved the quality of condensable products that can be used as potential fuels or feedstocks. When used tires were thermally pyrolyzed, a decrease of 33.5%wt in the solid product fraction (char and unreacted polymer) compared with pure HDPE was observed. In the case of catalytic pyrolysis of used tires, the increase of gaseous products is not as pronounced as in pure HDPE. Moreover, the carbon number distribution under catalytic pyrolysis was significantly different compared to that obtained for polyolefins. These results give evidence about the strong effect of both polymer microstructure and mixture on the pyrolysis processes.

1. INTRODUCTION

In recent years, chemical recycling has become more important since it is one of the few solutions to the problems associated with either waste plastic mixtures or tires.[1] Most research about chemical recycling of plastics focuses on polyolefins, mainly high density (HDPE)/low density (LDPE) polyethylenes and polypropylene (PP), because their high levels of production lead to a substantial volume of waste.[2] For instance, polyolefins are mostly used in packaging, one of the largest segments in the plastic market where materials are discarded immediately after use.[3] On the other hand, a large amount of tires are discarded every year and their production shows no sign of diminishing in the future.[4] These characteristics of both polyolefins and tires, along with the environmental regulations, make the chemical recycling of their wastes an important issue.

Pyrolysis is a chemical recycling process where polymers are degraded thermally in an inert atmosphere, and it is widely studied due to its potential to produce high quality fuels.[5,6] In thermal pyrolysis the temperature is the main variable associated with products yield,[7−10] getting values in the range 400−800 °C. Usually the products obtained by thermal pyrolysis cannot be used directly as fuels because they do not meet the required quality standards[11−13] and hydrocarbons formed presented a wide carbon number distribution.[5,6] For this reason, and because of the high operating temperatures, the use of catalysts has been studied. Many of the catalysts used in pyrolysis come from the petrochemical industry, such as solid acid catalysts that are the most widely studied in the literature, particularly those having a zeolitic structure.[14] For instance, HZSM-5 is one of the most effective zeolites for pyrolyzing polyolefins.[15−17] At lower temperatures and residence times than those of thermal pyrolysis, the same yields can be

obtained.[18−21] Moreover, catalytic pyrolysis provides a better control of the products distribution,[22−27] increasing the selectivity to gasoline range products.[18,28,29] In the case of used tires, there are much fewer studies about their catalytic pyrolysis[30,31] because the thermosetting characteristic of rubber does not allow the proper direct contact between the polymer and the catalyst. In this case, the pyrolysis should be performed in a two-stage fixed bed process where thermal pyrolysis takes place first and then the gaseous product are upgraded by the use of a catalyst.[32−34] Different rubbers were pyrolyzed under these conditions, yielding a decrease in the oil yield, which was associated with an increased gaseous fraction.[32,34−36] In addition, HZSM-5 zeolites can decrease the molecular weight of the liquid products obtained from pyrolysis of scrap tires, improving the production of commercially interesting products.[37]

Due to the cost related to sorting polymer wastes, attention has been given to both the effect of polymer structure and the interactions between different plastics in the pyrolysis processes.[38−43] Some authors have already studied the increasing decomposition rate of PP and LDPE as a result of tertiary carbons associated with the presence of methyl groups or branches.[29,44−46] Tertiary carbon provides favorable positions for initiation of degradation; therefore, more moderate temperatures are required than in the case of linear polymers. Jing et al.[38−40] studied the interactions between PP, LDPE, and HDPE, showing a significant effect of PP in the

degradation of the mixture. The presence of PP was able to decrease the cracking temperature of the mixture and the viscosity of the oil products as well as provide more radicals at lower temperatures, enhancing the PE degradation through chain transfer reactions. However, some studies did not find any evidence of interactions between PP and PE stating that the results obtained were equivalent to the sum of the pyrolysis of each polyolefin separately.[47−49] In the case of catalytic pyrolysis of polyolefin mixtures, Serrano et al.[43] reported the presence of steric hindrances between the catalyst and polymers. In particular, the presence of methyl groups in PP introduced steric hindrances, implying that linear molecules (HDPE) enter and diffuse through catalyst pores easier.[29,45] Accordingly, the highest activities were obtained for the catalysts that present a higher proportion of external acid sites and a more favorable diffusion regime producing lighter hydrocarbons. Regarding rubber polymers, the effect of their structure was confirmed by studying styrene−butadiene rubbers (SBR). Pyrolysis of SBR produced oils with a higher proportion of aromatics compared to polyolefins, attributed in part to recombination reactions that take place among aliphatic and aromatic free radicals coming from the degradation of aromatics structures in the polymer.[50] These results highlighted the effect of polymer structures and interactions between them on the pyrolysis processes.

The products obtained from the pyrolysis of plastic wastes are able to be used directly as a fuel because they meet some quality standards.[51−53] Nevertheless, other authors have studied the hydroreforming of plastic pyrolysis oils to obtain high quality fuels that can be included in the formulation of transportation fuels.[54−56] In the case of oils from used tires, they should be upgraded by hydrotreating, and these can only be used as a component of fuel oils.[57]

Since the polymer determines the behavior of pyrolysis reactions and their products, the aims of this paper are to discuss the role of the polymer structures on thermal and catalytic pyrolysis reactions of a mixture of HDPE, LDPE, and PP in a ratio similar to that found in plastic solid wastes. The catalysts used were two commercial HZSM-5 zeolites with different Si/Al ratios. Finally, pyrolysis of used tires was performed and contrasted with results from a polyolefins mixture to verify the influence of bulky polymers in the degradation reactions and its products.

2. EXPERIMENTAL SECTION

2.1. Materials. The polyolefins used were high density polyethylene (HDPE), low density polyethylene (LDPE), and polypropylene (PP). In the case of HDPE, both virgin and waste plastics were studied. Virgin HDPE was supplied in pellet form by Ipiranga Petroquímica S.A., and waste polyolefins were obtained from household wastes. Both were processed in an analytical mill (110 VAC/60 Hz, Cole-Parmer) and then sieved in the particle size fraction below 250 μm (mesh number 60). This was done to have a better mixture of polyolefins and catalyst in the reactor. Based on reported data for plastic wastes in the United States, the polyolefin mixture consisted of 27.6%wt of HDPE, 36.6%wt of LDPE, and 35,8%wt of PP.[58] In addition, used tires derived from passenger cars, free of steel, carcass, and textiles, were further studied. These were shredded to granules of the size range 2−5 mm.

The catalysts used were HZSM-5 zeolites supplied by Tosoh Corporation. The properties were provided by the manufacturer, except for BET area, which was obtained by N_2 adsorption−desorption (Micromeritics ASAP 2010). These properties are shown in Table 1.

In the case of used tires, the catalysts were pelletized, crushed, and sieved using 850 and 500 μm sieves.

Table 1. Properties of Zeolites Used in This Work

	Product name	Si/Al ratio	Particle Size [μm]	BET area [m^2/g]
HZSM-5(1)	HSZ-840	38	10	282.3
HZSM-5(2)	HSZ-822	23.8	10	289.3

2.2. Pyrolysis system and experimental procedure. Thermal and catalytic pyrolysis reactions were performed in a fixed bed reactor under nitrogen atmosphere. The reactor is a 20 mL Pyrex glass tube in U-form. The condensable products were collected in an expansion tube and a cold trap immersed in a mixture of salt and ice. The gaseous products were stored in a 1.5 L Tedlar bag. After the pyrolysis experiment, solid residues remained in the reactor. A scheme of the pyrolysis system is given in Figure 1.

1. **Fixed Bed Reactor**   4. *Schlenk* Tube
2. **Vertical Tube Furnace**   5. *Dewar* Flask
3. **Expansion tube**
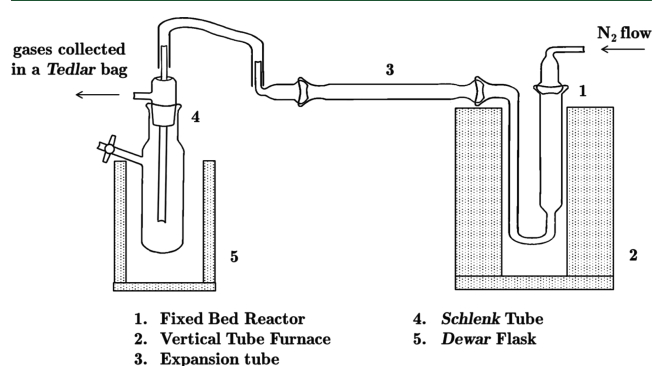
Figure 1. Scheme of the pyrolysis system.

Initially all glassware was weighed, and then 0.5 g of polymer was put into the reactor over a glass wool. In the case of polyolefins, when catalyst was used, 0.5 g of HZSM-5 zeolite was added and then mixed with the polyolefin. Regarding used tires, first pelletized HZSM-5 zeolite was loaded into the reactor and then the granules of used tires, both separated by glass wool. Next, the system was assembled, the temperature was set at 450 °C, and N_2 flow was adjusted to about 1 mL/s. A heating rate of 10 °C/min was used, and the reaction time started once the set temperature was reached. Finally, when the reaction time was ended (40 min for polyolefins, 10 min for used tires), all glassware was again weighed and a mass balance was determined to obtain the yields of gases, condensables, and solids. These values represent the product distribution of the pyrolysis reaction.

2.3. Thermogravimetric analysis. Thermogravimetric analysis (TGA) was done for HDPE, polyolefin mixtures, and used tire samples with (using a NETZSCH TG 209 F1 Libra). The experiments were carried out under dynamic conditions with a nitrogen flow of 20 mL/min and a heating rate of 20 K/min. For used tires, a DTG curve was obtained at 10 K/min. Samples (about 5−10 mg) were heated from room temperature to 600 °C. Onset (T_o), inflection (T_i), and end of degradation (T_f) temperature were reported. To analyze the effect of the catalyst in thermoplastic samples, a weight ratio of 1:1 was used between polymer and catalyst.

2.4. Product characterization. The carbon number distribution of the products was analyzed with chromatography tools. The analyses of the gaseous products (C1−C6) were performed in a PerkinElmer Clarus 500 gas chromatograph (GC) equipped with a flame ionization detector (FID) and using a HP-PLOT column (30 m × 0.32 mm; df = 0.25 μm). Helium flow was adjusted to 20 mL/min, and the injector temperature was set at 250 °C. The temperature program started at 45 °C, was held for 2.1 min, followed by a ramp of 19.4 °C/min to 170 °C, and a hold for another 5 min. The gaseous products were previously diluted from 25 to 100 μL with nitrogen. The injection volumen was 25 μL.

Aliphatic hydrocarbons (C10−C40) in condensable products were detected using a Shimadzu GC-2010 Plus equipped with a FID and

using a RTX-5 column (30 m × 0.32 mm; df = 0.25 μm). Nitrogen flow was adjusted to 30 mL/min, and the injector temperature was set at 280 °C. The temperature program started at 60 °C, was held for 1 min, followed by a ramp of 12 °C/min to 300 °C, and then a ramp at 6 °C/min to 330 °C, and a hold for another 2 min. The samples of about 10 mg were diluted in 2.5 mL of hexane. Injections of 1 μL were used with a split ratio of 50:1. The identity of the peaks was determined using a Restek NJDEP EPH 10/08 Rev.02 Aliphatics Calibration Standard (20 components).

1H-NMR spectroscopy (Bruker Avance III HD-400, CDCl3) was performed to determine the hydrocarbon types in condensable products and to provide an indication of product quality. Aromatics, paraffins, and olefins were estimated using the literature correlations defined elsewhere.[59]

3. RESULTS AND DISCUSSION

3.1. Pyrolysis of individual polyolefins. The onset (T_o), inflection point (T_i), and end of degradation (T_e) temperatures of virgin and waste HDPE samples obtained from TGA are summarized in Table 2. Our results show that the thermal

Table 2. Thermogravimetric Analysis of Virgin and Waste HDPE

|	Virgin HDPE			Waste HDPE		
	T_o	T_i	T_e	T_o	T_i	T_e
Thermal	457.4	482.3	493.9	463.9	486.9	499.4
HZSM-5(1)	361.4	392.9	403.5	365.0	399.8	429.8
HZSM-5(2)	279.1	307.0	345.9	303.4	368.5	389.7

degradation behavior is similar to both virgin and waste HDPE with differences less than 6.5 °C between characteristic temperatures. Ciliz et al.[60,61] found that the presence of impurities in waste polyolefins decreased the characteristic temperatures obtained by TGA. In the current study, negligible effects of impurities were detected in the thermal degradation of waste polyolefins. Catalytic analyses were carried out with two HZSM-5 zeolites having different Si/Al ratios. The characteristic temperatures were drastically reduced compared with thermal degradation, proving the significant capability of HZSM-5 zeolites to crack polyolefins. The reduction in degradation temperatures depended on the type of zeolite, with HZSM-5(2) having the largest effect with differences as high as 170 °C because of its larger number of active sites (lower Si/Al ratio). It is noteworthy that the catalyst behavior was affected by the polymer used with lower activity in waste HDPE, likely because of impurities that induce its deactivation[62] and enhance the char forming reactions.[61]

Due to the practical relevance in recycling, hereafter the results were focused on waste polyolefins in order to further study their degradation behavior. TGA curves for each waste polyolefin are shown in Figure 2. Regarding pure thermal analysis, the lowest degradation temperatures were obtained for PP in agreement with previous studies stating that the presence of methyl groups in the chain increased the number of tertiary carbons.[29,45] Adjacent to tertiary carbons are the weaker C−C bonds, which enhance random scission of the polymer chains.[63] LDPE also has tertiary carbons in its structure due to the presence of branches, but their amount is much less than that in PP, which has methyl groups on alternate carbons of its chains.[64] Therefore, PP has the lowest degradation temperature followed by LDPE, and the most stable polymer is HDPE because of its linear structure.[29,46,65]
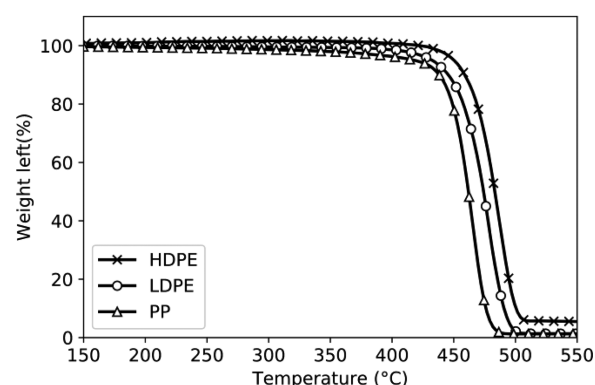
Figure 2. Thermogravimetrical analysis of individual waste polyolefins.

Both HZSM-5 zeolites were efficient for waste polymer degradation, shifting the curves to lower temperatures (Figure 3). However, the effect depended on the polymer tested with
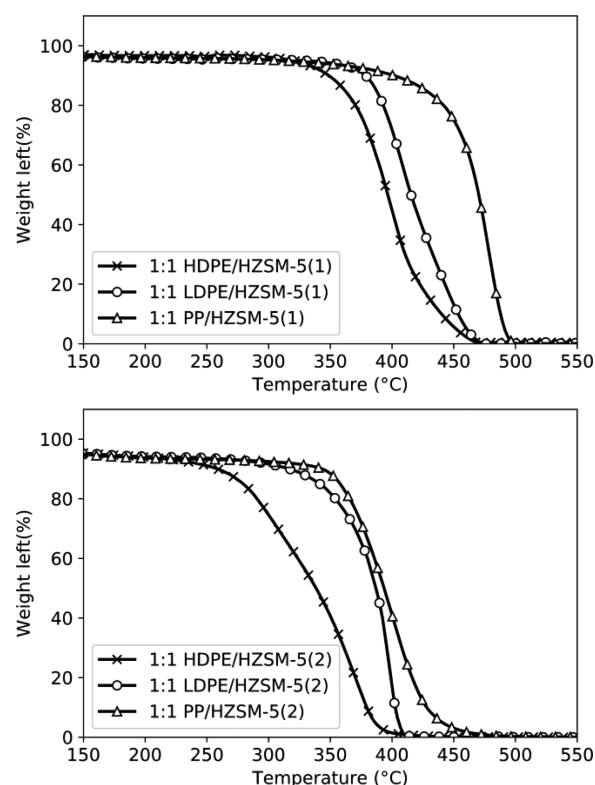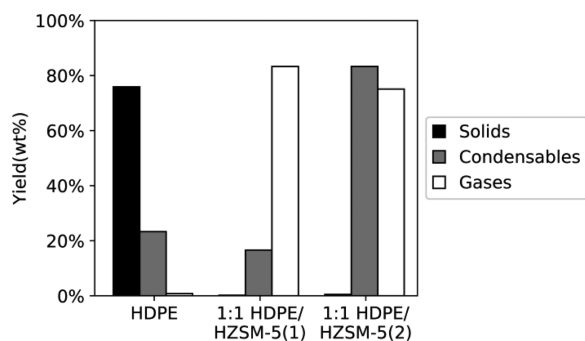

Figure 3. Thermogravimetrical analysis of individual waste polyolefins using HZSM-5 zeolite catalysts (polymer/catalyst ratio of 1:1).

PP showing the lowest reduction in degradation temperatures. In this case, the temperatures were decreased about 79 °C by using HZSM-5(2), and even with HZSM-5(1) no changes were noted. PP chains present a great cross-sectional area (bulky structure), inducing steric hindrances preventing the access to active sites;[45] therefore, zeolites containing very few or no active sites, that is, with higher Si/Al ratio, do not have a significant influence on degradation of PP. It has been reported that silicalite, the siliceous form of ZSM-5 (Si/Al > 1000), has a very minimal effect on PP degradation,[66] and as the Si/Al ratio increases, the effect decrease.[17] With LDPE the decrease of degradation temperatures by using HZSM-5 zeolites was about 63−89 °C, which is lower than with HDPE (90−157 °C).

Marcilla et al.[67] found that the high number of chain ends associated with branches in LDPE reach more easily the HZSM-5 zeolite pores, accessing more active sites. As discussed above, the waste LDPE used in this work has impurities promoting the formation of coke, which makes the penetration of chain ends into the pores of the zeolite more difficult. Therefore, the degradation reactions in LDPE were mainly carried out on the external surface area. In addition, the branched structure of LDPE also could induce steric hindrances. As can be noted from Figure 3, the catalytic effect was enhanced by using HZSM-5(2), having a higher external surface area and lower Si/Al ratio than HZSM-5(1); therefore, it has more readily available active sites.

Based on TGA results using catalyst, pyrolysis reactions of waste HDPE were performed in a fixed bed reactor at 450 °C. The product distribution in thermal degradation is displayed in Figure 4 showing that the solid fraction, composed of unreacted

Figure 5. Carbon number distribution of gaseous products obtained in the pyrolysis of waste HDPE (polymer/catalyst ratio of 1:1) at 450 °C.

Figure 4. Yields obtained in thermal and catalytic pyrolysis (polymer/catalyst ratio of 1:1) of waste HDPE at 450 °C.

polymer and char, was significantly larger (75.9 wt %) than the condensable (oil and waxes) and gaseous fractions, with the latter being negligible. This is in agreement with the HDPE linear structure, meaning that the energy required to break C−C bonds in the polymer backbone is high.[63] By using HZSM-5(1) and HZSM-5(2), a marked decrease of the solid fraction was noted, and therefore, high yields of gases were obtained with values of 83.3%wt and 75.1%wt, respectively. It has already been reported that, with HZSM-5 zeolites, high yields of gases are obtained, decreasing substantially the oils and waxes produced.[68−70] Although TGA showed that with HZSM-5(2) the degradation temperatures were more reduced than with HZSM-5(1), in pyrolysis reactions the gaseous product fraction was higher by using this latter zeolite displaying a higher degradation rate. This confirms that HZSM-5(2) has more readily available active sites, and therefore, it started to deactivate earlier.

The carbon number distribution from the gaseous and oil products obtained from thermal and catalytic pyrolysis is shown in Figure 5 and Figure 6. These carbon selectivities were normalized to the sum of the peak areas of C1 to C6 and C10 to C40, respectively. In thermal pyrolysis C3, C4, and C6 are the three main components of the gaseous products while a wide carbon number distribution was obtained for the oil products. This is similar to the results reported by Marcilla et al.[71] for LDPE and HDPE, where C3, C4, and C6 were rather produced in the range C1−C6. However, considering the whole range (C1−C42), there is no selectivity under this process. Regarding catalytic pyrolysis, in gaseous products C6 compounds were significantly decreased by about 48% and C3
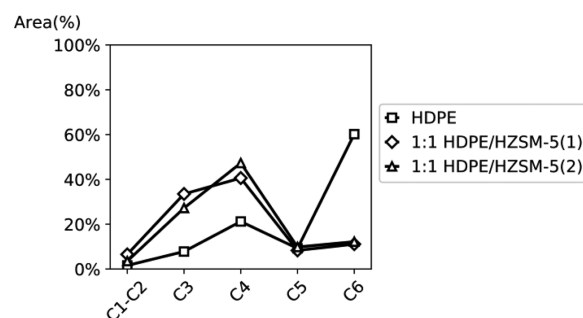
and C4 were increased by about 20%. In oil products, otherwise, C10 compounds were markedly increased, reducing the fraction of C20−C40 compounds. These results are in agreement with previous findings reporting that HZSM-5 zeolites provide selectivity in carbon number distribution to lighter hydrocarbon gases and oils.[68,70,72]

3.2. Pyrolysis of polyolefin mixture. TGA curves for waste polyolefin mixtures are displayed in Figure 7. In the case of thermal degradation, the curve is shifted about 8 °C toward lower degradation temperatures compared to the individual HDPE. As above-mentioned, PP and LDPE have tertiary carbons in their structures and therefore more radicals are formed, enhancing the decomposition reactions of HDPE in the mixture. Jing et al. found a synergetic effect between PE and PP possibly related to intermolecular radical transfer by hydrogen abstraction and complex secondary reactions of the cracked products of PE and PP, reducing the degradation temperature by about 20 °C. They also found that a significant interaction occurs when the mass fraction of PP exceeded 40% wt.[38,39] In our study, a mild effect was noticed at a PP mass fraction of 35.8 wt % in the mixture. In addition, tertiary carbons from branching in LDPE could also contribute to the higher degradation rate,[29,46,65] providing radicals that promote the destabilization of the more stable polymer (HDPE) by intermolecular radical transfer.[73]

In relation to the catalytic degradation, the degradation temperatures were reduced by 74 °C using HZSM-5(1) and by 122 °C using HZSM-5(2), meaning a lower effect of the catalyst than in pure HDPE. This can be associated with steric hindrances caused by PP blocking the access to active sites of the catalyst as observed in waste PP in Figure 3. Serrano et al. reported the presence of steric hindrances in the catalytic cracking of a polyolefin mixture and found that the highest activities are obtained when zeolites with a high proportion of external surface area were used.[43] Thus, as well as both pure PP and LDPE, the effect of steric hindrances in polyolefin mixtures is diminished by using the zeolite with higher external surface area and lower Si/Al ratio.

The presence of PP and LDPE in the waste polyolefin mixture also has an effect in the product distribution obtained from thermal pyrolysis at 450 °C, as shown in Figure 8. An increase of more than 23%wt in condensable products with respect to that obtained with pure HDPE was observed due to the enhancement of decomposition induced by the radicals from degraded PP and LDPE. However, in catalytic pyrolysis no major differences were observed for the product distribution obtained of pure HDPE and of a polyolefin mixture. This confirms that the external surface area of the zeolite was high enough to minimize steric hindrances caused by the bulky
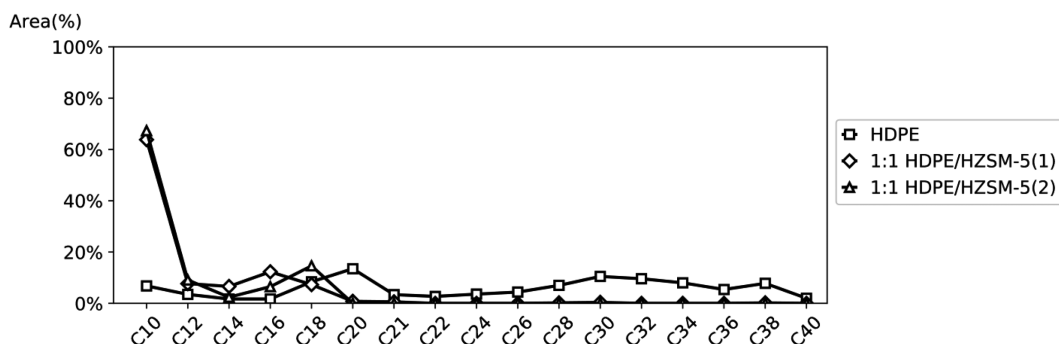
Figure 6. Carbon number distribution of condensable products obtained in the pyrolysis of waste HDPE (polymer/catalyst ratio of 1:1) at 450 °C.
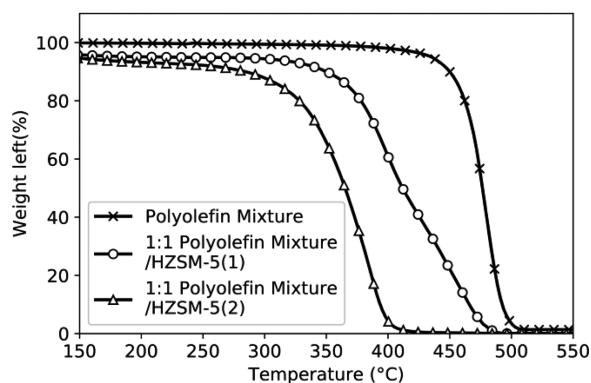

Figure 7. Thermogravimetrical analysis of a waste polyolefin mixture (27.6%wt of HDPE, 36.6%wt of LDPE, and 35,8%wt of PP) using HZSM-5 zeolite catalysts (polymer/catalyst ratio of 1:1).
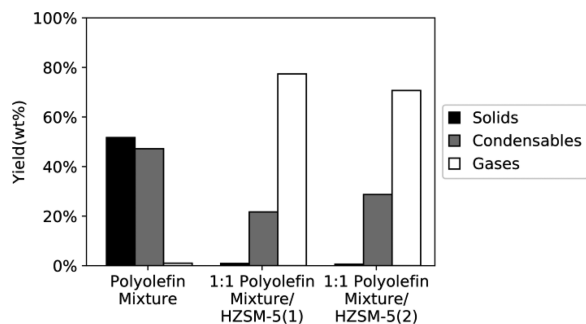

Figure 9. Carbon number distribution of gaseous products obtained in the thermal pyrolysis of a waste polyolefin mixture, HDPE and PP at 450 °C.

Figure 8. Yields obtained in thermal and catalytic pyrolysis (polymer/catalyst ratio of 1:1) of a polyolefin mixture (27.6%wt of HDPE, 36.6% wt of LDPE, and 35,8%wt of PP) at 450 °C.

structures of PP at 450 °C. Aguado et al.[74] also reported that light hydrocarbons were the main products obtained in pyrolysis of a polyolefin mixture over zeolites with both a high external surface area and high acid strength.

Regarding the differences between the carbon number distribution of the products, the gases obtained by thermal pyrolysis of the polyolefin mixture showed an increase of 6.2% and 15.2% for C3 and C4, respectively, compared to that obtained with pure HDPE (Figure 9), indicating that the presence of PP promotes intermolecular hydrogen abstraction and facilitates the formation of radicals from PE.[38] It has been reported that the pyrolysis of PP in comparison with PE yields significantly higher amounts of C3 and C4 compounds,[61] as shown in Figure 9. In the case of oil products from PP (Figure 10), the amount of hydrocarbons in the range C24−C40 was negligible, and consequently, the presence of this polyolefin in
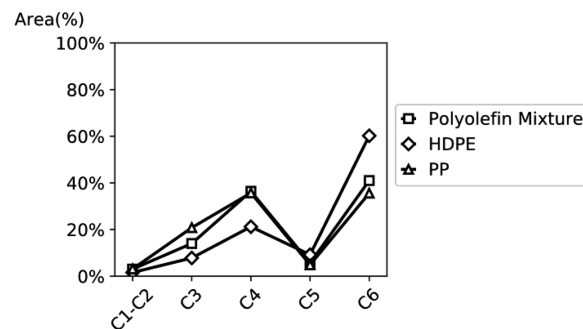
the mixture caused a slight decrease in the range C24−C40, increasing the fraction of lighter hydrocarbons (C10−C20). Jing et al.[39] also noticed an improvement in the lighter hydrocarbons formation, proposing that the presence of PP promotes the chain scission reactions.

Due to the steric hindrances produced by PP, the carbon number distribution of gases obtained in catalytic pyrolysis of a polyolefin mixture (Figure 11) exhibits a change compared to that obtained with HDPE. In particular, with a polyolefin mixture, a decrease of 13% (HZSM-5(1)) and 11% (HZSM-5(2)) in C4 compounds with respect to that obtained with HDPE was observed. In the case of oil products (Figure 12), a major selectivity toward lighter hydrocarbons (C10−C16) was obtained because the degradation reactions over HZSM-5 zeolites mainly occur by end chain scission.[43,74,75] However, like in the case of gaseous products, PP has an influence on the production of oils, obtaining a lower increase of C10−C12 compounds compared to those obtained from HDPE.

Hydrocarbon types in condensable products were determined using ^{1}H NMR analysis, where the results are presented in vol %, as explained elsewhere.[59] The condensable product obtained by thermal degradation is mainly composed by paraffins (59.4 vol %) and olefins (37.4 vol %), as seen in Figure 13. Olefins were decreased to 12.2 vol % using HZSM-5(1) and 1.3 vol % using HZSM-5(2), and aromatics were increased to 30.3 vol % using HZSM-5(1) and 70.9 vol % using HZSM-5(2). The above demonstrates that using HZSM-5 zeolites the content of aromatics in condensable products is increased, confirming that these particles can induce the cyclization from olefins to aromatics.[16] Moreover, a higher content of aromatics was produced in HZSM-5(2) because of its lower Si/Al ratio, increasing the total number of acid sites.[76] The conversion of olefin into aromatics could not be completed
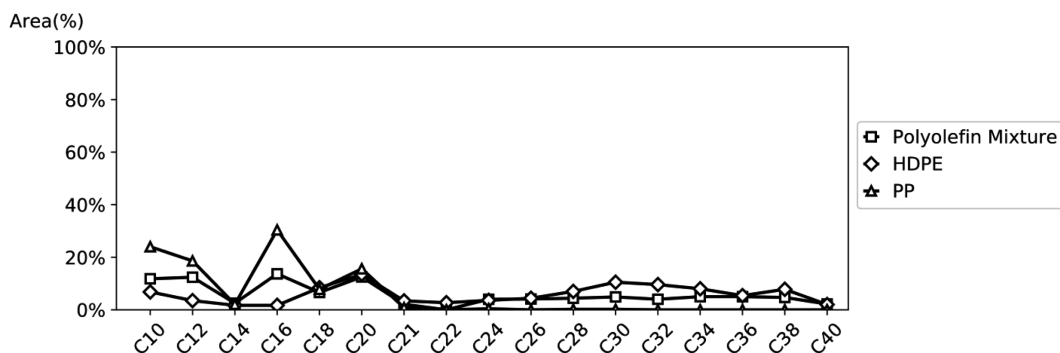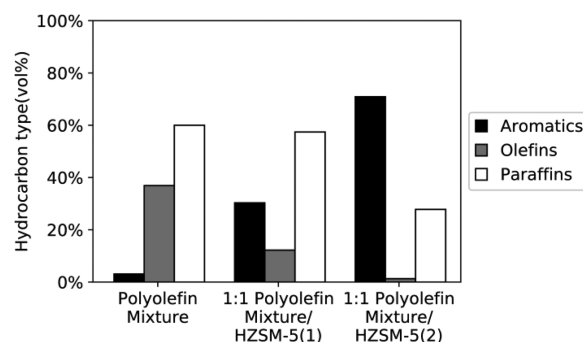
Figure 10. Carbon number distribution of condensable products obtained in the thermal pyrolysis of a waste polyolefin mixture, HDPE and PP at 450 °C.
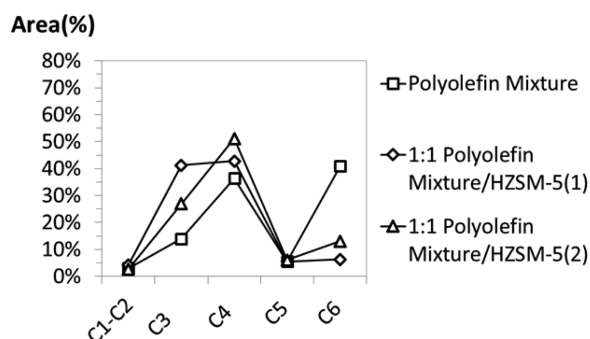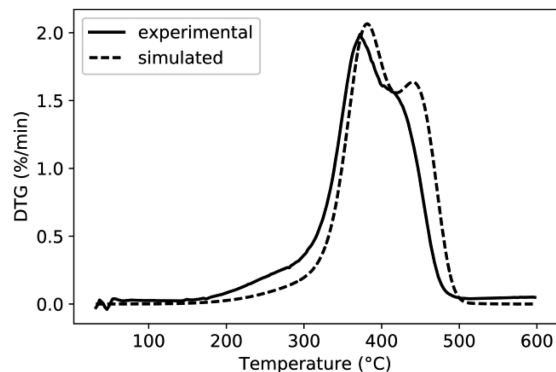

Figure 11. Carbon number distribution of gaseous products obtained in the pyrolysis of a waste polyolefin mixture (polymer/catalyst ratio of 1:1) at 450 °C.

Figure 13. Hydrocarbon types in condensable products obtained in the pyrolysis of a waste polyolefin mixture (polymer/catalyst ratio of 1:1) at 450 °C.

on a single acid site, and therefore, intermediates should be desorbed from the acid sites and readsorbed on other acid sites to be transformed into aromatics.[77] This mechanism needs catalysts with a large amount of acid sites, such as HZSM-5(2). With HZSM-5(1) a gasoline range product was obtained with a similar composition to that determined by ref 78; therefore, high Si/Al ratio zeolites are suitable to produce this type of hydrocarbons.

3.3. Pyrolysis of used tires. In order to observe the effect of bulky structures in the degradation of polymers, used tire was further analyzed. A TGA at 10 K/min was performed, obtaining the DTG curve for a tire sample (Figure 14). By using the method of identifying and quantifying elastomers, the presence of NR and SBR was confirmed following the shape of the DTG curve.[79] From the simulation of this curve, the rubber composition was estimated to be 46 wt % NR, 44 wt % SBR,


Figure 14. Identification of rubber component from used tires by simulation of the DTG curve.
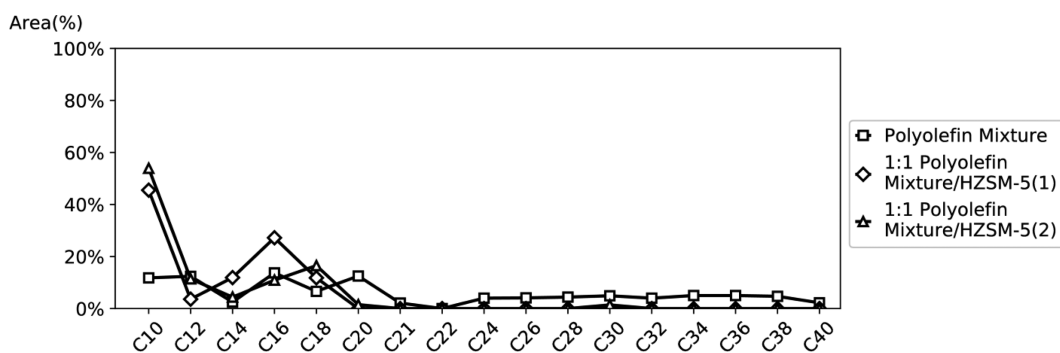
Figure 12. Carbon number distribution of condensable products obtained in the pyrolysis of a waste polyolefin mixture (polymer/catalyst ratio of 1:1) at 450 °C.

and 10 wt % oil (rubber process oil used in the manufacturing of tires). This is consistent with the reported by ref 80. Regarding the TGA curve (Figure 15) of the used tire sample,
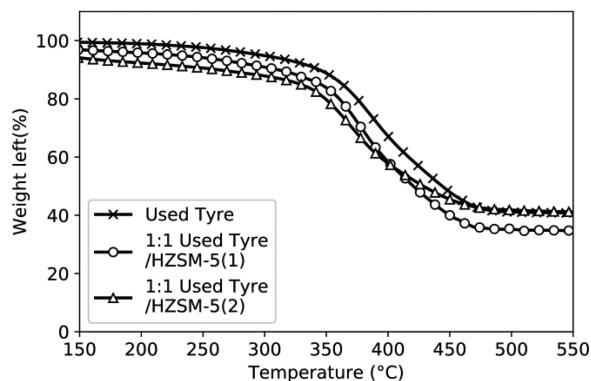
Figure 15. Thermogravimetrical analysis of used tires using HZSM-5 zeolite catalysts (polymer/catalyst ratio of 1:1).

one weight loss event was mainly observed, attributed to the operation conditions used (heating rate of 20 K/min).[81] Used tires started to degrade at about 120 °C less than that for polyolefins, due to the presence of a high number of double bonds in the chains of rubbers, resulting in weaker bonds in the β position.[63,82,83] The remaining product observed in Figure 15 corresponds to carbon black filler currently used in tires. Despite the thermosetting characteristic of tires, TGA curves for a 1:1 ratio with catalysts were also carried out, observing slight decreases of about 18 and 23 °C for HZSM-5(1) and HZSM-5(2), respectively, as compared to thermal degradation. This demonstrates the hindrances produced by the bulky phenyl groups of SBR. Moreover, this could indicate the occurrence of heat transfer limitations; therefore, the solid sample temperature can be lower than the measured temperature, which corresponds to that of the gas.[84]

The solid product fraction of used tires is composed primarily of carbon black,[50] which is present in tires up to 30−46 wt %;[80] therefore, the percentage of solid residues observed in Figure 16 (36.2 wt %) is hardly derived from
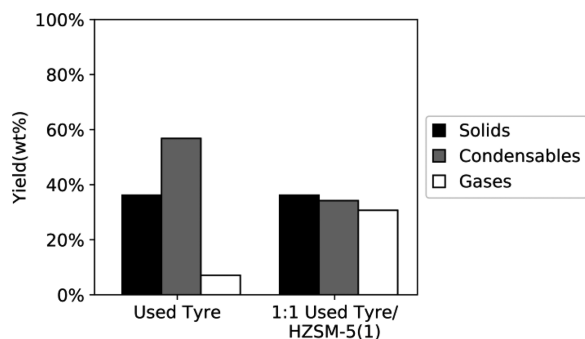

Figure 16. Yield obtained in thermal and catalytic pyrolysis (polymer/catalyst ratio of 1:1) of used tires at 450 °C.

degradation of rubbers. A significant decrease of this fraction is noticed in used tires as compared with that obtained in pure HDPE thermal pyrolysis (75.9 wt %). As indicated above, this is because the structure of rubbers present in used tires leads to lower degradation temperatures than that for pure HDPE. In the case of catalytic pyrolysis of used tires, since the rubbers

structure presents problems related to the interaction with zeolite catalysts and heat transfer, the product distribution was studied performing pyrolysis reactions in a two-stage fixed bed. Some authors[32,33,85] showed that the two-stage fixed bed pyrolysis maximized the interaction time between both the thermally degraded compounds and the catalyst, improving the quality of the products obtained. An increase of 23.6 wt % in gaseous products is observed when HZSM-5 zeolite was used as compared with the pure thermal process (Figure 16). Nevertheless, the increase is not as pronounced as in pure HDPE, and this is probably due to the fact that the thermally degraded compounds of tires could proceed by a different pathway, taking advantage of the moderate capacity of this catalyst for condensation reactions.

The carbon number distribution for used tires displayed in Figure 17 and Figure 18 proves that in the case of gaseous
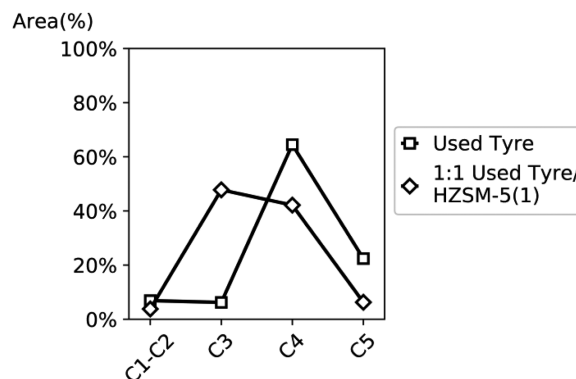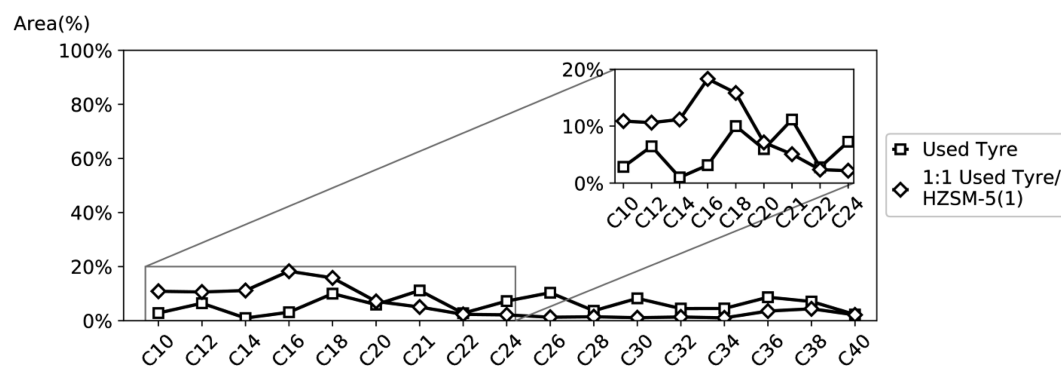

Figure 17. Carbon number distribution of gaseous products obtained in the pyrolysis of used tires (polymer/catalyst ratio of 1:1) at 450 °C.

products the HZSM-5 zeolites decrease the molecular weight but in condensable products the effect is nearly unnoticeable compared to that obtained with polyolefins. Qu et al.[33] obtained a similar result, but in their process catalyst directly contacts tires and then steric hindrances were induced. This shows that our system does not overcome all limitations. In addition, it has been reported that the oils produced from catalytic pyrolysis of used tires are characterized by the high presence of aromatic compounds[50] and the catalysts have influence mainly in the aromatic and aliphatic proportions, decreasing the amount of the latter.[32,86] This is shown in Figure 19, where hydrocarbon types in condensable products are reported, obtained from ^{1}H NMR spectra. An increase of 16.5 vol % in aromatics compounds is observed using HZSM-5(1) zeolites. Olefins were decreased by about 13 vol %, but paraffins do not exhibit a significant change. As in the case of condensable products from polyolefin mixtures, the results prove the formation of aromatics from olefins. Using HZSM-5(1) zeolites, condensable products with a potential use as a fuel are obtained but probably require a hydrodesulfurization treatment, as other authors suggest.[87,88]

4. CONCLUSIONS

The thermal and catalytic pyrolyses of different polymers were studied to determine the influence of their structures on the degradation reactions. TGA results for both virgin and waste HDPE showed that the origin of polymer used does not affect thermal degradation, unlike what occurs in catalytic degrada-

Figure 18. Carbon number distribution of condensable products obtained in the pyrolysis of used tires (polymer/catalyst ratio of 1:1) at 450 °C.
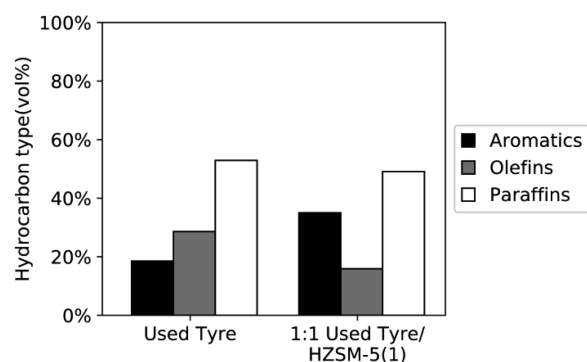
Figure 19. Hydrocarbon types in condensable products obtained in the pyrolysis of used tires (polymer/catalyst ratio of 1:1) at 450 °C.

tion, where the impurities of waste HDPE induce the deactivation of zeolite catalyst.

HDPE is the most stable polyolefin, with the highest degradation temperatures, because of its linear structure and because its degradation reactions are enhanced by using HZSM-5 zeolites, obtaining high yields of gases. Although PP and branched polyolefins promote the C−C bond scission reactions at lower temperatures, in catalytic degradation, its structures cause steric hindrances interfering with the catalytic activity. However, by using HZSM-5 zeolites with a higher external surface area and lower Si/Al ratio, these constraints are reduced.

Regarding the polyolefin mixture, a mild effect was noticed, shifting TGA curves 8 °C to lower temperatures and increasing condensable products with respect to that obtained with pure HDPE. This shows a synergetic effect between HDPE, LDPE, and PP where tertiary carbons from branching in PP and LDPE lead to the formation of more radicals that promote the destabilization of the more stable polymer (HDPE). In catalytic pyrolysis the temperatures are less reduced than in pure HDPE, confirming that the presence of both PP and LDPE induce steric hindrances. Nevertheless, at 450 °C no major differences were observed between the product distributions obtained for pure HDPE and for the polyolefin mixture, showing that zeolites with a high external surface area minimize some effects of branched structures. Depending on the zeolite used, gasoline range products or aromatic feedstocks can be obtained.

Used tires were thermally pyrolyzed, obtaining lower degradation temperatures and solid residues compared to those obtained with polyolefins, because of the presence of double bonds in the chains of rubbers. In catalytic pyrolysis the effect on gaseous and oil products is not as marked as in

polyolefins because of the bulky side groups of tires, proving the relevance of polymer structures. The composition of condensable products showed that they can be used as fuels but after being desulfurized.

AUTHOR INFORMATION

Corresponding Author
*E-mail: macolet@ing.uchile.cl.

ORCID

Madeleine Colet: 0000-0003-0834-7570

Notes

The authors declare no competing financial interest.

ABBREVIATIONS

HDPE = high density polyethylene
LDPE = low density propylene
PP = polypropylene
TGA = thermogravimetrical analysis
DTG = difference thermogravimetry

REFERENCES

(1) Ignatyev, I. A.; Thielemans, W.; Vander Beke, B. Recycling of polymers: a review. *ChemSusChem* **2014**, *7* (6), 1579−1593.
(2) Panda, A. K.; Singh, R. K.; Mishra, D. K. Thermolysis of waste plastics to liquid fuel: A suitable method for plastic waste management and manufacture of value added products—A world prospective. *Renewable Sustainable Energy Rev.* **2010**, *14* (1), 233−248.
(3) Plastics Europe (2015, November 09). Plastics - the Facts 2015. Retrieved from http://www.plasticseurope.org/cust/documentrequest.aspx?DocID=65435.
(4) Tire Business Staff (2015, December 23). Global tire demand to rise 4% annually − Freedonia. Retrieved from http://www.tirebusiness.com/article/20151223/NEWS/151229969/global-tire-demand-to-rise-4-annually-freedonia.
(5) Al-Salem, S. M.; Lettieri, P.; Baeyens, J. The valorization of plastic solid waste (PSW) by primary to quaternary routes: From re-use to energy and chemicals. *Prog. Energy Combust. Sci.* **2010**, *36* (1), 103−129.
(6) Aguado, J.; Serrano, D. P. *Feedstock recycling of plastic wastes*; Royal Society of Chemistry: 1999; Vol. 1.
(7) Conesa, J. A.; Font, R.; Marcilla, A.; Garcia, A. N. Pyrolysis of polyethylene in a fluidized bed reactor. *Energy Fuels* **1994**, *8* (6), 1238−1246.

(8) Kodera, Y.; Ishihara, Y.; Kuroki, T. Novel process for recycling waste plastics to fuel gas using a moving-bed reactor. *Energy Fuels* **2006**, *20* (1), 155−158.

(9) Williams, P. T.; Besler, S.; Taylor, D. T. The pyrolysis of scrap automotive tyres: The influence of temperature and heating rate on product composition. *Fuel* **1990**, *69* (12), 1474−1482.

(10) Mastral, J. F.; Berrueco, C.; Gea, M.; Ceamanos, J. Catalytic degradation of high density polyethylene over nanocrystalline HZSM-5 zeolite. *Polym. Degrad. Stab.* **2006**, *91* (12), 3330−3338.

(11) Kaminsky, W.; Kim, J. S. Pyrolysis of mixed plastics into aromatics. *J. Anal. Appl. Pyrolysis* **1999**, *51* (1), 127−134.

(12) Kim, S. S.; Kim, S. Pyrolysis characteristics of polystyrene and polypropylene in a stirred batch reactor. *Chem. Eng. J.* **2004**, *98* (1), 53−60.

(13) Nabi, A. R.; Masud, M. H.; Alam, Q. I. Purification of TPO (Tire Pyrolytic Oil) and its use in diesel engine. *IOSR Journal of Engineering* **2014**, *4* (3), 1.

(14) Park, D. W.; Hwang, E. Y.; Kim, J. R.; Choi, J. K.; Kim, Y. A.; Woo, H. C. Catalytic degradation of polyethylene over solid acid catalysts. *Polym. Degrad. Stab.* **1999**, *65* (2), 193−198.

(15) López, A.; De Marco, I.; Caballero, B. M.; Laresgoiti, M. F.; Adrados, A.; Aranzabal, A. Catalytic pyrolysis of plastic wastes with two different types of catalysts: ZSM-5 zeolite and Red Mud. *Appl. Catal., B* **2011**, *104* (3), 211−219.

(16) Vasile, C.; Pakdel, H.; Mihai, B.; Onu, P.; Darie, H.; Ciocâlteu, S. Thermal and catalytic decomposition of mixed plastics. *J. Anal. Appl. Pyrolysis* **2001**, *57* (2), 287−303.

(17) Durmuş, A.; Koç, S. N.; Pozan, G. S.; Kaşgöz, A. Thermal-catalytic degradation kinetics of polypropylene over BEA, ZSM-5 and MOR zeolites. *Appl. Catal., B* **2005**, *61* (3), 316−322.

(18) Park, D. W.; Hwang, E. Y.; Kim, J. R.; Choi, J. K.; Kim, Y. A.; Woo, H. C. Catalytic degradation of polyethylene over solid acid catalysts. *Polym. Degrad. Stab.* **1999**, *65* (2), 193−198.

(19) Ding, W.; Liang, J.; Anderson, L. L. Thermal and catalytic degradation of high density polyethylene and commingled post-consumer plastic waste. *Fuel Process. Technol.* **1997**, *51* (1), 47−62.

(20) Ohkita, H.; Nishiyama, R.; Tochihara, Y.; Mizushima, T.; Kakuta, N.; Morioka, Y.; Tanifuji, S. Acid properties of silica-alumina catalysts and catalytic degradation of polyethylene. *Ind. Eng. Chem. Res.* **1993**, *32* (12), 3112−3116.

(21) Lee, S. Y.; Yoon, J. H.; Kim, J. R.; Park, D. W. Catalytic degradation of polystyrene over natural clinoptilolite zeolite. *Polym. Degrad. Stab.* **2001**, *74* (2), 297−305.

(22) Aguado, J.; Serrano, D. P.; Escola, J. M.; Garagorri, E. Catalytic conversion of low-density polyethylene using a continuous screw kiln reactor. *Catal. Today* **2002**, *75* (1), 257−262.

(23) Park, J. W.; Kim, J. H.; Seo, G. The effect of pore shape on the catalytic performance of zeolites in the liquid-phase degradation of HDPE. *Polym. Degrad. Stab.* **2002**, *76* (3), 495−501.

(24) Hwang, E. Y.; Choi, J. K.; Kim, D. H.; Park, D. W.; Woo, H. C. Catalytic degradation of polypropylene I. Screening of catalysts. *Korean J. Chem. Eng.* **1998**, *15* (4), 434−438.

(25) Hwang, E. Y.; Kim, J. R.; Choi, J. K.; Woo, H. C.; Park, D. W. Performance of acid treated natural zeolites in catalytic degradation of polypropylene. *J. Anal. Appl. Pyrolysis* **2002**, *62* (2), 351−364.

(26) Bagri, R.; Williams, P. T. Fluidised-bed catalytic pyrolysis of polystyrene. *Journal of the Institute of Energy* **2002**, *75* (505), 117−123.

(27) Kim, J. R.; Yoon, J. H.; Park, D. W. Catalytic recycling of the mixture of polypropylene and polystyrene. *Polym. Degrad. Stab.* **2002**, *76* (1), 61−67.

(28) Audisio, G.; Silvani, A.; Beltrame, P. L.; Carniti, P. Catalytic thermal degradation of polymers: Degradation of polypropylene. *J. Anal. Appl. Pyrolysis* **1984**, *7* (1−2), 83−90.

(29) Aguado, J.; Serrano, D. P.; Escola, J. M.; Garagorri, E.; Fernandez, J. A. Catalytic conversion of polyolefins into fuels over zeolite beta. *Polym. Degrad. Stab.* **2000**, *69* (1), 11−16.

(30) San Miguel, G.; Aguado, J.; Serrano, D. P.; Escola, J. M. Thermal and catalytic conversion of used tyre rubber and its polymeric constituents using Py-GC/MS. *Appl. Catal., B* **2006**, *64* (3), 209−219.

(31) Arabiourrutia, M.; Olazar, M.; Aguado, R.; Lopez, G.; Barona, A.; Bilbao, J. HZSM-5 and HY zeolite catalyst performance in the pyrolysis of tires in a conical spouted bed reactor. *Ind. Eng. Chem. Res.* **2008**, *47* (20), 7600−7609.

(32) Williams, P. T.; Brindle, A. J. Catalytic pyrolysis of tyres: influence of catalyst temperature. *Fuel* **2002**, *81* (18), 2425−2434.

(33) Qu, W.; Zhou, Q.; Wang, Y. Z.; Zhang, J.; Lan, W. W.; Wu, Y. H.; Wang, D. Z. Pyrolysis of waste tire on ZSM-5 zeolite with enhanced catalytic activities. *Polym. Degrad. Stab.* **2006**, *91* (10), 2389−2395.

(34) Boxiong, S.; Chunfei, W.; Binbin, G.; Rui, W. Pyrolysis of waste tyres with zeolite USY and ZSM-5 catalysts. *Appl. Catal., B* **2007**, *73* (1), 150−157.

(35) Salmasi, S. S. Z.; Abbas-Abadi, M. S.; Haghighi, M. N.; Abedini, H. The effect of different zeolite based catalysts on the pyrolysis of poly butadiene rubber. *Fuel* **2015**, *160*, 544−548.

(36) Aguado, R.; Arrizabalaga, A.; Arabiourrutia, M.; Lopez, G.; Bilbao, J.; Olazar, M. Principal component analysis for kinetic scheme proposal in the thermal and catalytic pyrolysis of waste tyres. *Chem. Eng. Sci.* **2014**, *106*, 9−17.

(37) Olazar, M.; Arabiourrutia, M.; López, G.; Aguado, R.; Bilbao, J. Effect of acid catalysts on scrap tyre pyrolysis under fast heating conditions. *J. Anal. Appl. Pyrolysis* **2008**, *82* (2), 199−204.

(38) Jing, X.; Zhao, Y.; Wen, H.; Xu, Z. Interactions between low-density polyethylene (LDPE) and polypropylene (PP) during the mild cracking of polyolefin mixtures in a closed-batch reactor. *Energy Fuels* **2013**, *27* (10), 5841−5851.

(39) Jing, X.; Yan, G.; Zhao, Y.; Wen, H.; Xu, Z. Study on mild cracking of polyolefins to liquid hydrocarbons in a closed batch reactor for subsequent olefin recovery. *Polym. Degrad. Stab.* **2014**, *109*, 79−91.

(40) Jing, X.; Yan, G.; Zhao, Y.; Wen, H.; Xu, Z. Cocracking Kinetics of PE/PP and PE/Hydrocarbon Mixtures (I) PE/PP Mixtures. *Energy Fuels* **2014**, *28* (8), 5396−5405.

(41) Pek, W. K.; Ghosh, U. K. Effect of binary mixture of waste plastics on the thermal behavior of pyrolysis process. *Environ. Prog. Sustainable Energy* **2015**, *34* (4), 1113−1119.

(42) Muhammad, C.; Onwudili, J. A.; Williams, P. T. Thermal degradation of real-world waste plastics and simulated mixed plastics in a two-stage pyrolysis−catalysis reactor for fuel production. *Energy Fuels* **2015**, *29* (4), 2601−2609.

(43) Serrano, D. P.; Aguado, J.; Escola, J. M. Catalytic cracking of a polyolefin mixture over different acid solid catalysts. *Ind. Eng. Chem. Res.* **2000**, *39* (5), 1177−1184.

(44) Mikulec, J.; Vrbova, M. Catalytic and thermal cracking of selected polyolefins. *Clean Technol. Environ. Policy* **2008**, *10* (2), 121−130.

(45) Marcilla, A.; Gómez-Siurana, A.; Berenguer, D. Study of the influence of the characteristics of different acid solids in the catalytic pyrolysis of different polymers. *Appl. Catal., A* **2006**, *301* (2), 222−231.

(46) Marcilla, A.; Gómez, A.; García, Á. N.; Olaya, M. M. Kinetic study of the catalytic decomposition of different commercial polyethylenes over an MCM-41 catalyst. *J. Anal. Appl. Pyrolysis* **2002**, *64* (1), 85−101.

(47) Costa, P.; Pinto, F.; Ramos, A. M.; Gulyurtlu, I.; Cabrita, I.; Bernardo, M. S. Study of the pyrolysis kinetics of a mixture of polyethylene, polypropylene, and polystyrene. *Energy Fuels* **2010**, *24* (12), 6239−6247.

(48) Westerhout, R. W. J.; Waanders, J.; Kuipers, J. A. M.; Van Swaaij, W. P. M. Recycling of polyethene and polypropene in a novel bench-scale rotating cone reactor by high-temperature pyrolysis. *Ind. Eng. Chem. Res.* **1998**, *37* (6), 2293−2300.

(49) Westerhout, R. W. J.; Kuipers, J. A. M.; Van Swaaij, W. P. M. Experimental determination of the yield of pyrolysis products of polyethene and polypropene. Influence of reaction conditions. *Ind. Eng. Chem. Res.* **1998**, *37* (3), 841−847.

(50) de Marco Rodriguez, I.; Laresgoiti, M. F.; Cabrero, M. A.; Torres, A.; Chomon, M. J.; Caballero, B. Pyrolysis of scrap tyres. *Fuel Process. Technol.* **2001**, *72* (1), 9−22.

(51) Sharma, B. K.; Moser, B. R.; Vermillion, K. E.; Doll, K. M.; Rajagopalan, N. Production, characterization and fuel properties of alternative diesel fuel from pyrolysis of waste plastic grocery bags. *Fuel Process. Technol.* **2014**, *122*, 79−90.

(52) Kaimal, V. K.; Vijayabalan, P. A study on synthesis of energy fuel from waste plastic and assessment of its potential as an alternative fuel for diesel engines. *Waste Manage.* **2016**, *51*, 91−96.

(53) Kunwar, B.; Moser, B. R.; Chandrasekaran, S. R.; Rajagopalan, N.; Sharma, B. K. Catalytic and thermal depolymerization of low value post-consumer high density polyethylene plastic. *Energy* **2016**, *111*, 884−892.

(54) Escola, J. M.; Aguado, J.; Serrano, D. P.; García, A.; Peral, A.; Briones, L.; Fernandez, E. Catalytic hydroreforming of the polyethylene thermal cracking oil over Ni supported hierarchical zeolites and mesostructured aluminosilicates. *Appl. Catal., B* **2011**, *106* (3), 405−415.

(55) Escola, J. M.; Aguado, J.; Serrano, D. P.; Briones, L.; Díaz de Tuesta, J. L.; Calvo, R.; Fernandez, E. Conversion of polyethylene into transportation fuels by the combination of thermal cracking and catalytic hydroreforming over Ni-supported hierarchical beta zeolite. *Energy Fuels* **2012**, *26* (6), 3187−3195.

(56) Escola, J. M.; Serrano, D. P.; Aguado, J.; Briones, L. Hydroreforming of the LDPE Thermal Cracking Oil over Hierarchical Ni/Beta Catalysts with Different Ni Particle Size Distributions. *Ind. Eng. Chem. Res.* **2015**, *54* (26), 6660−6668.

(57) Hita, I.; Aguayo, A. T.; Olazar, M.; Azkoiti, M. J.; Bilbao, J.; Arandes, J. M.; Castaño, P. Kinetic modeling of the hydrotreating and hydrocracking stages for upgrading Scrap Tires Pyrolysis Oil (STPO) toward high-quality fuels. *Energy Fuels* **2015**, *29* (11), 7542−7553.

(58) U.S. Environmental Protection Agency Office of Resource Conservation and Recovery (2014, February). Municipal Solid Waste Generation, Recycling, and Disposal in the United States Tables and Figures for 2012. Retrieved from https://www.epa.gov/sites/production/files/2015-09/documents/2012_msw_dat_tbls.pdf.

(59) Myers, M. E.; Stollstelmer, J.; Wims, A. M. Determination of hydrocarbon-type distribution and hydrogen/carbon ratio of gasolines by nuclear magnetic resonance spectrometry. *Anal. Chem.* **1975**, *47*, 2010−2015.

(60) Kiran, N.; Ekinci, E.; Snape, C. E. Recyling of plastic wastes via pyrolysis. *Resources, Conservation and Recycling* **2000**, *29* (4), 273−283.

(61) Ciliz, N. K.; Ekinci, E.; Snape, C. E. Pyrolysis of virgin and waste polypropylene and its mixtures with waste polyethylene and polystyrene. *Waste Manage.* **2004**, *24* (2), 173−181.

(62) Serrano, D. P.; Aguado, J.; Escola, J. M. Developing advanced catalysts for the conversion of polyolefinic waste plastics into fuels and chemicals. *ACS Catal.* **2012**, *2* (9), 1924−1941.

(63) Tsuchiya, Y.; Sumi, K. Thermal decomposition products of polyethylene. *J. Polym. Sci., Part A-1: Polym. Chem.* **1968**, *6* (2), 415−424.

(64) Aguado, J.; Sotelo, J. L.; Serrano, D. P.; Calles, J. A.; Escola, J. M. Catalytic conversion of polyolefins into liquid fuels over MCM-41: Comparison with ZSM-5 and amorphous SiO2-Al2O3. *Energy Fuels* **1997**, *11* (6), 1225−1231.

(65) González-Pérez, J. A.; Jiménez-Morillo, N. T.; de La Rosa, J. M.; Almendros, G.; González-Vila, F. J. Pyrolysis-gas chromatography−isotope ratio mass spectrometry of polyethylene. *Journal of Chromatography A* **2015**, *1388*, 236−243.

(66) Lin, Y. H.; Yang, M. H. Chemical catalysed recycling of polypropylene over a spent FCC catalyst and various commercial cracking catalysts using TGA. *Thermochim. Acta* **2008**, *470* (1), 52−59.

(67) Marcilla, A.; Beltrán, M. I.; Hernández, F.; Navarro, R. HZSM5 and HUSY deactivation during the catalytic pyrolysis of polyethylene. *Appl. Catal., A* **2004**, *278* (1), 37−43.

(68) Sharratt, P. N.; Lin, Y. H.; Garforth, A. A.; Dwyer, J. Investigation of the catalytic pyrolysis of high-density polyethylene over a HZSM-5 catalyst in a laboratory fluidized-bed reactor. *Ind. Eng. Chem. Res.* **1997**, *36* (12), 5118−5124.

(69) Huang, W. C.; Huang, M. S.; Huang, C. F.; Chen, C. C.; Ou, K. L. Thermochemical conversion of polymer wastes into hydrocarbon fuels over various fluidizing cracking catalysts. *Fuel* **2010**, *89* (9), 2305−2316.

(70) Manos, G.; Garforth, A.; Dwyer, J. Catalytic degradation of high-density polyethylene over different zeolitic structures. *Ind. Eng. Chem. Res.* **2000**, *39* (5), 1198−1202.

(71) Marcilla, A.; Beltrán, M. I.; Navarro, R. Thermal and catalytic pyrolysis of polyethylene over HZSM5 and HUSY zeolites in a batch reactor under dynamic conditions. *Appl. Catal., B* **2009**, *86* (1), 78−86.

(72) Garforth, A. A.; Lin, Y. H.; Sharratt, P. N.; Dwyer, J. Production of hydrocarbons by catalytic degradation of high density polyethylene in a laboratory fluidised-bed reactor. *Appl. Catal., A* **1998**, *169* (2), 331−342.

(73) Albano, C.; de Freitas, E. Thermogravimetric evaluation of the kinetics of decomposition of polyolefin blends. *Polym. Degrad. Stab.* **1998**, *61* (2), 289−295.

(74) Aguado, J.; Serrano, D. P.; Sotelo, J. L.; Van Grieken, R.; Escola, J. M. Influence of the operating variables on the catalytic conversion of a polyolefin mixture over HMCM-41 and nanosized HZSM-5. *Ind. Eng. Chem. Res.* **2001**, *40* (24), 5696−5704.

(75) Serrano, D. P.; Aguado, J.; Escola, J. M.; Rodriguez, J. M.; Peral, A. Catalytic properties in polyolefin cracking of hierarchical nanocrystalline HZSM-5 samples prepared according to different strategies. *J. Catal.* **2010**, *276* (1), 152−160.

(76) Costa, C.; Dzikh, I. P.; Lopes, J. M.; Lemos, F.; Ribeiro, F. R. Activity−acidity relationship in zeolite ZSM-5. Application of Brönsted-type equations. *J. Mol. Catal. A: Chem.* **2000**, *154* (1), 193−201.

(77) Song, Y.; Zhu, X.; Xu, L. Study on the process of transformation of olefin into aromatics over HZSM-5. *Catal. Commun.* **2006**, *7* (4), 218−223.

(78) Burri, J.; Crockett, R.; Hany, R.; Rentsch, D. Gasoline composition determined by 1 H NMR spectroscopy. *Fuel* **2004**, *83* (2), 187−193.

(79) Yang, J.; Kaliaguine, S.; Roy, C. Improved quantitative determination of elastomers in tire rubber by kinetic simulation of DTG curves. *Rubber Chem. Technol.* **1993**, *66* (2), 213−229.

(80) Quek, A.; Balasubramanian, R. Liquefaction of waste tires by pyrolysis for oil and chemicals—a review. *J. Anal. Appl. Pyrolysis* **2013**, *101*, 1−16.

(81) Williams, P. T.; Besler, S. Pyrolysis-thermogravimetric analysis of tyres and tyre components. *Fuel* **1995**, *74* (9), 1277−1283.

(82) Chen, F.; Qian, J. Studies on the thermal degradation of cis-1, 4-polyisoprene. *Fuel* **2002**, *81* (16), 2071−2077.

(83) Choi, S. S. Characterization of bound rubber of filled styrene-butadiene rubber compounds using pyrolysis-gas chromatography. *J. Anal. Appl. Pyrolysis* **2000**, *55* (2), 161−170.

(84) Lanteigne, J. R.; Laviolette, J. P.; Tremblay, G.; Chaouki, J. Predictive kinetics model for an industrial waste tire pyrolysis process. *Energy Fuels* **2013**, *27* (2), 1040−1049.

(85) Williams, P. T.; Brindle, A. J. Aromatic chemicals from the catalytic pyrolysis of scrap tyres. *J. Anal. Appl. Pyrolysis* **2003**, *67* (1), 143−164.

(86) Olazar, M.; Aguado, R.; Arabiourrutia, M.; Lopez, G.; Barona, A.; Bilbao, J. Catalyst effect on the composition of tire pyrolysis products. *Energy Fuels* **2008**, *22* (5), 2909−2916.

(87) Jantaraksa, N.; Prasassarakich, P.; Reubroycharoen, P.; Hinchiranan, N. Cleaner alternative liquid fuels derived from the hydrodesulfurization of waste tire pyrolysis oil. *Energy Convers. Manage.* **2015**, *95*, 424−434.

(88) Al-Lal, A. M.; Bolonio, D.; Llamas, A.; Lapuerta, M.; Canoira, L. Desulfurization of pyrolysis fuels obtained from waste: Lube oils, tires and plastics. *Fuel* **2015**, *150*, 208−216.