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Paula Osorio-Vargas (Conceptualization) (Investigation) (Formal analysis) (Validation) (Methodology) (Data curation) (Project administration) (Funding acquisition) (Writing - original draft), Tamara Menares (Investigation) (Formal analysis) (Validation) (Methodology) (Data curation), Daniela Lick (Resources) (Data curation) (Writing - review and editing), Monica L. Casella (Resources) (Data curation), Romina Romero (Conceptualization) (Methodology) (Validation) (Data curation), Romel Jiménez (Conceptualization) (Writing - review and editing), Luis E. Arteaga-Pérez (Conceptualization) (Methodology) (Writing - review and editing) (Project administration) (Funding acquisition) (Visualization) (Supervision)

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**Tuning the product distribution during the catalytic pyrolysis of waste tires: The effect of the nature of metals and the reaction temperature**

Paula Osorio-Vargas <sup>1,\*</sup> posorio@ubiobio.cl, Tamara Menares <sup>1,2</sup>, Daniela Lick <sup>3</sup>, Monica L. Casella <sup>3</sup>, Romina Romero <sup>2,4</sup>, Romel Jiménez <sup>5</sup>, Luis E. Arteaga-Pérez <sup>1,2,\*</sup> larteaga@ubiobio.cl,

<sup>1</sup> *Laboratory of Thermal and Catalytic Processes (LPTC), Wood Engineering Department, University of Bio-Bio, Concepción, Chile*

<sup>2</sup> *Universidad de Concepción, Unidad de Desarrollo Tecnológico, UDT, Coronel, Chile*

<sup>3</sup> *CINDECA (CCT La Plata-CONICET, UNLP), Universidad Nacional de La Plata, Facultad de Ciencias Exactas, 47 N°257, 1900 La Plata, Argentina*

<sup>4</sup> *Laboratorio de Investigaciones Medioambientales de Zonas Áridas (LIMZA), Depto. Ingeniería Mecánica, Facultad de Ingeniería, Universidad de Tarapacá, Arica, Chile.*

<sup>5</sup> *Carbon and Catalysis Laboratory (CarboCat), Department of Chemical Engineering, Universidad de Concepción, Concepción, Chile*

\*Corresponding authors:

Luis E. Arteaga-Pérez

Universidad del Bio Bio, Escuela de Ingeniería Química, Chile

Tel: (+5641) 311 1691

e-mail:

Paula Osorio-Vargas

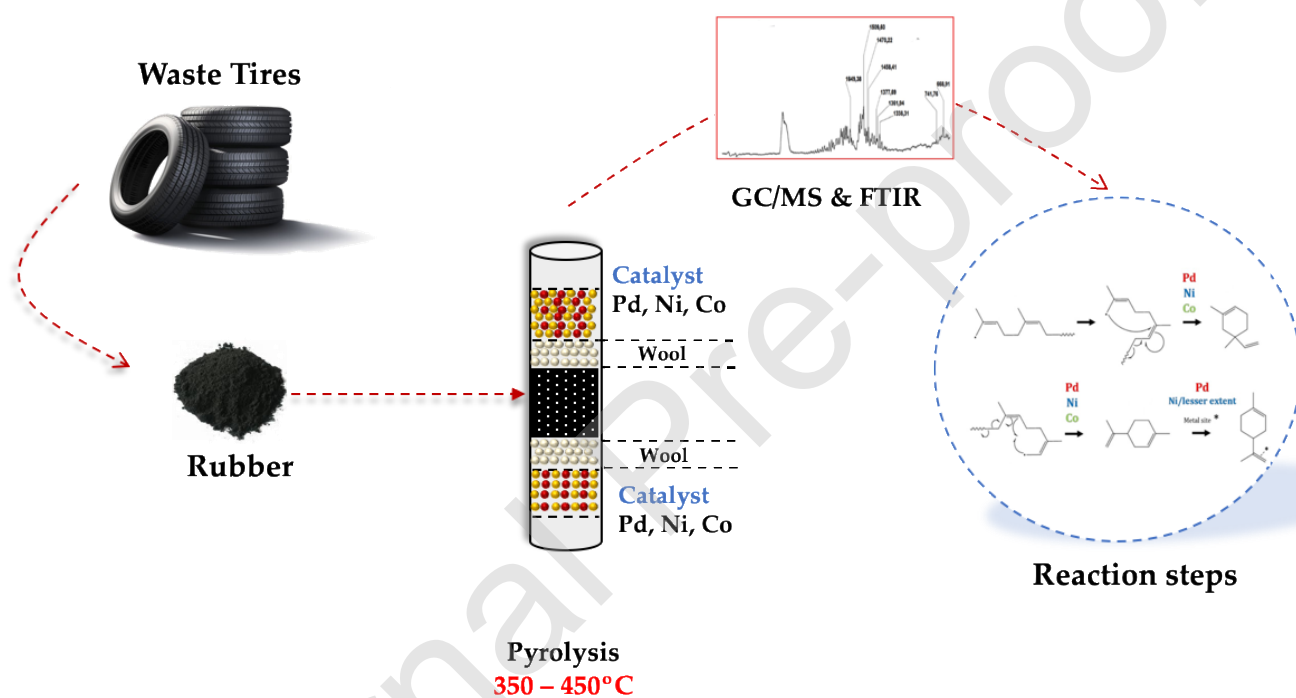
Universidad del Bio Bio, Escuela de Ingeniería Química, Chile

Tel: (+5641) 311 1161

e-mail:

## Graphical Abstract

**Title:** Tuning the product distribution during the catalytic pyrolysis of waste tires: The effect of the nature of metals and the reaction temperature.



## Highlights

- Pyrolysis of waste tires using supported metal catalysts was investigated.
- (Pd, Ni or Co)/SiO<sub>2</sub> favor the aromatization and cracking reactions at low temperature
- Pd/SiO<sub>2</sub> catalyst promoted the reactions toward the formation of aromatic compounds
- (Ni or Co)/SiO<sub>2</sub> catalysts drive mainly to alkenes formation in the pyro-oil
- (Pd, Ni or Co)/SiO<sub>2</sub> catalysts leads to a pyro-oil enriched in valuable hydrocarbons

**Abstract**

Metal catalysts based on Ni, Co, and Pd supported on SiO<sub>2</sub> were evaluated in the catalytic pyrolysis of waste tires using pyrolysis experiments coupled to gas chromatography/mass spectrometry (Py-GC/MS) and thermogravimetric analysis coupled with Fourier Transform Infrared spectrometer (TGA-FTIR) techniques. The effect of temperature and the nature of metals on the product distribution and reaction pathways was determined. Catalytic pyrolysis promoted aromatization and cracking reactions at particularly low temperatures ca. 350 °C, leading mainly to the formation of alkenes (isoprene), aromatic terpenes (p-cymene), aliphatic terpenes (d,l-limonene), and other aromatic compounds such as benzene, toluene, and xylenes (BTX). The Pd/SiO<sub>2</sub> catalyst was the most selective toward aromatic compounds (around 40%), owing to its well-known hydrogenation/dehydrogenation capacity, while C-C bond cleavage reactions, leading to alkenes, were more favored on the Ni/SiO<sub>2</sub> and Co/SiO<sub>2</sub> catalysts. In all cases, high selectivity to limonene and isoprene was observed at low temperature. Above 400 °C, no significant differences in product distribution were observed between catalyzed and uncatalyzed pyrolysis. Herein, selectivity toward high-value hydrocarbons (i.e., d,l-limonene, isoprene, BTX, and p-cymene) during the catalytic pyrolysis of waste tires was tuned by the nature of the supported transition metals (i.e., Ni, Co, Pd) and the reaction temperature (e.g., <400 °C). The results demonstrate that the use of these catalysts is a promising strategy to valorize waste tires into high added-value products.

**Keywords:** catalytic pyrolysis; waste tires; high added-value products; BTX; supported metal catalysts

## 1. Introduction

Human activities produce tons of non-biodegradable wastes that have a detrimental effect on the environment and human health. One of these residues is that of waste tires, which remain unaltered in the environment for long periods of time. Often, tire residues are disposed of in landfills or waste concentration centers, converting them into breeding grounds for mosquitoes and a potential source of fires. In Chile alone, almost 140,000 tons of regular scrap tires are generated each year, plus approximately 32,000 tons of giant tires from industrial mining activities, of which only 23% are recycled as rubber granulates [1]. In recent years, the growing interest in the care of the environment, along with more restrictive regulations, has led to searching for economically viable and environmentally friendly solutions for the disposal/valorization of residual tires.

The methods used for waste tire management are mainly based on mechanical grinding and its subsequent use as a source of asphalt additive, rubber recovery, combustion, and, more recently, feedstock for pyrolysis processes. Among the several alternatives, pyrolysis of tires' polymer component (rubber) seems to be a promising strategy. Tires are mainly composed of rubber (45–60 wt.%), carbon black (20–30 wt.%), and a variety of organic and inorganic additives, including plasticizers, antioxidants, sulfur, vulcanization accelerators, zinc oxide, etc. [2]. The rubber fraction consists of a blend of two or three types of rubbers, namely, natural rubber (NR), butadiene rubber (BR), and styrene–butadiene rubber (SBR). The pyrolysis of such polymeric material comprises of thermal degradation (500–900 °C) in the absence of oxygen, leading to the formation of a gas ( $C_1$ – $C_4$  hydrocarbons and  $H_2$ ), and has a solid (recovered carbon black, rCB) and a liquid phase (oil). In this latter phase, a mixture

of organic compounds, such as dipentene (d,l-limonene), isoprene, benzene, toluene, mixed-xylene, ethylbenzene, styrene, and some polycyclic aromatic hydrocarbons, such as naphthalene, among others, can often be found [2–4]. These chemical compounds can be recovered and used as energy sources or as building blocks in the synthesis of pharmaceuticals, cosmetics, petrochemicals, and polymers, making this process more attractive from both an economic and environmental perspective. In fact, in the United States, some European countries, Japan, and China, industrial-scale plants exist for processing around 10–24 tons of waste tire residues per day through pyrolysis, yielding 45%–50% of pyrolytic oil [5,6]. However, despite the maturity of this process and its indubitable economic and environmental contributions, its greater expansion strongly depends on the potential use of its derived oil, which is often hindered by the physical–chemical complexity of the product mixture obtained. Consequently, a significant number of papers about waste tire pyrolysis have been published recently [7–13], which are primarily focused on the yield and selectivity toward certain reaction products present in the gas and/or liquid fraction.

The use of catalysts during pyrolysis has been one of the strategies that have been evaluated in order to drive the reaction toward the desired products. In this framework, zeolites have been the most studied catalysts [9–12,14–20], mainly with the objective of increasing the selectivity toward aromatic hydrocarbons. All investigations agree that properties such as (a) acidity/basicity, (b) pore channel structure, (c) size, and (d) Si/Al ratio in zeolites would affect the production of valuable hydrocarbons such as benzene, toluene, xylenes, ethylbenzene, and styrene. Most of these studies suggest that zeolites may favor aromatization reactions compared to non-catalytic pyrolysis, and may increase gas yield and light fractions in the pyrolytic oil by favoring cracking reactions. Moreover, metal doping of

zeolites has also been evaluated by some authors in order to enhance these reactions. In two reported studies where Fe (HMOR, HBeta, HZSM-5, KL) [19] and Ni (HMOR, HZSM-5) [12] were evaluated, the authors agreed that the acidic properties and the shape selectivity of zeolites, rather than the nature of the metals, play a fundamental role in the selectivity toward aromatic compounds and light alkenes. Moreover, Ni doping of HBeta zeolite [12] was shown to favor the formation of heavier oils with high amounts of di-, poly-, and polar aromatics instead of monoaromatics. The presence of Pt over HBeta and HMOR zeolites was used to decrease selectivity to sulfur-containing polar aromatic compounds [18]. These authors have found that raising the temperature leads to a higher production of these compounds (light and heavy); however, conversely, the presence of a catalyst decreases the number of polar aromatic hydrocarbons in the oil phase due to cracking reactions. Meanwhile, the addition of Pd into the zeolite Hbeta structure increased pyrolysis gas yield by favoring hydrocarbon cracking which was attributed to its capability for inducing hydrogenation/dehydrogenation reactions [21]. Recently, Tavera- Ruiz et al. [22] reported the use of catalysts other than zeolites; three different heteropolyacids ( $H_3PW_{12}O_{40}$ ,  $H_3PMo_{12}O_{40}$ , and  $H_4PMo_{11}VO_{40}$ ) supported on commercial silica (CARIACT Q-10) were evaluated for cymene production from catalytic pyrolysis of scrap tire rubber. The authors showed that the highest amount of cymene was obtained with molybdenum-based catalysts, which exhibited the highest ratio of Lewis/Bronsted acid sites, while the lowest yield was obtained using tungsten-based catalysts with a higher number of Bronsted acid sites and a strong acidity, leading to cracking reactions. As can be observed in these studies, the products obtained during the catalytic pyrolysis of waste tires strongly depends on the type of catalysts used, in addition to the reaction conditions. Although a significant number of studies have already been published in this field, the use of other types of catalysts as opposed to zeolites



that selectively allow the valorization of this waste toward products of commercial interest remains less explored.

A good understanding of the individual roles of different catalysts on the distribution of pyrolytic products and reaction pathways for each catalytic system will allow the development of new catalysts with suitable properties to drive reactions toward the desired products. In this sense, considering that the main reaction mechanisms for the pyrolysis of waste tires involves reactions such as depolymerization, cracking, isomerization, and dehydrogenation of the polymeric fraction, herein, the use of metallic catalysts based on Pd, Ni, and Co supported over SiO<sub>2</sub> is put forward. These transition metals were selected because of their well-known catalytic activity in hydrogenation/dehydrogenation and cracking reactions [23,24]; therefore, it is expected that the proposed catalysts will promote the formation of added-value products such as d,l-limonene, isoprene, and aromatic compounds (i.e., benzene, toluene, mixed-xylene (BTX), and p-cymene), all reported to be pyrolytic products of waste tires. BTX, which are well known, are derived from petroleum-based naphtha; thus, in an endeavor to increase the intrinsic sustainability of these compounds, their production from waste materials is a subject of great interest for society at large, according to the circular economy concept. Another chemical compound with tremendous potential is limonene [25], which is considered as being a high-value fine chemical that can be used as a solvent in industrial applications to produce resins and adhesives, as well as a dispersing agent for pigments. In addition, its six-member ring can be aromatized, making it a suitable candidate for substituting the aromatic intermediates. Moreover, isoprene, a monomer of natural rubber (one of the constituents of tires), has been added to the list of potential target structures [26]. Finally, p-cymene is used as an intermediate in industrial fine chemical

synthesis in terms of fragrances, flavorings, herbicides, pharmaceuticals, and p-cresol synthesis [27], and it is usually synthesized by Friedel–Crafts alkylation of benzene with methyl and isopropyl halides using  $\text{AlCl}_3$  as an acid catalyst, or from toluene with isopropyl alcohol. However, p-cymene can also be produced from limonene [27,28], which creates an opportunity for its recovery from waste tire pyrolysis oil.

Therefore, instead of focusing on a specific compound, the catalytic transformation of waste tires via pyrolysis should point to the production of an oil, enriched with several compounds of marketable value. This can also be achieved by tailoring the catalyst and reaction conditions to guide the selectivity to within the desired products. With this aim, Ni, Co, and Pd catalysts supported on  $\text{SiO}_2$  were evaluated in the catalytic pyrolysis of the rubber fraction of waste tires.  $\text{SiO}_2$  was chosen as a support owing to its thermal stability and low acidity, which ensure that it does not participate in the reaction. Thus, the role of the metallic phase on the selectivity toward valuable products can be isolated from the effect of the support. The isolated role of metallic phase has been insufficiently explored since the acid supports with intrinsic activity are commonly used in these reactions. This kind of catalysts where only metallic phase A combination of the TGA–FTIR and Py–GC/MS techniques was used to comprehensively study thermal decomposition behavior, product distribution, and reaction pathways of waste tire pyrolysis.

## **2. Experiment**

### ***2.1. Raw material and catalyst preparation***

The raw material (waste tires) used in this study was collected from the Polambiente S.A company as granulated material and was screened (8" Gilson sieve) into particle sizes between 180 and 300  $\mu\text{m}$ . The catalysts were prepared by the incipient wetness impregnation

of the support ( $\text{SiO}_2$  sieved to 180-125  $\mu\text{m}$ ) with a suitable volume of the corresponding metal salts. Water was used as solvent for  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{PdCl}_2$  (adding triethanolamine (TEA,  $\geq 99.0\%$ , Merck) and  $\text{HCl}$  ( $\text{HNO}_3$  (aq.)  $\geq 37.0\%$  Merck), to control solubility). The metallic load and impregnation volume were adjusted to obtain 5%w/w for Ni and Co, and 2%w/w for Pd loadings. Subsequently, the samples were dried and calcined at 500  $^\circ\text{C}$  for 2 h (2  $^\circ\text{C min}^{-1}$ ). Thereafter, the precursors were treated under a  $\text{H}_2$  flow (20  $\text{mL min}^{-1}$ , 99,9999% Airliquide, Chile) at 500  $^\circ\text{C}$  for Co and Ni catalysts, and 300  $^\circ\text{C}$  for the catalyst.

## **2.2. Raw material and catalyst characterization**

The specific BET surface area, pore volume, and diameter of the catalysts were determined from nitrogen adsorption/desorption at  $-196$   $^\circ\text{C}$  using a Micromeritics Gemini VII 2390t instrument. Temperature-programmed reduction ( $\text{H}_2$ -TPR) analysis was performed on a ChemBet 3000 instrument. Typically, 100 mg of oxidized catalysts ( $180 < dp < 300$   $\mu\text{m}$ ) was deposited in a quartz tube (4 mm diameter) and dried under He flow at 200  $^\circ\text{C}$  for 0.5 h and then heated from room temperature (RT) to 700  $^\circ\text{C}$  at 5  $^\circ\text{C min}^{-1}$  in a 5%  $\text{H}_2/\text{Ar}$  mixture (30  $\text{mL min}^{-1}$ ). The size and distribution of the metallic particles were studied by transmission electron microscopy (TEM; JOEL JEM 1200 EXII), with an acceleration voltage of 120 kV. The images were processed with ImageJ software to obtain the particle size distributions. Total acidity was evaluated by the temperature-programmed desorption of ammonia ( $\text{NH}_3$ -TPD) technique. Before analysis, samples (100 mg) were pre-treated under a He flow at 100  $^\circ\text{C}$  up to baseline stabilization, and were then subsequently ammonia-saturated at RT using  $\text{NH}_3$  pulses. Once the surface was saturated, the weakly adsorbed  $\text{NH}_3$  was removed by flowing He at 100  $^\circ\text{C}$  for 0.5 h. Subsequently, desorption was carried out using a linear

heating rate of  $10\text{ }^{\circ}\text{C min}^{-1}$  from 100 to  $800\text{ }^{\circ}\text{C}$ . All desorption profiles were normalized per gram of catalyst. The experiments were carried out with a semiautomatic Micromeritics TPD/TPR 2900 apparatus equipped with a TCD. Specific surface area metal was measured by  $\text{H}_2$  chemisorption on a Micromeritics ASAP 2020 unit. All samples were dried at  $200\text{ }^{\circ}\text{C}$  for 1 h and reduced under in situ  $\text{H}_2$  for 2 h at the corresponding temperature. Subsequently, the samples were placed under vacuum for 1 h at  $350\text{ }^{\circ}\text{C}$ . Then, the systems were brought to room temperature and hydrogen isotherms were carried out to calculate the metallic surface area.

The proximate analysis was performed according to the ASTM D3172 Standard, while the elemental composition was determined in a Leco CHNS 628 elemental analyzer. Trace inorganic elements were quantified by inductively coupled plasma optical emission spectrometry (ICP-OES) using a PerkinElmer Optima 7000 DV ICP-OES series instrument. Further details of methods and equipment can be found in [13]. The TGA measurements were carried out using a Shimadzu DT 50 Thermal Analyzer to evaluate the thermal events during tire decomposition. The thermogravimetric analyses were performed under He ( $50\text{ mL min}^{-1}$ ) using 2 mg of the sample and a heating rate of  $25\text{ }^{\circ}\text{C min}^{-1}$ . The studied temperature range was  $20\text{--}600\text{ }^{\circ}\text{C}$ .

### **2.3. Experimental Methods**

#### *2.3.1 Thermogravimetric analysis coupled with Fourier Transform Infrared spectrometer (TGA-FTIR)*

The thermogravimetric analyzer (TA Instruments thermobalance model Q50) was coupled to the FTIR (Thermo Scientific infrared spectrometer model Nicolet is10, DTGS detector and KBr windows) to investigate the mass loss of the evaluated materials (catalyst-to-tire ratio of 8:1) and the formation of typical products at the same time. This catalyst-to-tire ratio

was established in previous systematic studies to guarantee an adequate response of the analytic techniques used. In the TGA experiment, the sample was heated to 600 °C (25 °C min<sup>-1</sup>) under nitrogen flow (100 mL min<sup>-1</sup>) for thermal decomposition of the sample. The gases evolved were analyzed by FTIR, which was set to collect 32 interferograms at a resolution of 8 wavenumbers and a spectral range of 4000–400 cm<sup>-1</sup>. The buoyancy effect during the TGA experiments was avoided by subtracting a blank baseline curve from each experiment.

### 2.3.2. Pyrolysis experiments coupled to gas chromatography/mass spectrometry (Py-GC/MS)

Fast pyrolysis of tires, with and without catalysts, was performed in a CDS 5200 pyroprobe (CDS Analytical) (Figure S1). The reactor was a quartz tube (25 mm length and 1.9 mm ID), which was inserted inside a probe and electrically heated using a Pt coil. In a typical experiment, 1 ± 0.1 mg of raw material (AD 6000 Ultra MicroBalance Perkin Elmer) was placed within the reactor, along with the catalyst bed with a catalyst-to-tire ratio of 8:1 (Figure S1). Both the catalyst and tire were separated by quartz wool, in this way the direct contact tire-catalyst is avoided and the whole catalytic effect could be ascribed to purely *ex-situ* operation. Catalyst was placed on both sides of the reaction bed to ensure that all pyrolysis products pass through the catalytic bed. In the reaction zone, a flow of He gas (pure 99.996%, BOC) of 20 mL min<sup>-1</sup> was maintained to push volatiles into the analysis area (GC/MS), and the heating rate varied according to the reaction temperature (350, 400, and 450 °C), considering a residence time of 12 s. Before entering the GC, the volatiles passed by a Tenax trap (pre column Perkin Elmer) at 280 °C and a heated transfer line (CDS Analytical) set at 280 °C and connected to the chromatograph gases. The separation system

consisted of an Elite 1701 column ( $30\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$ ) and He as the carrier gas at  $15\text{ mL min}^{-1}$ . The GC column was heated from  $45$  to  $280\text{ }^\circ\text{C}$  at  $2.5\text{ }^\circ\text{C min}^{-1}$ . The compounds were identified by their mass spectra with an  $m/z$  range of  $30$ – $600$  Da. The MS spectra obtained were compared with the standard spectra of the compounds found in the NIST library. As the amount of tire was strictly controlled, the ratio of relative peak areas ( $\text{Area}_{\text{compound}(i)}/\text{Area}_{\text{All detected compounds}}$ ) can be used as a representation of the selectivity to the products. Aiming to provide a more specific value of selectivity, this parameter was expressed per active metal sites. The conversion was calculated with respect to the amount of tire mass loss upon completion of the pyrolysis experiment ( $X_i(\%)$ ).

### 3. Results and Discussion

#### 3.1. Characterization of the catalysts and raw material

The reduction profiles measured by TPR for the calcined M/SiO<sub>2</sub> catalysts are depicted in Figure 1. For the Ni catalyst, a broad reduction peak in the range of  $300$ – $600\text{ }^\circ\text{C}$  was observed, which had two shoulder peaks—one at  $250\text{ }^\circ\text{C}$  and the other extending up to  $800\text{ }^\circ\text{C}$ . The reduction profile between  $250$  and  $600\text{ }^\circ\text{C}$  can be associated to reduction of amorphous and crystalline NiO and Ni<sup>2+</sup> species having weak to medium interaction with the support. The presence of reduction peaks observed at higher temperatures ( $>600\text{ }^\circ\text{C}$ ) may be related to the reduction of Ni<sup>2+</sup> species—present as nickel silicate—which are not easily reduced [29]. The reduction profile of Co/SiO<sub>2</sub> catalyst was similar to those already reported [30,31], in which different reduction stages between  $200$  and  $500\text{ }^\circ\text{C}$  were observed due to the reduction of Co<sup>2+</sup> species to Co metal. Afterward, an additional reduction peak was observed between  $500$  and  $720\text{ }^\circ\text{C}$ , which could be attributed to hardly reducible species such as Co<sub>2</sub>SiO<sub>4</sub> [30,31]. As has been validated by other researchers, the anchoring effect of Ni<sup>2+</sup>

and  $\text{Co}^{2+}$  between the metal and support interface could help in forming more stable metal clusters due to the enhanced metal–support interactions [32,33]. The Pd/SiO<sub>2</sub> catalyst exhibited a typical negative peak at 50 °C due to the decomposition of Pd hydride formed at room temperature during the reduction of PdO [34]. The peaks detected between 50 and 100 °C can be ascribed to the reduction of PdO. The metallic catalysts then prepared by reduction at 500 °C for Ni and Co and 300 °C for Pd exhibited a specific surface area similar to the support, as shown in Table 1. The slight decrease in the surface area and pore volume could be due to the pores plugging the support during metal impregnation. The TEM micrographs and average particle diameters are shown in Figure 2 and Table 1, respectively. The particle size distribution was obtained by measuring more than 200 individual particles. All the catalysts had a wide range of distribution, ranging between 2 and 20 nm (inserts of Figure 2). In addition, the standard deviation for the mean particle sizes was relatively high (Table 1), which implies that there is not a significant difference for this parameter among the used catalysts. The specific surface area of the metals was established by H<sub>2</sub> chemisorption (Table 1) and the distribution of the products obtained in the reaction for each catalyst was reported based on it. The NH<sub>3</sub>-TPD measurements (Figure S2) indicated that all of the catalysts presented a very low acidity; therefore, it could be suggested that the catalytic behavior of the synthesized materials evaluated here may be mainly attributed to the metallic phase.

Regarding the sample of waste tires, the proximate analysis displayed an organic carbon content—representing volatile matter—of around 58.8% (Table 2). The fixed carbon (non-volatile) and ash fractions of the waste tires correspond to carbon black and inorganics that other than steel, respectively. The elemental analysis shows the presence of N ( $0.47 \pm 0.03\%$ ) and sulfur ( $1.48 \pm 0.06\%$ ), which are commonly used as a vulcanizing agent. Metallic

elements such as aluminum, iron, calcium, potassium, and sodium were also detected at low proportions. These elements could promote some reactions during fast pyrolysis; however, their low concentrations in the raw material may rule out significant participation in the pyrolysis reactions. The results for the regular thermogravimetric analysis carried out from ambient temperature to 600 °C at 25 °C min<sup>-1</sup> are presented in Figure 3 and Table 2. The TGA profile allows assessment of the pyrolysis behavior, establishing a suitable temperature range for the pyrolysis reaction. An extended discussion about this issue has been published elsewhere [13]. The TGA and DTG curves show that four thermal events occurred between 100 and 600 °C. The mass loss observed below 220 °C (first thermal event) is attributed to the decomposition of the volatile matter, such as plasticizers and additives, used in tire fabrication. The highest mass loss appears centered at 370 °C, with a shoulder at about 450 °C. These second and third thermal events observed in the DTG analysis (Figure 3) can be assigned to the tire–natural rubber decomposition, in agreement with previously reported thermogravimetric analyses of natural rubber [35,36]. The thermal event at 460 °C may also be related to the degradation of styrene–butadiene rubber (SBR) and butadiene rubber (BR) components in tires [35,36]. The last statement is based on previous reports demonstrating that thermal degradation of SBR started at ca. 350–370 °C and finished between 480 and 570 °C; meanwhile, for BR, it started at ca. 450–520 °C and ended at ca. 550 °C [35,36]. Therefore, the mass loss at around 560 °C can be attributed to BR decomposition. The remaining residue after the pyrolysis process was 39%, which corresponds to the carbon residues and non-decomposable inorganic fillers, in agreement with the proximal analysis (Table 2).

### *3.2. Catalytic pyrolysis of waste tires: Product identification and selectivity*



### *3.2.1. Catalytic pyrolysis reaction evaluated by thermogravimetric analysis coupled with Fourier Transform Infrared spectrometer (TGA–FTIR)*

The catalysts' effect on the thermal decomposition of the used tires was evaluated by TGA–FTIR measurements under extrapure N<sub>2</sub> at a heating rate of 25 °C min<sup>-1</sup> (Figure 4). A slight shifting to lower temperatures in respect to non-catalyzed pyrolysis was observed, indicating that tire degradation was favored in the presence of the catalysts. A loss of mass around 70% was observed in all cases. The volatile compounds from the thermal decomposition of the rubber tires were detected in real time by using FTIR to detect the functional groups of evolved products. The experimental conditions were controlled to simulate pyrolysis (catalyst-to-tire ratio of 8:1). The spectra exhibited in Figure 5 indicate that alkenes and aromatic compounds [37] were the main products liberated during pyrolysis. The large peak observed at 1510 cm<sup>-1</sup> in all cases, along with the heat treatment, can be attributed to C=C bond stretch absorptions in the aromatic ring. The presence of aromatics during the reaction can be confirmed by peaks at both ca. 740 and 670 cm<sup>-1</sup>, corresponding to symmetric out-of-plane bending of the ring hydrogens and out-of-plane ring bend, respectively. The former was mainly observed on the Pd and Ni catalysts. On the other hand, the methyl and methylene groups that were present as substituents of the aromatic ring or in the aliphatic hydrocarbons were identified by the peaks between 1340 and 1490 cm<sup>-1</sup>, representing the bending vibration of -CH<sub>3</sub> and -CH<sub>2</sub>. The peaks at ca. 1460 and 1375 cm<sup>-1</sup> are due to -CH<sub>3</sub> asymmetric and symmetric bending, respectively, while the -CH<sub>2</sub> groups were identified by a peak at about 1470 cm<sup>-1</sup>, which was attributed to scissoring bending.

The appearance of a doublet between 1350 and 1390  $\text{cm}^{-1}$  was attributed to branched alkanes or gem dimethyl. The peak centered at 1654  $\text{cm}^{-1}$  represents the C=C stretching vibration in aliphatic hydrocarbons, confirming the presence of alkenes in the evolved products. The peaks at around 2320 and 2360  $\text{cm}^{-1}$  are characteristic signals attributed to  $\text{CO}_2$ ; as the temperature increased, the intensity of these signals increased (Figure 5), in agreement with the reports of a previous study [38], indicating that the release of  $\text{CO}_2$  took place at a relatively high temperature. In all cases, during short heating times of 5 min (125 °C), IR-signals attributed to gases generated by tire thermal decomposition were observed. As the temperature rose, all these signals exhibited an important increase in intensity. Around 400 °C, an increase in intensity of the characteristic signals for  $-\text{CH}_3$  and  $-\text{CH}_2$  stretching (2800 and 3100  $\text{cm}^{-1}$ ) (Figure 5) was observed in the reaction without the catalysts, most likely indicating the formation of aliphatic hydrocarbons, contrary to the catalyzed reactions where band vibrations corresponding to aromatic compounds were showed greater increases in intensity. These results point out that the catalysts favored the formation of aromatic compounds at this temperature.

### *3.2.2. Catalytic pyrolysis experiments coupled to gas chromatography/mass spectrometry (Py-GC/MS)*

#### *3.2.2.1. Product distribution in the catalytic pyrolysis of waste tires*

The catalytic activity of the M/SiO<sub>2</sub> catalysts (M: Pd, Ni, and Co) for the pyrolysis of waste tires was measured at 450 °C, according to the results obtained via thermogravimetric analysis (Figure 3 and Section 3.2.1), where, below this temperature, the highest mass loss was registered. Table 3 shows the main compounds identified by GC/MS ( $\pm 90\%$  accuracy

according to the NIST database) during the pyrolysis experiments. Those peaks that were not identified due to their low resolution were grouped as “others.” The identified species corresponded to more than 50% of the total products obtained. As can be seen in Table 3, waste tire pyrolysis produces a mixture of valuable chemical compounds, namely, cycloalkenes, alkenes (e.g. isoprene), aromatic terpenes (p-cymene and p-cymenene), aliphatic terpenes (limonene, terpinolene, and  $\alpha$ - and  $\gamma$ -terpinene), benzene, and alkylbenzenes (toluene, p-xylene, styrene, and 1,3,5-trimethyl benzene). Pd/SiO<sub>2</sub> led to the highest percentage (93.8%) of identifiable compounds, and the lowest was obtained with the Co/SiO<sub>2</sub> catalyst (56%). Although the same compounds were observed with or without a catalyst, in some cases, selectivity toward certain products was affected by the presence and the nature of the catalysts.

The highest selectivity was obtained toward limonene (regardless of the presence or the nature of the catalyst), which makes up more than 17% of the total area of all of the products in the following order: Ni (30.6 %) > Pd (28.8%) > non-catalyzed (24.5%) > Co (17.7%). In addition, a high selectivity to isoprene was obtained in all cases. A large number of studies have also reported that limonene is the major product of waste tire pyrolysis [39,8,13,14,35]. Limonene is produced by degradation of cis-1,4-polyisoprene (natural or synthetic rubber) through a radical-mediated reaction, initiated by  $\beta$  bond scission with respect to the double bonds of the main polymer chain [25,40]. The allylic radical thus formed subsequently undergoes an intramolecular cyclization and  $\beta$  bond scission to form d,l-limonene.

The presence of alkenes, cycloalkenes, and aliphatic terpenes observed in this study (Table 3) in the presence or absence of catalysts could be due to the isomerization and cracking of

limonene and to the depolymerization of styrene–butadiene and butadiene rubber [25,41]. In addition to the above-mentioned substances, N- and/or S-containing compounds, such as 1,3-benzothiazole and 2,4-dimethyl-quinoline (Table 3) appear. This is most likely due to the thermal degradation of organic additives, or to the chemical agents and accelerators used during the vulcanization process [42]. Although these S-containing heteroatomic molecules represent an obstacle for later use of the oil, the relative selectivity found in the pyrolytic product was lower than 1.2%. It has been reported [25,43] that between 350 and 850 °C, approximately half of the initial sulfur remains in the solid char rather than in the condensed vapor phase, which could explain the low selectivity toward S-containing species observed here.

The formation of high-value hydrocarbons such as limonene, isoprene, benzene, toluene, xylenes, and p-cymene shows that waste tire pyrolysis confers an undoubted added value to these types of residues. Indeed, recovering chemical compounds from waste tires will contribute to establishing a circular economic concept, instead of the traditional linear model of production–use–disposal.

#### *3.2.2.2. Effect of temperature on selectivity to high-value hydrocarbons*

The effect of temperature on the product distribution in the volatile fractions from the waste tire pyrolysis using M/SiO<sub>2</sub> catalysts is shown in Figure 6. At the lowest temperature (350 °C), the highest selectivity to limonene was obtained for the Co catalyst (52%), and the lowest was found using Pd/SiO<sub>2</sub>, where only 2.7% limonene was obtained and a high selectivity toward benzene was detected—43% of the total identified compounds. Mixture of alkenes

and cycloalkenes (Table 3) were only identified on the Ni and Co catalysts at up to 8.2% and 4.0%, respectively. The aromatic compounds did not represent more than 12% of products with these catalysts and without catalyst. When raising the temperature to 400 °C, reactions leading to alkenes, cycloalkenes, and aromatic compounds were favored in all of the experiments; however, for the Co/SiO<sub>2</sub> catalyst, limonene and isoprene remained the main products out of those identified. It is interesting to note that only on Pd/SiO<sub>2</sub> was p-cymene significantly generated (11.2%). Selectivity toward alkenes (different from isoprene) and cycloalkenes followed the order of Ni (20.2%) > Co (7.1%) > Pd (4.2%) > non-catalyzed (2.5%), while for aromatic compounds represented by BTX, it was Pd (30.1%) > Ni (22.2%) > Co (10.2%) > non-catalyzed (8.8%). An increase in temperature (450 °C) resulted in the appearance of more compounds in all cases (in the presence or absence of a catalyst). At 450 °C, only the Pd-based catalyst showed important differences related to selectivity toward aromatic compounds such as BTX (20.1%) and p-cymene (13%), while in the other cases, the generation of p-cymene and aromatic compounds was below 2% and 6%, respectively (Figure 6).

Tire conversion progressively increased with temperature, being 27% at the lowest temperature, regardless of whether catalysts were present or not. In all cases, and when the temperature increased to 400 °C, conversion was around 50%. The maximum conversion was obtained at 450 °C, with a value of 65.7%, which was in agreement with the results of mass loss established by TGA (Section 3.2.1) and proximate analysis (Table 2).

### *3.2.2.3. Effect of the nature of the catalyst on selectivity to high-value hydrocarbons*

The effect of the nature of the catalyst on pyrolysis selectivity was more evident at the lowest temperatures ( $T \leq 400$  °C) (Figure 6). The Co/SiO<sub>2</sub> catalyst showed a remarkably high selectivity (52%) to limonene, indicating that the formation of this terpene was favored at 350 °C by the presence of Co sites. Conversely, on the Pd catalyst, a high selectivity to benzene was detected (43%). Furthermore, other aromatic compounds such as xylene and toluene were also detected. Below 400 °C, aromatization reactions were mostly favored on a Pd/SiO<sub>2</sub> catalyst, increasing selectivity to p-cymene and BTX (41.3%). On the other hand, the C–C bond cleavage reactions mainly occurred on the Ni catalyst, as shown by a higher formation of alkenes and cycloalkenes from 350 °C (compared to the other cases); however, aromatization reactions were also identified when using this catalyst (24.3% to BRX and p-cymene). For the Co/SiO<sub>2</sub> catalyst, mild-cracking reactions were detected, since a high selectivity toward limonene was observed up to 400 °C. The lack of alkenes and aliphatic terpenes liberated in the reaction without a catalyst clearly indicates an effect of the catalyst on isomerization and cracking reactions at low temperature during waste tire pyrolysis. When the temperature increases (450 °C), the effect caused by the presence of a catalyst and its nature is less important in terms of the product distribution compared with the results from the non-catalyzed experiments. This suggests that the reaction is thermodynamically controlled at higher temperatures. As can be observed, at 450 °C (Figure 6), only the Pd/SiO<sub>2</sub> catalyst showed some differences with respect to the reaction carried out without the catalyst; the Pd catalyst favored the formation of benzene, toluene, xylene, and p-cymene. These compounds represent 33.1% of the detected species during Pd-catalyzed pyrolysis, while for uncatalyzed reactions and those performed with other catalysts, the amount of aromatic compounds formed did not exceed more than 8%. The observed trend in selectivity is clearly related to the nature of the metals. The well-known dehydrogenation capacity of Pd [24]

promoted aromatization reactions, while Ni and Co favored cracking reactions, being to a lesser extent for Co. Furthermore, Ni is also known to be very active in hydrogenation/dehydrogenation reactions [24], so that this catalyst also promoted the formation of aromatic compounds.

### *3.3. Reaction pathways for the pyrolysis of waste tires on SiO<sub>2</sub>-supported Ni, Co, and Pd catalysts*

Taking into account the product distribution obtained by Py-GC/MS (Table 3) and detected by TGA-FTIR (Figure 5), the effect of temperature (Figure 6), and the available data in the literature [9,23,25,41], an analysis of the possible reaction pathways is provided (Figure 7). When waste tire pyrolysis is carried out, the reaction initiates from the  $\beta$ -bond homolytic rupture of the cis-1,4-polyisoprene or natural rubber (**A**), leading to the formation of two radical chains (**B** and **C**). Both of them can undergo an intramolecular cyclization, followed by scission yielding 1-methyl-4-(1-methylethenyl)-cyclohexene or d,l-limonene (**E**) from **C** and 1,5-dimethyl-5-ethenyl-cyclohexene (**D**) from **B** [44]. The highest amount of d,l-limonene obtained is partly due to steric hindrance of the methyl group, preventing the cyclization reaction in radical **B**, and partly to a higher stability of radical **C** by hyperconjugation [40]. However, although the selectivity to **D** was consistently lower, it was observed in all cases. In addition, both **B** and **C** radicals can unzip toward the isoprene monomer (**J**). This compound is part of the potential target structure [26], so its isolation is interesting, as was already mentioned. Another reaction route for the production of limonene that has been argued by some authors and also reported by us [13] is the dimerization of two isoprene monomers via a Diels-Alder addition reaction [25]. However, this mechanism is

controversial, since it can also lead to significant amounts of 1-methyl-5-(1-methylethenyl)cyclohexene (diprene) [45], which was not observed within the reaction products (Table 3). A computational study carried out by Kar et al. [45] suggested that diprene and d,l-limonene are products that are equally favored by isoprene dimerization; therefore, since diprene was not observed as a product and limonene selectivity was always high in our reactions, this indicates that intramolecular cyclization was the favored reaction in this case. Menares et al. [13] suggested this reaction route because when the pyrolysis temperature increased above 600 °C, a notable decrease in the amount of isoprene was observed with a simultaneous increase in the amount of limonene.

Once limonene is formed (**E**), this may undergo further isomerization reactions, resulting in the production of its isomers such as terpinolene (**F**) and  $\alpha$ - and  $\gamma$ -terpinene (**G** and **H**), which were detected in the pyrolysis products in all cases (Table 3). Subsequently, these terpenes can undergo dehydrogenation, leading to p-cymene (**I**), a product detected mainly on the Pd catalyst. All of these reactions can be promoted by acid and metallic sites or by bifunctional acid/metal catalysts, as was explained by Corma et al. [46]. In the case of the catalysts used in this study, on metal sites, olefins (as limonene) could be adsorbed by electron donation from their  $\pi$  orbitals to the d-type orbitals of metal centers and simultaneous electro back-donation from full d-type orbitals of metals to empty  $\pi^*$ -antibonding orbitals [24]. In this way, the exocyclic double bond of d,l-limonene could be adsorbed on a catalyst metal site, which is preferable to the endocyclic, given its lower steric hindrance, although the latter cannot be ruled out. Thereafter, the dehydrogenation reaction gives rise to the formation of terpinolene (**F**), as shown schematically (Figure 7). In turn, the terpinolene (**F**) can isomerize to  $\alpha$ - and  $\gamma$ -terpinene (**G** and **H**) by double-bond migration, and subsequent dehydrogenation



reactions would result in aromatization of these species, leading to p-cymene (**I**). The dehydrogenation occurs in the vicinity of the  $\pi$ -allylic interaction by scission of a nearby C–H bond. A key factor favoring this reaction is the ability to adsorb hydrogen, which would be a determining step of dehydrogenation reactions [24]. This could explain the greater selectivity toward p-cymene observed when using the Pd/SiO<sub>2</sub> catalyst compared to the others, given the well-reported hydrogenation/dehydrogenation ability of Pd [46,47]. In fact, p-cymene has already been produced from limonene over Pd-supported catalysts [27,28,47]. The presence of p-cymenene (Table 3) in byproduct reactions—an aromatic terpene that retains the exocyclic double bond—could indicate that a limonene–catalyst interaction through the endocyclic double bond is possible. The participation of the acid sites of a catalyst in the aforementioned reactions was ruled out, given the insignificant acidity observed in these catalysts (Figure S2). As a result, the observed selectivity was only attributable to the catalyst metallic sites.

Cycloalkenes, alkenes, and alkylbenzenes found as waste tire pyrolysis reaction byproducts (Table 3) resulted from the cracking and aromatization of limonene (**E**) (Figure 8). Scission of the C–C bond of the limonene ring in the  $\beta$  position gave rise to a diradical diene, which was transformed to an alkatriene by intramolecular hydrogen transfer (**K**). Isomerization of this alkatriene to its conjugate form (**L**) and further cyclization could result in some cycloalkenes identified in the reaction products such as 5-ethyl-1,5-dimethylcyclohexa-1,3-diene (**M**) and/or 1,5,5,6-tetramethyl 1,3-cyclohexadiene (**N**). Then, the aromatization reaction of the latter produces 1,2,3-trimethyl-benzene (**O**), which was also observed. The subsequent dealkylation of these alkylbenzenes was indicated by the presence of the xylenes (**P**), toluene (**Q**), and benzene (**R**) observed in the reaction products. These dealkylation

reactions on metals have been studied for a long time, and their mechanism involves the participation of a metal hydride [48]; thus, in the present study, the Pd and Ni catalysts could favor them, such as was observed in the product distribution (Figure 6). These alkylbenzenes could also be produced from cymene (**I**) dealkylation, as has been reported before [49], which could have been favored over Pd/SiO<sub>2</sub>. Moreover, isoprene (**J**) can also be formed from diradical diene of limonene by its allylic rearrangement and  $\beta$  scission.

On the other hand, styrene-butadiene rubber decomposition could be responsible for the presence of styrene in the pyrolysis products (Table 3 and Figure 6), even at the lowest temperature (350 °C), taking into account that SBR rubber thermal decomposition begins at around 350 °C [35,36]. This was further indicated by the TGA results, which showed that rubber decomposition was favored in the presence of catalysts. Styrene is also susceptible to dealkylation, leading to the aforementioned BTX compounds [50]. When the temperature of the pyrolysis increased to 450 °C, new cycloalkenes, such as 1,3-cycloheptadiene and 4-vinyl cyclohexene, were detected at retention times of 4.90 and 7.7 min, respectively (Table 3), which were associated with the cyclization of butadiene rubber depolymerized radicals [9,50].

The well-known hydrogenation/dehydrogenation capacity of Pd [24] effectively favored the formation of aromatic compounds from the isomerization and dehydrogenation of limonene, and subsequent dealkylation of the p-cymene and alkylbenzenes formed (Figure 7 and 8). The Ni catalyst mainly promoted cracking reactions due to its C–C bond scission ability [26] as well as subsequent aromatization reactions (Figure 7 and 8), while on the Co catalyst, a mild-cracking could be observed, leading mainly to limonene and isoprene. Consequently,

considering that there is not a significant difference in the metallic surface between the catalysts (Table 1), it is possible that the catalytic activity observed can be mainly attributed to the nature of the catalyst itself. The selectivity toward aromatic compounds such as benzene, toluene, and xylene found here over the Pd and Ni catalysts was similar to those already reported using zeolites [9,11]; however, the reaction temperature in our case was lower ( $\leq 400$  °C).

#### 4. Conclusions

The use of Pd, Ni, and Co metal catalysts supported on SiO<sub>2</sub> for waste tire pyrolysis favored aromatization and cracking reactions at low temperatures (below 400 °C) compared to non-catalyzed pyrolysis. The Pd/SiO<sub>2</sub> catalyst was the most selective to aromatic compounds (around 40%), such as benzene, toluene, xylenes, and p-cymene, which could be related to its well-known hydrogenation/dehydrogenation capacity. However, over Ni/SiO<sub>2</sub> catalyst a significant selectivity to BTX was also observed (around 20%). On the other hand, the Ni/SiO<sub>2</sub> and Co/SiO<sub>2</sub> catalysts promoted cracking reactions, leading to the formation of alkenes and cycloalkenes, due to its greater C–C bond scission ability—although, a mild-cracking was observed on the Co catalyst. Below 400 °C, selectivity toward alkenes and cycloalkenes followed the order of Ni (20.2%) > Co (7.1%) > Pd (4.2%) > non-catalyzed (2.5%), while for aromatic compounds represented by BTX, it was Pd (30.1%) > Ni (22.2%) > Co (10.2%) > non-catalyzed (8.8%). In all cases, high selectivity to limonene and isoprene was found. This work demonstrates that the selectivity toward high-value hydrocarbons such as limonene, isoprene, benzene, toluene, xylenes, and p-cymene during the catalytic pyrolysis

of waste tires can be controlled by a suitable selection of catalyst and reaction temperature. Herein, it was confirmed that catalytic pyrolysis over easy-to-prepare metal catalysts based on transition metals is a feasible alternative for the valorization of waste tires at low temperatures. However, the results obtained at analytical level in this study, must be scaled-up in order to validate the fundamentals developed here. The evaluation of the catalysts stability in long-term operation is also a major challenge which should be addressed.

### **Credit Authors Statement**

**Paula Osorio-Vargas:** Conceptualization, Investigation, Formal Analysis, Validation, Methodology, Data curation, Project Administration, Funding Acquisition and Writing Original Draft. **Tamara Menares:** Investigation, Formal Analysis, Validation, Methodology and Data curation. **Daniela Lick:** Resources, Data Curation Writing Review & Editing. **Monica L. Casella:** Resources and Data Curation. **Romina Romero:** Conceptualization, Methodology, Validation and Data curation. **Romel Jiménez:** Conceptualization, Writing Review & Editing. **Luis E. Arteaga-Pérez:** Conceptualization, Methodology, Writing Review & Editing, Project Administration, Funding Acquisition, Visualization, Supervision.

Conflict of interests

The authors have no conflicts of interest to declare.

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**Figure captions**

**Figure 1.** Temperature-programmed reduction (H<sub>2</sub>-TPR) profiles of (a) Ni, (b) Co, and (c) Pd supported on SiO<sub>2</sub>. Dashed red line deconvolution.

**Figure 2.** Transmission electron microscopy (TEM) micrographs of (a) Ni, (b) Co, and (c) Pd supported on SiO<sub>2</sub>. Insert figure: particle size distribution.

**Figure 3.** Thermogravimetric (TG, blue line) and derivative thermogravimetric (DTG, black line) analyses corresponding to the thermal degradation of waste tires.

**Figure 4.** DTG curves of waste tire decomposition over M/SiO<sub>2</sub> catalysts at 25 °C min<sup>-1</sup> carried out using thermogravimetric analysis coupled with Fourier Transformed Infrared spectrometer (TGA–FTIR). DTG curve for non-catalytic experiment is named as tire (black line).

**Figure 5.** FTIR of TGA evolved gas, representing absorbance with respect to time (min) and wavenumber (cm<sup>-1</sup>) of waste tires over M/SiO<sub>2</sub> catalysts: (a) Non-cat, (b) Ni/SiO<sub>2</sub>, (c) Co/SiO<sub>2</sub>, and (d) Pd/SiO<sub>2</sub>

**Figure 6.** Product distribution for catalytic waste tire pyrolysis over M/SiO<sub>2</sub> catalysts (M: Ni, Co, and Pd) at 350, 400, and 450 °C determined by pyrolysis experiments coupled to gas chromatography/mass spectrometry (Py–GC/MS). X (%) = conversion.

**Figure 7.** Suggested reaction pathways of waste tire pyrolysis leading to d,l-limonene, isoprene, and aromatic and aliphatic terpenes. (A) Cis-1,4-polyisoprene, (B) radical oligomer of cis-1,4-polyisoprene, (C) radical oligomer of cis-1,4-polyisoprene, (D) 1,5-dimethyl-5-

ethenyl-cyclohexene, (E) d,l-limonene, (F) terpinolene, (G)  $\gamma$ -terpinene, (H)  $\alpha$ -terpinene, (I) p-cymene, and (J) isoprene.

**Figure 8.** Suggested reaction pathways of waste tire pyrolysis leading to alkenes, cycloalkenes, and mono-aromatic compounds. (K) Alkatriene, (L) conjugate alkatriene, (M) 5-ethyl-1,5-dimethylcyclohexa-1,3-diene, (N) 1,5,5,6-tetramethyl 1,3-cyclohexadiene, (O) 1,2,3-trimethyl-benzene, (P) xylenes, (Q) toluene, and (R) benzene.

Figures

Figure 1

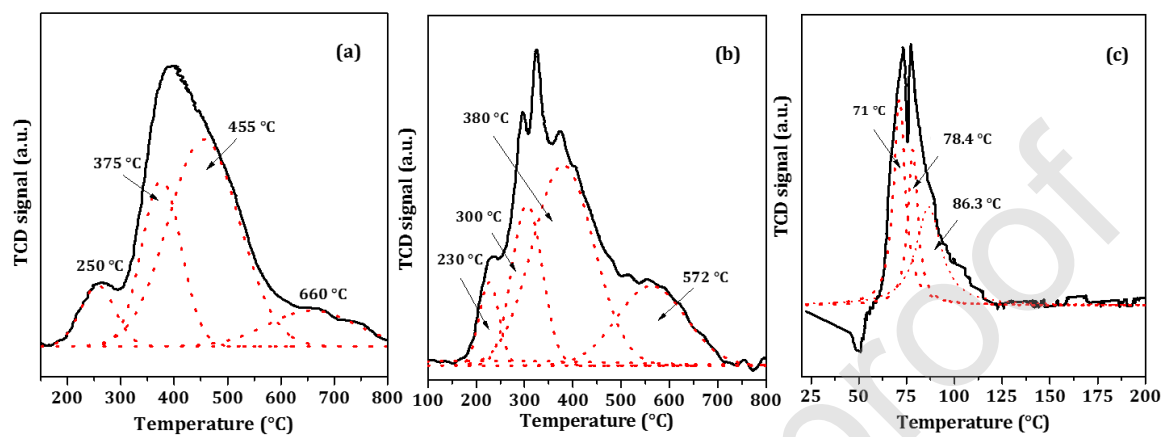


Figure 2

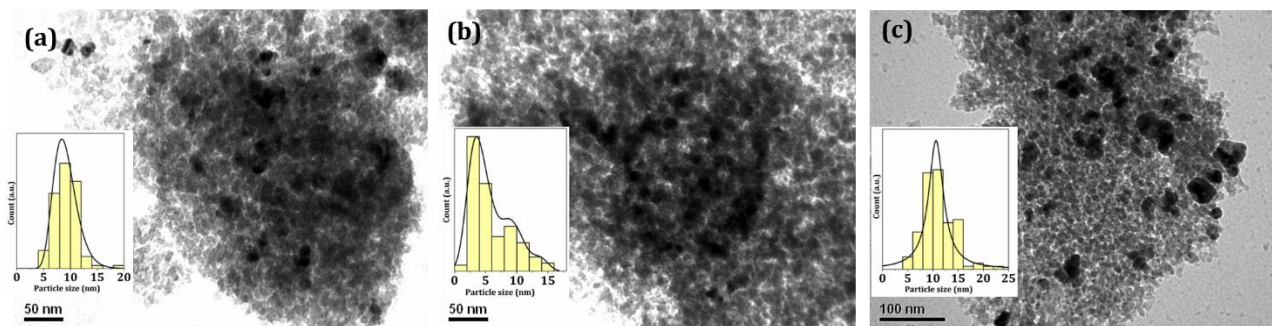


Figure 3.

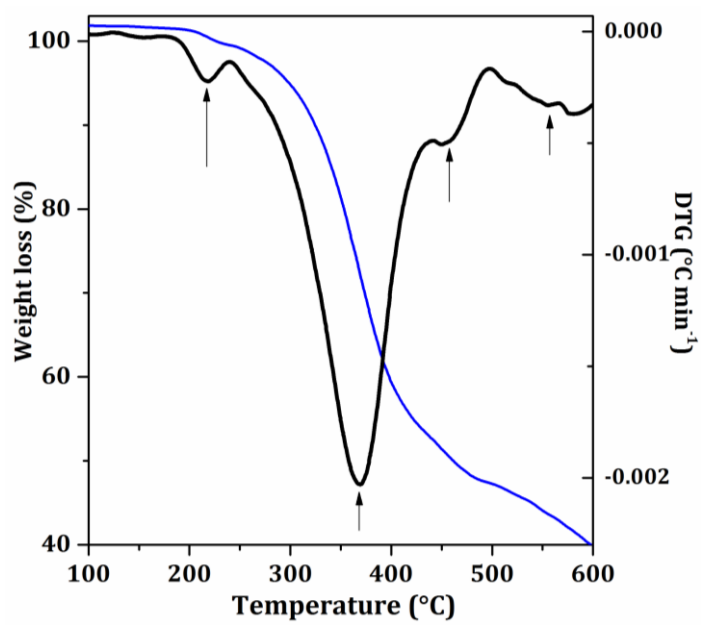




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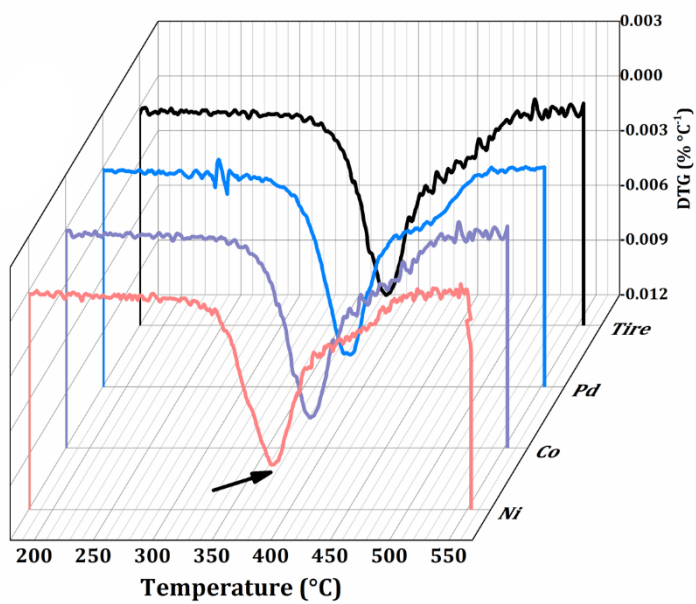


Figure 5.

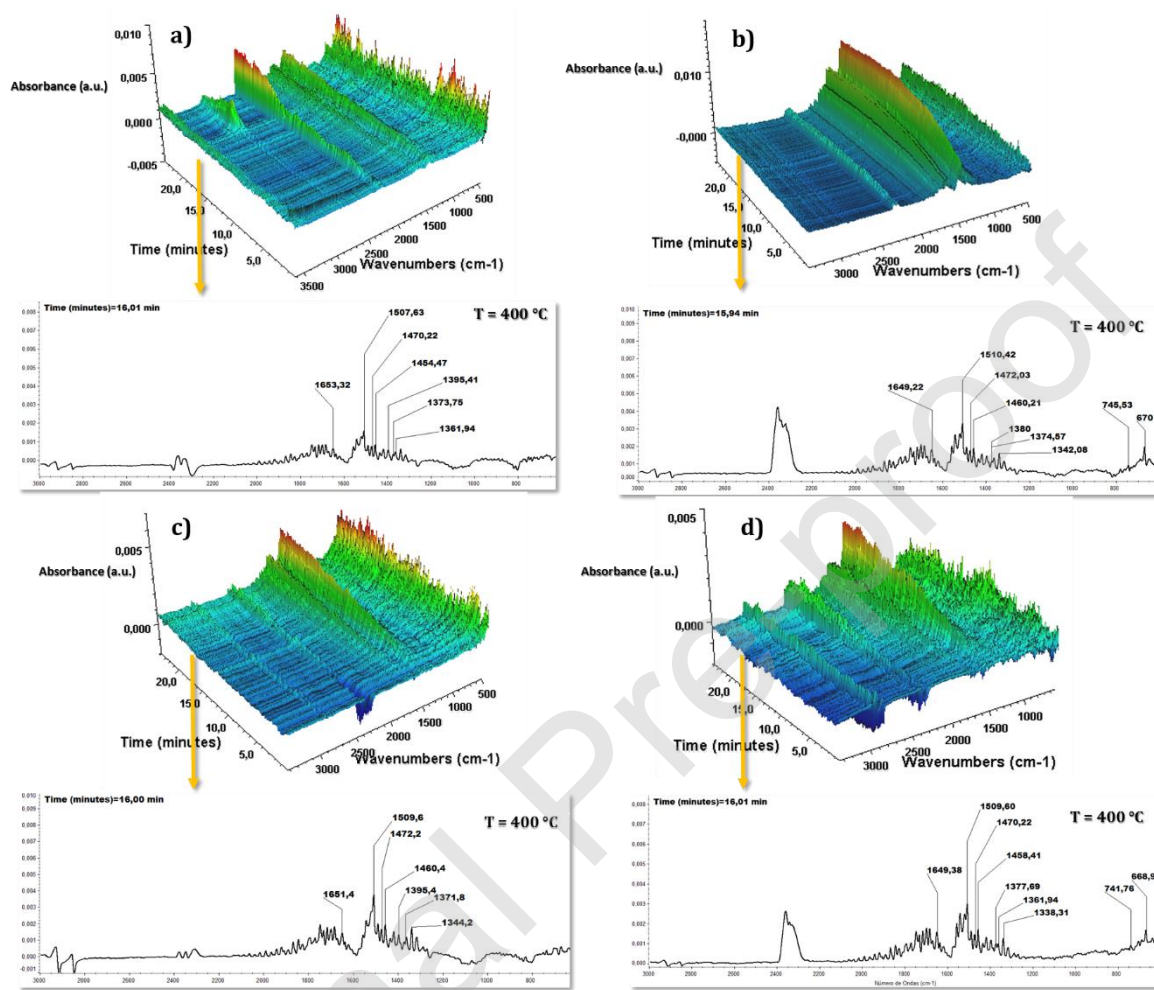


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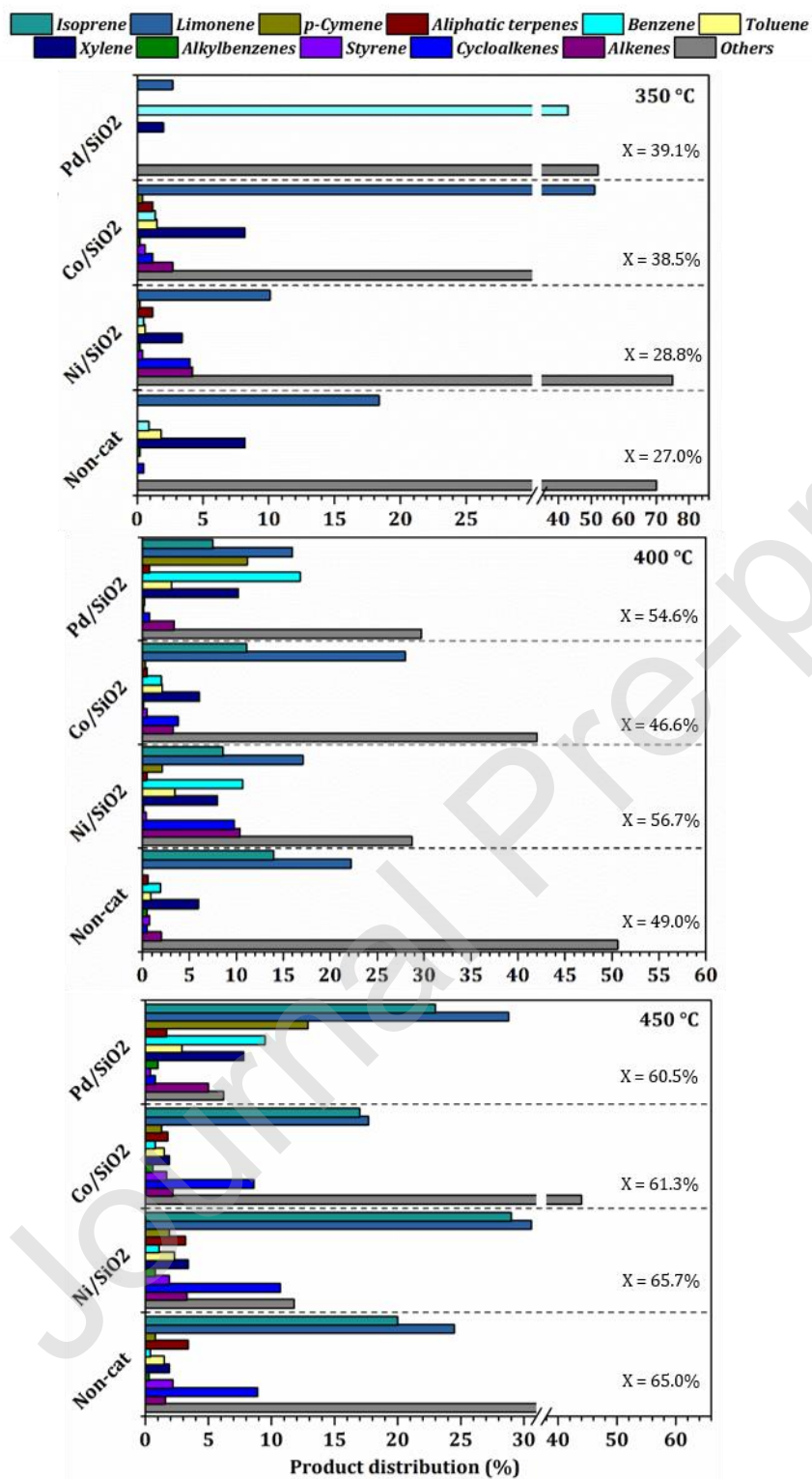


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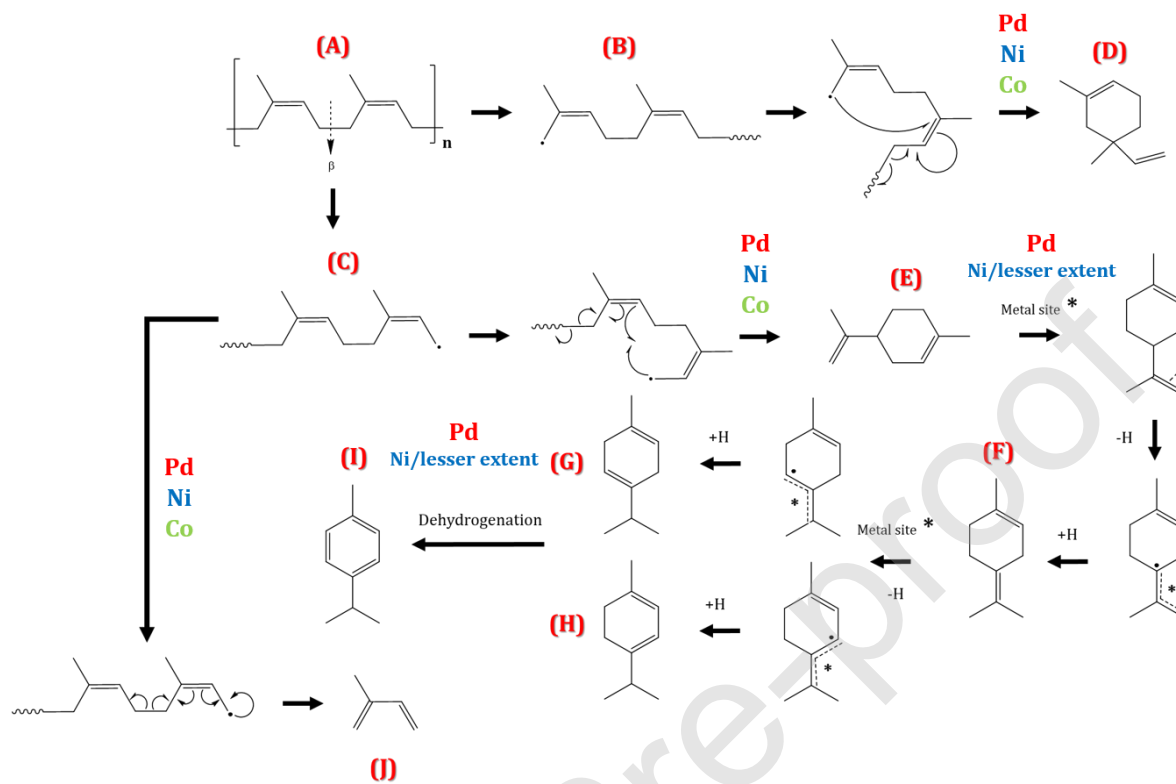
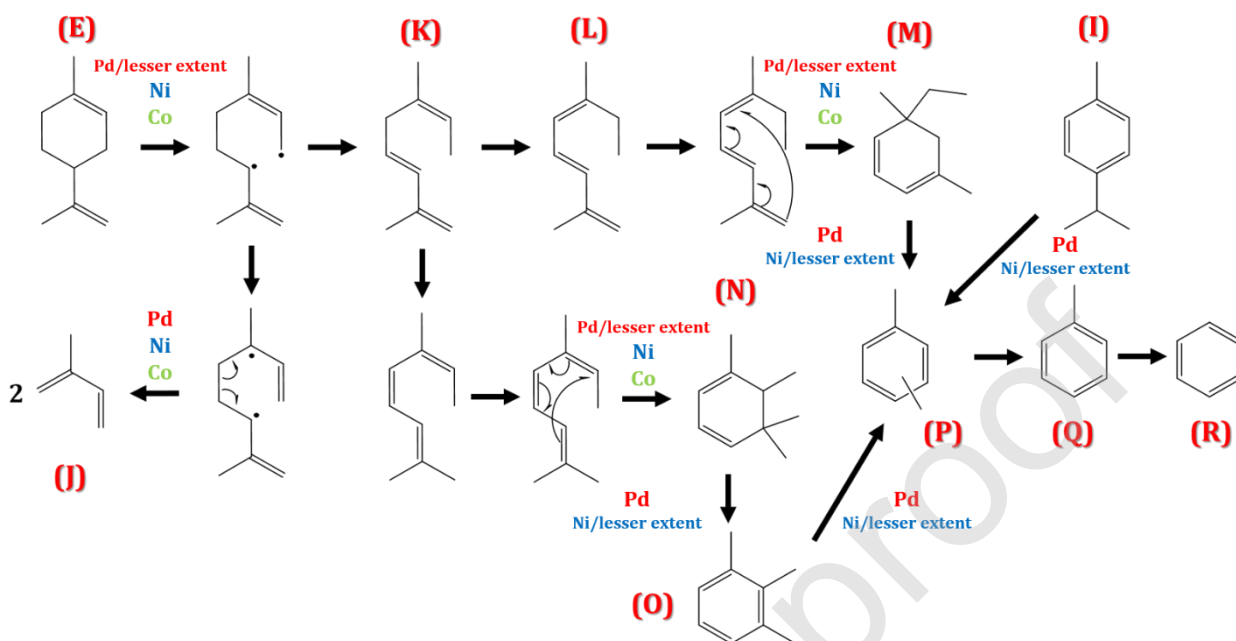


Figure 8.



Tables

**Table 1.** Textural properties of M/SiO<sub>2</sub> catalysts (M: Ni, Co, and Pd).

Catalysts	wt. %	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	V <sub>pore</sub> (cm <sup>3</sup> g <sup>-1</sup> )	S <sub>M</sub> (m <sup>2</sup> g <sup>-1</sup> ) <sup>a</sup>	dp (nm) <sup>b</sup>
SiO <sub>2</sub>		228.4	0.27		
Ni/SiO <sub>2</sub>	5	204.5	0.24	257	9.14 ± 2.16
Co/SiO <sub>2</sub>	5	217.2	0.24	200	5.93 ± 3.40
Pd/SiO <sub>2</sub>	2	210.5	0.24	248	10.8 ± 3.20


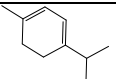

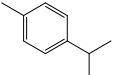

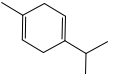



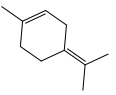

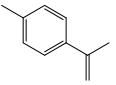
<sup>a</sup>Metal specific surface area obtained from H<sub>2</sub> chemisorption.<sup>b</sup>Average particle size obtained from transmission electron microscopy (TEM) images.


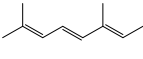

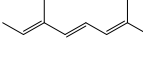
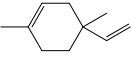




**Table 2.** Proximate and elemental analysis composition and thermogravimetric study of waste tires.

Proximate Analysis (wt.%)	Elemental Analysis					TGA	
		(wt.%)	(mg/kg)			Temperature (°C)	Weight loss (%)
Moisture content	1.2	C	79.54	Al	1352	100–300	4.83
Volatile matter	58.76	H	7.33	Ca	1152	300–470	50.3
Fixed carbon	30.15	N	0.47	Fe	1117	470–600	5.88
Ash	9.89	S	1.48	K	509		
		O <sup>a</sup>	2.77	Na	508		

<sup>a</sup> Oxygen is calculated by the difference from C, H, N, S, and Ash

**Table 3.** Products resulting from catalytic waste tire pyrolysis on SiO<sub>2</sub>-supported Ni, Co and Pd catalysts determined by pyrolysis experiments coupled to gas chromatography/mass spectrometry (Py–GC/MS) at 450 °C.

Compounds		tr (min)	Compounds		tr (min)
Isoprene		2.1	$\alpha$ -Terpinene		16.7
Cyclohexene		3.2	p-Cymene		17.1
Benzene		3.4	$\gamma$ -Terpinene		17.5
1,3-Cycloheptadiene		4.9	1,2,3-Trimethyl benzene		17.8
Toluene		5.9	Terpinolene		18.2
4-vinyl cyclohexene		7.7	p-Cymenene		19.1

p-Xylene		11.5	3,7-Dimethyl 2,4,6-octatriene		19.5
Styrene		13.3	2,6-Dimethyl 2,4,6-octatriene		19.9
4-Ethenyl-1,4-dimethylcyclohexene		14.0	1,3-Benzothiazole		23.2
1,5,5,6-tetramethyl 1,3-cyclohexadiene		15.0	2,4-Dimethylquinoline		26.8
Limonene		16.5	Others		

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We certify that the following article

**Tuning the product distribution during the catalytic pyrolysis of waste tires: Effect of metal nature and reaction temperature**

**Paula Osorio Vargas**

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