Data in Brief

Dataset from analytical pyrolysis assays for converting waste tires into valuable chemicals in the presence of noble-metal catalysts

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A B S T R A C T

About 25.7 million tons of waste tires (WT) are discarded each year worldwide causing important environmental, and health problems. This waste is difficult to manage and dispose due to its huge rate of generation and its extremely slow biodegradation. Therefore, many efforts are being made to valorise WTs into a series of marketable products under a circular economy framework. In the attempt to convert WT into higher-value products, thermochemical decomposition by pyrolysis has emerged as a promising process [1]. The pyrolysis is a thermochemical transformation (under an oxygen-depleted atmosphere) of the tire’s polymeric constituents: natural rubber (NR), styrene-butadiene rubber (SBR), and butadiene rubber (BR) into three major fractions. These fractions are a gas (10–35%, TPG) which is usually used as a heat source (50 MJ kg⁻¹), a solid consisting mainly of recovered carbon black (12–45%, rCB), and a liquid fraction (35–65%, TPO) containing a complex mixture of organic compounds. Among the high-value compounds that can be found

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in the TPO are D,L-limonene, isoprene, benzene, toluene, mixed-xylene, ethylbenzene, styrene, p-cymene, and some polycyclic aromatic hydrocarbons. This mixture is commonly used as a diesel substitute and owing to its complex composition it rarely is seen as a source for more valuable products. To overcome such a complexity, and selectively produce specific chemical identities, different types of catalysts have been used [2,3].

Herein, we provide a dataset from a systematic study about catalytic pyrolysis of WT for selectively producing benzene, toluene, and xylenes (BTX) and p-cymene on noble metals (Pd, Pt, Au) supported on titanate nanotubes (NT-Ti). The comprehensive analysis of this data was recently published, thus, the analytical techniques, experimental conditions and dataset are given in the present paper as a complement to that publication [1]. The reaction was evaluated in an analytical pyrolysis unit consisting in a micropyrolyzer coupled to a mass spectrometer (Py-GC/MS) operating at temperatures between 400 and 450 °C in a fast pyrolysis regime (12 s). The effectivity of catalysts was measured in terms of selectivity to monoaromatics as BTX and p-cymene, under non-catalytic and for catalytic pyrolysis conditions. Moreover, the reaction was conducted on individual rubbers (Polyisoprene, Polybutadiene, and Styrene-Butadiene) and D,L-limonene, to get deep insights into the transformation behaviour and reaction pathways. Therefore, the reader will find a data-in-brief paper containing some characterizations of the WTs used for the investigation, along with a complete dataset of Py-GC/MS results. Finally, the original files for the interpretation of the MS results are also provided, so that the reader can easily use this information to further expand the study to their own interest (industrial or scientific).

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### Specifications Table

| Subject                  | Chemistry: Chemical Engineering, Catalysis |
|--------------------------|-------------------------------------------|
| Specific subject area    | Conversion of wastes into valuable chemicals via catalytic fast pyrolysis. |
| Type of data             | Tables and Figures                        |
| How the data were acquired| The data was measured in a micro-pyrolysis reactor (CD55200, CDS Analytical Co Ltd.) coupled to a gas chromatograph (Clarus 690, Perkin Emer) equipped with a quadrupole mass detector (SQ8, Perkin Emer). The waste tires were characterized in an elemental analyser (CHNS 628, Leco) and thermogravimetric analysis (Netzsch, model STA 409 PC). Compound identification was done by comparison with the National Institute of Standards and Technology database (NIST, v2016) with the software TurboMass™ v5.4. |
| Data format              | Raw (TurboMass files and *.xls files). |
| Description of data collection | Filtered (Tables with compounds ids, retention times, etc.). |
| Data source location     | Institution: Universidad del Bio-Bio City/Town/Region: Concepción/Concepción/Biobío Country: Chile |

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Value of the Data

- Waste tire pyrolysis is a sustainable solution to the problems associated to WTs management and valorisation. Therefore, analytical data is of paramount importance to defining potential marketable products.
- Industrials and scientific groups devoted to the understanding and analysis of pyrolysis processes can benefit from this data, which includes regular and catalytic pyrolysis experiments of WTs and its constituent polymers.
- The data presented here can be used for expanding analysis on product distribution, kinetics and as a basis for scaling-up the process.

1. Data Description

Waste tire pyrolysis is attracting the attention of industrials and the scientific community worldwide, hence the availability of experimental data is mandatory for defining production strategies in a circular economy framework. Here we provide raw data (linked) and filtered results for analytical pyrolysis experiments.

1.1. Material characterization

This paper presents the composition, and the thermal characterization parameters -gathered from thermogravimetric analysis- for waste tires coming from light vehicles (Table 1 and Fig. 1). Moreover, the area-related composition of pyrolysis vapours produced from natural rubber (CAS N° 104389-31-3), butadiene rubber (CAS N° 9003-17-2) and styrene-butadiene rubber (CAS N° 9003-55-8) is also provided for two temperatures (400 °C and 450 °C) in Tables 2 and 3. Deconvolution of DTG curves allows estimating the polymeric composition of the tires which is fundamental to understand reaction pathways, thus the TGA data and characteristic DTG temperatures are also provided [5].

1.2. Catalytic pyrolysis assays

The Tables 4 to 5 presents the results of catalytic pyrolysis experiments for waste tires on Pd/NT-Ti, Pt/NT-Ti and Au/NT-Ti at 400 °C and 450 °C, respectively. Each table indicate the retention times, chromatographic area percentage and the assignation of compounds ids according to the comparison of the ionization patterns with the NIST database.

Supplementary datafiles: The Supplementary information to this manuscript includes raw data in (.xls) format along with the original TruboMass v5.6 data files, both can be freely used by expert to re-process the results. In addition, TGA and DTG data are also included, which could
Table 1
Elemental and proximate composition of waste tires.

| Proximate Analysis (wt.%) | Ultimate Analysis (wt.%) | Alkali Metals (mg/kg) |
|---------------------------|-------------------------|----------------------|
| (a.r.)                    | (d.b.)                  |                      |
| Moisture content (MC)     | 1.2                     | C                    | 79.54 ± 0.17 | Al | 1352 |
| Volatile matter (VM)      | 58.76                   | H                    | 7.33 ± 0.03 | Ca | 1152 |
| Fixed carbon (FC)         | 30.15                   | N                    | 0.47 ± 0.03 | Fe | 1117 |
| Ash                       | 9.89                    | S                    | 1.48± 0.06 | K  | 509  |
| HHV* (MJ/kg) d.b.         | 36.55                   | O**                  | 1.29        | Na | 508  |

Natural Rubber (BR) 22.9 T_peak (°C) 380
Butadiene Rubber (BR) 43.4 T_initial (°C) 327
Styrene-Butadiene (SBR) 33.7 T1/T2 (°C) 456/506

* HHV (MJ/kg) = 35.2C +116.2H + 6.3N + 10.5S - 11.1O, where C, H, O, S, N are fractional elemental composition of carbon, hydrogen and oxygen, respectively [6].

** Oxygen is calculated by difference from O = 100 - C% - N% - H% - S% - ASH%.

*** Metal content was measured by inductively coupled plasma optical emission spectrometry (ICP-OES) using a PerkinElmer Optima 7000 DV ICP-OES series instrument.

allow performing further kinetic analyses or other valuable interpretation of the results. This is shared as a MendeleyData repository to facilitate the access and sharing of the information.

2. Experimental Design, Materials and Methods

Sample preparation: The waste tires were provided by a local enterprise as polymeric granules (free of steel). Then, the WT granules were crushed, and sieved in sizes between 180 and 300 μm (Gilson ASTM E11), before being dried at 100 °C, during 12 h in static air (LabTech, LDO-150F). Dry samples were stored until use in hermetic plastic bags.

Waste tire characterization: Elemental composition and proximate analysis of waste tire were carried out in an elemental analyzer (Leco CHNS 628), and a muffle (Thermo Scientific F6020C) following the ASTM D3176 and D3172 standards, respectively. The inorganic elements were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) using a PerkinElmer Optima 7000 DV series instrument and the UOP389-15. Thermogravimetric analysis (TGA) was carried out for 25 mg of WTs between 20 and 650 °C at 10 °C min⁻¹ heating.

Fig. 1. TGA/DTG characterization of waste tires with characteristic peaks identification (T_peak, T_initial and T_final).
Table 2
Py-GC/MS results for individual polymers and waste tires under regular pyrolysis conditions (non-catalytic). Conditions $T = 400 \, ^\circ\text{C}$, time = 12 s, mass = 1 mg.

| Peak N° | time (min) | NR   | BR   | SBR  | WT   | IUPAC Compound id                      |
|--------|------------|------|------|------|------|----------------------------------------|
| 1      | 1.718      | 0.0% | 4.71%| 4.93%| 0.0% | 1,3-Butadiene                          |
| 2      | 1.922      | 19.30%| 1.28%| 1.60%| 21.82%| Isoprene                                |
| 3      | 2.486      | 0.05%| 0.64%| 0.69%| 0.03%| cyclohexene                             |
| 4      | 3.136      | 0.07%| 1.20%| 1.83%| 0.15%| Benzene                                 |
| 5      | 4.05       | 0.49%| 0.33%| 0.10%| 0.55%| 3,5-Dimethylcyclopentene               |
| 6      | 4.789      | 0.92%| 0.30%| 0.09%| 0.57%| 1-Methyl-1,4-cyclohexadiene            |
| 7      | 5.378      | 0.35%| 0.79%| 1.05%| 0.61%| Toluene                                 |
| 8      | 6.961      | 0.0% | 69.47%| 59.99%| 0.52%| 4-Ethenyl-cyclohexene                  |
| 9      | 7.6        | 0.02%| 0.58%| 0.47%| 0.09%| 2,6-Dimethyl-1,6-heptadiene            |
| 10     | 8.4        | 0.15%| 0.01%| 0.01%| 0.08%| (E,E,E)-2,4,6-Octatriene               |
| 11     | 10.2       | 0.08%| 0.01%| 0.06%| 0.01%| Ethylbenzene                            |
| 12     | 10.726     | 0.55%| 0.40%| 0.41%| 2.77%| Xylenes                                 |
| 13     | 12.2       | 0.0% | 0.29%| 0.07%| 0.00%| 1,5,5,6-tetramethyl-1,3-cyclohexadiene |
| 14     | 12.912     | 0.39%| 1.06%| 0.42%| 0.09%| Styrene                                 |
| 15     | 13.009     | 0.37%| 0.01%| 0.73%| 0.02%| 2,5,5-trimethyl-1,6-Heptadiene         |
| 16     | 13.414     | 5.03%| 0.69%| 0.01%| 1.99%| 4-ethyl-1,4-dimethyl-cyclohexene       |
| 17     | 14.024     | 0.23%| 0.01%| 0.31%| 1.08%| 2,5,6-trimethyl-1,3,6-Heptatriene      |
| 18     | 14.497     | 0.45%| 0.29%| 0.03%| 0.13%| 2,6-dimethyl-2,6-Octadiene             |
| 19     | 14.747     | 0.76%| 0.09%| 0.08%| 0.35%| Benzenes, 1-ethyl-3-methyl-             |
| 20     | 15.0       | 0.13%| 0.01%| 0.14%| 0.16%| 5-ethyl-1,5-dimethyl-1,3-cyclohexadiene|
| 21     | 15.192     | 0.32%| 0.14%| 0.04%| 0.10%| 3,7-dimethyl-2,4,6-octatriene          |
| 22     | 15.4       | 0.24%| 0.0% | 0.00%| 0.00%| 2,6-dimethyl-1,6-octadiene             |
| 23     | 15.501     | 0.97%| 0.0% | 0.16%| 0.43%| 2,6-Dimethyl13,5,7octatetra            |
| 24     | 15.6       | 0.0% | 0.11%| 0.00%| 0.21%| 1,6-Dimethyl-hepta-1,3,5-triene        |
| 25     | 15.8       | 0.06%| 0.04%| 2.81%| 0.74%| 3,7-dimethyl-1,3,6-octatriene          |

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| Peak No. | time (min) | NR  | BR  | SBR | WT  | IUPAC Compound id                                      |
|---------|------------|-----|-----|-----|-----|------------------------------------------------------|
| 26      | 16.042     | 55.50% | 1.48% | 0.06% | 50.37% | Limonene                                             |
| 27      | 16.323     | 2.21%  | 0.07% | 0.01% | 0.82%  | 1,3,6-Heptatriene, 2,5,6-trimethyl-                 |
| 28      | 16.53      | 0.27%  | 0.06% | 0.00% | 0.40%  | p-Cymene                                             |
| 29      | 17.616     | 0.30%  | 0.07% | 0.12% | 0.29%  | γ-Terpinene                                          |
| 30      | 17.8       | 0.12%  | 0.10% | 3.31% | 0.30%  | Toluene, p-ethyl-                                   |
| 31      | 17.9       | 0.06%  | 4.01% | 0.76% | 0.05%  | α-Terpinene                                          |
| 32      | 18.515     | 0.38%  | 0.20% | 0.00% | 0.01%  | 1,3,6-Heptatriene, 2,5,6-trimethyl-                 |
| 33      | 19.5       | 0.02%  | 0.83% | 0.19% | 0.05%  | Dodecane                                             |
| 34      | 20.911     | 1.06%  | 0.36% | 5.34% | 0.04%  | Dodecane, 2,6,11-trimethyl-                          |
| 35      | 21.1       | 0.02%  | 5.80% | 2.85% | 0.01%  | Dodecane, 2,6,10-trimethyl-                          |
| 36      | 21.308     | 0.02%  | 0.21% | 0.56% | 0.06%  | Benzene, 1,4-bis(11-dimethyl)                        |
| 37      | 22.507     | 0.40%  | 0.50% | 0.35% | 2.03%  | Dodecane, 2,6,11-trimethyl-                          |
| 38      | 22.615     | 0.37%  | 0.15% | 0.06% | 0.23%  | 1,5-Cycloundecadiene, 8,8-dimethyl-9-methylene-     |
| 39      | 22.694     | 0.61%  | 0.0%  | 0.06% | 0.32%  | 1,5-Cycloundecadiene, 9-(1-methyl-3-hexylidene)-    |
| 40      | 23.074     | 0.31%  | 0.07% | 0.01% | 0.06%  | Tetradecane                                          |
| 41      | 23.443     | 0.71%  | 0.01% | 0.11% | 0.28%  | 1,5-Cyclodecadiene, 15-dimethyl-8-(1-methylethylidene)- |
| 42      | 23.687     | 1.22%  | 0.10% | 0.04% | 0.52%  | 1-Cycloheptene, 1,4-dimethyl-3-(2-methyl-1-propene-1-yl)-4-vinyl- |
| 43      | 23.84      | 1.71%  | 0.01% | 0.02% | 0.46%  | Bicyclo[5.2.0]nonane, 4-methylene-2,8,8-trimethyl-2-vinyl- |
| 44      | 24.015     | 0.45%  | 0.01% | 0.63% | 0.26%  | Cyclohexane, 1-ethenyl-1-methyl-2,4-bis-1-methylethyl- |
| 45      | 24.183     | 1.26%  | 0.04% | 0.33% | 0.81%  | Cyclohexane, 1-ethenyl-1-methyl-2-(1-methylethyl)-4-(1-methylethylidene)- |
| 46      | 26.2       | 0.12%  | 0.08% | 1.05% | 0.23%  | Hexadecane                                          |
| 47      | 26.346     | 0.59%  | 0.31% | 0.38% | 5.74%  | Quinoline, 1,2-dihydro-2,2,4-trimethyl-              |
| 48      | 28.91      | 0.04%  | 0.32% | 0.30% | 0.25%  | Octadecane                                          |
| 49      | 30.245     | 0.19%  | 0.25% | 0.06% | 1.02%  | β-D-Glucopyranose, 1,6-anhydro-                     |
| 50      | 30.534     | 0.11%  | 0.27% | 0.15% | 0.22%  | (E,E,E)-3,7,11,15-Tetramethylhexadeca-1,3,6,10,14-pentaene |
| 51      | 30.645     | 0.13%  | 0.48% | 1.08% | 0.29%  | 1,5,5-Trimethyl-6-(3-methyl-buta-1,3-dienyl)-cyclohexene |
| 52      | 31.008     | 0.88%  | 1.64% | 0.53% | 1.41%  | Cyclohexane, 1-ethenyl-1-methyl-2-(1-methylethyl)-4-(1-methylethylidene)- |
Table 3
Py-GC/MS results for individual polymers and waste tires under regular pyrolysis conditions (non-catalytic). Conditions T = 450 °C, time = 12 s, mass = 1 mg.

| Peak N° | time (min) | NR    | BR    | SBR   | WT    | IUPAC Compound id                        |
|---------|------------|-------|-------|-------|-------|------------------------------------------|
| 1       | 1.718      | 0.00% | 5.19% | 4.00% | 0.00% | 1,3-Butadiene                            |
| 2       | 1.922      | 19.39%| 1.41% | 1.30% | 22.56%| Isoprene                                 |
| 3       | 2.486      | 0.05% | 0.71% | 0.56% | 0.01% | cyclohexene                              |
| 4       | 3.136      | 0.07% | 0.00% | 1.49% | 0.19% | Benzene                                  |
| 5       | 4.05       | 0.49% | 0.36% | 0.04% | 0.68% | 3,5-Dimethylcyclopentene                |
| 6       | 4.789      | 0.32% | 0.33% | 0.07% | 0.62% | 1-Methyl-1,4-cyclohexadiene             |
| 7       | 5.378      | 0.35% | 0.87% | 0.85% | 0.72% | Toluene                                  |
| 8       | 6.961      | 0.01% | 76.60%| 48.74%| 0.13% | 4-Ethenyl- cyclohexene                  |
| 9       | 7.6        | 0.02% | 0.64% | 0.38% | 0.13% | 2,6-Dimethyl-1,6-heptadiene             |
| 10      | 8.4        | 0.15% | 0.01% | 0.01% | 0.17% | (E,E,E)-2,4,6-Octatriene                |
| 11      | 10.2       | 0.08% | 0.53% | 0.08% | 0.14% | Ethylbenzene                             |
| 12      | 10.726     | 0.55% | 0.44% | 0.34% | 2.12% | Xylenes                                  |
| 13      | 12.2       | 0.00% | 0.32% | 0.05% | 0.00% | 1,5,6-tetramethyl-1,3-cyclohexadiene     |
| 14      | 12.912     | 0.39% | 1.17% | 17.51%| 0.30% | Styrene                                  |
| 15      | 13.009     | 0.37% | 0.01% | 0.34% | 0.25% | 2,5,5-trimethyl-1,6-Heptadiene          |
| 16      | 13.414     | 5.05% | 0.77% | 0.59% | 3.69% | 4-ethyl-1,4-dimethyl- cyclohexene        |
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| 19      | 14.747     | 0.77% | 0.01% | 0.07% | 0.71% | Benzene, 1-ethyl-3-methyl-               |
| 20      | 15.0       | 0.53% | 0.01% | 0.03% | 0.45% | 5-ethyl-1,5-dimethyl-1,3-cyclohexadiene  |
| 21      | 15.192     | 0.32% | 0.16% | 0.11% | 0.34% | 3,7-dimethyl 2,4,6-octatriene            |
| 22      | 15.4       | 0.24% | 0.01% | 0.03% | 0.00% | 2,6-dimethyl-1,6-octadiene              |
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| 26      | 16.042     | 55.76%| 1.63% | 2.28% | 47.79%| Limonene                                 |
| 27      | 16.323     | 2.23% | 0.08% | 0.04% | 1.48% | 1,3,6-Heptatriene, 2,5,6-trimethyl-      |

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| 29      | 17.616     | 0.30%| 0.08%| 0.15%| 0.51%| γ-Terpinene                                                |
| 30      | 17.8       | 0.12%| 0.11%| 0.10%| 0.29%| Toluene, p-ethyl-                                          |
| 31      | 17.9       | 0.06%| 0.00%| 2.69%| 0.08%| α-Terpinene                                                |
| 32      | 18.515     | 0.57%| 0.97%| 2.56%| 1.03%| p-Cymenene                                                 |
| 33      | 19.5       | 0.02%| 0.91%| 4.56%| 0.02%| Dodecane                                                   |
| 34      | 20.911     | 1.07%| 0.53%| 0.15%| 0.03%| Dodecane, 2,6,11-trimethyl-                                |
| 35      | 21.1       | 0.12%| 0.50%| 4.34%| 0.24%| Dodecane, 2,6,10-trimethyl-                                |
| 36      | 21.308     | 0.01%| 0.23%| 2.31%| 0.08%| Benzene, 1,4-bis(1,1-dimethylethyl)-                        |
| 37      | 22.507     | 0.40%| 0.55%| 0.45%| 1.41%| Benzothiazole                                              |
| 38      | 22.615     | 0.37%| 0.17%| 0.28%| 0.24%| 1.5-Cycloundecadiene, 8,8-dimethyl-9-methylene-             |
| 39      | 22.694     | 0.61%| 0.00%| 0.05%| 0.34%| 1.5-Cycloundecadiene, 9-(1-methylethylidene)-              |
| 40      | 23.074     | 0.06%| 0.08%| 0.04%| 0.24%| Tetradecane                                                |
| 41      | 23.443     | 0.72%| 0.01%| 0.01%| 0.49%| 1.5-Cyclodecadiene, 1,5-dimethyl-8-(1-methylethylidene)-., (E,E)- |
| 42      | 23.687     | 1.23%| 0.05%| 0.09%| 0.83%| 1-Cycloheptene, 1,4-dimethyl-3-(2-methyl-1-propene-1-yl)-4-vinyl- |
| 43      | 23.84      | 0.72%| 0.02%| 0.14%| 0.67%| Bicyclo[5.2.0]nonane, 4-methylene-2,8,8-trimethyl-2-vinyl- |
| 44      | 24.015     | 0.45%| 0.01%| 0.01%| 0.48%| Cyclohexane, 1-ethyl-1-methyl-2,4-bis(1-methylethenyl)-., [15-(1α,2β,4β)]- |
| 45      | 24.183     | 1.26%| 0.54%| 0.07%| 0.91%| Cyclohexane, 1-ethyl-1-methyl-2-(1-methylethenyl)-4-(1-methylethylidene)- |
| 46      | 26.2       | 0.12%| 0.09%| 0.27%| 0.30%| 1-Cyclohexene, 1,2-dihydro-2,2,4-trimethyl-2,6-dimethyldien- |
| 47      | 26.346     | 0.70%| 0.36%| 0.85%| 3.48%| Quinoline, 1,2-dihydro-2,2,4-trimethyl-2,6-dimethyldien-   |
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Table 4
Py-GC/MS results for waste tires under catalytic pyrolysis on Pd/NT-Ti, Pt/NT-Ti and Au/NT-Ti. Conditions $T = 400 \, ^{\circ}C$, time = 12 s, mass of WT = 1 mg. Catalyst-to-WT ratio = 4.

| Peak N° | time (min) | Pd/NT-Ti | Pt/NT-Ti | Au/NT-Ti | IUPAC Compound id |
|---------|------------|----------|----------|----------|------------------|
| 1       | 1.8        | 0.00%    | 4.44%    | 4.49%    | Butadiene        |
| 2       | 2.1        | 13.52%   | 16.17%   | 16.34%   | Isoprene         |
| 3       | 2.97       | 0.71%    | 1.04%    | 1.05%    | Cyclohexene      |
| 4       | 3.14       | 6.96%    | 0.70%    | 0.71%    | Benzene          |
| 5       | 4.05       | 0.25%    | 0.45%    | 0.45%    | 3,5-Dimethylcyclopentene |
| 6       | 4.79       | 0.26%    | 0.46%    | 0.47%    | 1-Methyl-1,4-cyclohexadiene |
| 7       | 5.38       | 9.99%    | 7.35%    | 7.43%    | Toluene          |
| 8       | 6.98       | 0.05%    | 0.34%    | 0.35%    | 4-Ethenyl- cyclohexene |
| 9       | 7.6        | 0.05%    | 0.09%    | 0.09%    | 2,6-Dimethyl-1,6-heptadiene |
| 10      | 8.4        | 0.01%    | 0.01%    | 0.01%    | (E,E,E)-2,4,6-Octatriene |
| 11      | 10.2       | 0.30%    | 0.01%    | 0.01%    | Ethylbenzene     |
| 12      | 10.7       | 3.61%    | 3.22%    | 3.26%    | Xylenes          |
| 13      | 12.2       | 0.00%    | 0.01%    | 0.00%    | 1,5,5,6-tetramethyl-1,3-cyclohexadiene |
| 14      | 12.9       | 0.14%    | 0.03%    | 0.02%    | Styrene          |
| 15      | 13.0       | 0.04%    | 0.01%    | 0.01%    | 2,5,5-trimethyl-1,6-Heptadiene |
| 16      | 13.4       | 0.09%    | 0.76%    | 0.76%    | 4-ethenyl-1,4-dimethyl- cyclohexene |
| 17      | 14.0       | 0.96%    | 0.01%    | 0.01%    | 2,5,6-trimethyl-1,3,6-Heptatriene |
| 18      | 14.5       | 0.13%    | 0.00%    | 0.00%    | 2,6-dimethyl-2,6-Octadiene |
| 19      | 15.0       | 0.13%    | 0.16%    | 0.03%    | 5-ethyl-1,5-dimethyl-1,3-cyclohexadiene |
| 20      | 15.2       | 0.04%    | 0.32%    | 0.05%    | 3,7-dimethyl 2,4,6-octatriene |
| 21      | 15.4       | 0.12%    | 0.04%    | 0.21%    | 2,6-dimethyl-1,6-octadiene |
| 22      | 15.5       | 0.04%    | 0.21%    | 0.10%    | 2,6-Dimethyl1,3,5,7octatetriene |
| 23      | 15.6       | 0.06%    | 0.10%    | 0.01%    | 1,6-Dimethyl-hepta-1,3,5-triene |
| 24      | 15.8       | 0.26%    | 0.39%    | 0.40%    | 3,7-dimethyl-1,3,6-octatriene |
| 25      | 16.0       | 21.32%   | 26.15%   | 26.43%   | DL-Limonene      |
| 26      | 16.5       | 13.12%   | 11.05%   | 11.17%   | p-Cymene         |
| 27      | 17.6       | 0.13%    | 1.33%    | 1.34%    | y-Terpinene      |

(continued on next page)
| Peak N° | time (min) | Pd/NT-Ti | Pt/NT-Ti | Au/NT-Ti | IUPAC Compound id |
|--------|------------|----------|----------|----------|------------------|
| 28     | 17.8       | 0.07%    | 0.13%    | 0.02%    | Toluene, p-ethynyl- |
| 29     | 17.9       | 0.00%    | 0.04%    | 0.04%    | α-Terpine \(\alpha\)-Terpinene |
| 30     | 18.5       | 1.51%    | 1.84%    | 1.86%    | p-Cymene \(\beta\)-Cymene |
| 31     | 19.5       | 0.00%    | 0.04%    | 0.43%    | Dodecan \(\delta\)-Dodecan |
| 32     | 20.9       | 1.38%    | 0.41%    | 0.42%    | Dodecane, 2,6,11-trimethyl- |
| 33     | 21.1       | 0.04%    | 0.12%    | 0.01%    | Dodecane, 2,6,10-trimethyl- |
| 34     | 21.3       | 0.06%    | 0.63%    | 0.64%    | Benzene, 1,4-bis(1,1-dimethylethyl)- |
| 35     | 22.5       | 6.25%    | 9.41%    | 9.51%    | Benzothiazole |
| 36     | 22.6       | 0.08%    | 0.15%    | 0.15%    | 1,5-Cycloundecadiene, 8,8-dimethyl-9-methylene- |
| 37     | 22.7       | 0.04%    | 0.12%    | 0.02%    | 1,5-Cycloundecadiene, 9-(1-methylethylidene)- |
| 38     | 23.1       | 0.08%    | 0.70%    | 0.06%    | Tetradecane |
| 39     | 23.4       | 0.04%    | 0.10%    | 0.10%    | 1,5-Cyclodecadiene, 1,5-dimethyl-8-(1-methylethylidene)-, (E,E)- |
| 40     | 23.7       | 0.02%    | 0.01%    | 0.01%    | 1-Cycloheptene, 1,4-dimethyl-3-(2-methyl-1-propene-1-yl)-4-vinyl- |
| 41     | 23.8       | 0.31%    | 0.29%    | 0.30%    | Bicyclo[5.2.0]nonane, 4-methylene-2,8,8-trimethyl-2-vinyl- |
| 42     | 24.0       | 0.25%    | 0.18%    | 0.18%    | Cyclohexane, 1-ethenyl-1-methyl-2,4-bis(1-methylene)enyl)-, [1S-(1\(\alpha\),2\(\beta\),4\(\beta\)]- |
| 43     | 24.2       | 0.49%    | 0.33%    | 0.33%    | Cyclohexane, 1-ethenyl-1-methyl-2-(1-methylene)enyl)-4-(1-methylethylidene)- |
| 44     | 26.2       | 0.13%    | 0.12%    | 0.12%    | Hexadecane |
| 45     | 26.346     | 7.31%    | 9.57%    | 9.67%    | Quinoline, 1,2-dihydro-2,2,4-trimethyl- |
| 46     | 28.9       | 0.67%    | 0.34%    | 0.35%    | Octadecane |
| 47     | 30.245     | 2.40%    | 0.18%    | 0.18%    | β-D-Glucopyranose, 1,6-anhydro- |
| 48     | 30.5       | 2.28%    | 0.06%    | 0.06%    | (E,E,E)-3,7,11,15-Tetramethylhexadeca-1,3,6,10,14-pentaene |
| 49     | 30.7       | 0.36%    | 0.03%    | 0.03%    | 1,5,5-Trimethyl-6-(3-methyl-buta-1,3-dienyl)-cyclohexene |
| 50     | 31.0       | 3.94%    | 0.34%    | 0.34%    | Cyclohexane, 1-ethenyl-1-methyl-2-(1-methylene)enyl)-4-(1-methylethylidene)- |
Table 5
Py-GC/MS results for waste tires under catalytic pyrolysis on Pd/NT-Ti, Pt/NT-Ti and Au/NT-Ti. Conditions: T = 450 °C, time = 12 s, mass of WT = 1 mg. Catalyst-to-WT ratio = 4.

| Peak N° | time (min) | Pd/NT-Ti | Pt/NT-Ti | Au/NT-Ti | IUPAC Compound id |
|---------|------------|----------|----------|----------|-------------------|
| 1       | 1.8        | 0.00%    | 0.00%    | 0.00%    | Butadiene         |
| 2       | 2.1        | 19.87%   | 19.23%   | 21.71%   | Isoprene          |
| 3       | 2.97       | 0.12%    | 0.09%    | 0.47%    | Cyclohexene       |
| 4       | 3.14       | 2.91%    | 1.62%    | 0.66%    | Benzene           |
| 5       | 4.05       | 1.11%    | 1.43%    | 0.86%    | 3,5-Dimethylcyclopentene |
| 6       | 4.79       | 0.48%    | 0.49%    | 0.42%    | 1-Methyl-1,4-cyclohexadiene |
| 7       | 5.38       | 2.25%    | 2.39%    | 3.49%    | Toluene           |
| 8       | 6.98       | 1.01%    | 0.80%    | 0.75%    | 4-Ethenyl- cyclohexene |
| 9       | 7.6        | 0.34%    | 0.37%    | 0.33%    | 2,6-Dimethyl-1,6-heptadiene |
| 10      | 8.4        | 0.00%    | 0.00%    | 0.00%    | 1,3,4,5-tetramethyl-1,3-cyclohexadiene |
| 11      | 10.2       | 1.10%    | 0.49%    | 0.14%    | Ethylbenzene      |
| 12      | 10.7       | 4.34%    | 3.91%    | 2.72%    | Xylenes           |
| 13      | 12.2       | 0.03%    | 0.00%    | 0.00%    | 1,5,5,6-tetramethyl-1,3-cyclohexadiene |
| 14      | 12.9       | 0.26%    | 0.48%    | 0.33%    | Styrene           |
| 15      | 13.0       | 0.55%    | 0.55%    | 0.24%    | 2,5,5-trimethyl-1,6-Heptadiene |
| 16      | 13.4       | 4.98%    | 4.80%    | 2.70%    | 4-ethyl-1,4-dimethyl- cyclohexene |
| 17      | 14.0       | 0.20%    | 0.11%    | 0.01%    | 2,5,6-trimethyl-1,3,6-Heptatriene |
| 18      | 14.5       | 0.69%    | 0.00%    | 0.30%    | 2,6-dimethyl-2,6-Octadiene |
| 19      | 15.0       | 0.78%    | 0.66%    | 0.39%    | 5-ethyl-1,5-dimethyl-1,3-cyclohexadiene |
| 20      | 15.2       | 0.31%    | 0.27%    | 1.09%    | 3,7-dimethyl 2,4,6-octatriene |
| 21      | 15.4       | 0.00%    | 0.00%    | 0.00%    | 2,6-dimethyl-1,6-octadiene |
| 22      | 15.5       | 1.12%    | 0.91%    | 0.79%    | 2,6-Dimethyl1,3,5,7octatetriene |
| 23      | 15.6       | 0.41%    | 0.44%    | 0.22%    | 1,6-Dimethyl-hepta-1,3,5-triene |
| 24      | 15.8       | 0.26%    | 0.99%    | 1.12%    | 3,7-dimethyl-1,3,6-octatriene |
| 25      | 16.0       | 31.40%   | 31.90%   | 29.39%   | DL-Limonene       |
| 26      | 16.5       | 9.84%    | 9.81%    | 13.32%   | p-Cymene          |
| 27      | 17.6       | 0.89%    | 2.03%    | 1.86%    | y-Terpinene       |

(continued on next page)
| Peak N° | time (min) | Pd/NT-Ti | Pt/NT-Ti | Au/NT-Ti | IUPAC Compound id |
|--------|------------|----------|----------|----------|-------------------|
| 28     | 17.8       | 0.04%    | 0.30%    | 0.12%    | Toluene, p-ethynyl-|
| 29     | 17.9       | 0.17%    | 0.23%    | 0.15%    | α-Terpinene       |
| 30     | 18.5       | 4.50%    | 4.49%    | 2.65%    | p-Cymene         |
| 31     | 19.5       | 0.07%    | 0.19%    | 0.03%    | Dodecane         |
| 32     | 20.9       | 0.17%    | 0.24%    | 0.17%    | Dodecane, 2,6,11-trimethyl-|
| 33     | 21.1       | 0.00%    | 0.00%    | 0.00%    | Dodecane, 2,6,10-trimethyl-|
| 34     | 21.3       | 0.18%    | 0.36%    | 0.25%    | Benzene, 1,4-bis(1,1-dimethylethyl)-|
| 35     | 22.5       | 2.33%    | 2.36%    | 4.52%    | Benzothiazole     |
| 36     | 22.6       | 0.12%    | 0.18%    | 0.14%    | 1,5-Cyclodecadiene, 8,8-dimethyl-9-methylene-|
| 37     | 22.7       | 0.07%    | 0.08%    | 0.19%    | 1,5-Cyclodecadiene, 9-(1-methylethylidene)-|
| 38     | 23.1       | 0.19%    | 0.15%    | 0.47%    | Tetradecane       |
| 39     | 23.4       | 0.52%    | 0.48%    | 0.32%    | 1,5-Cyclodecadiene, 1,5-dimethyl-8-(1-methylethylidene)-, (E,E)-|
| 40     | 23.7       | 0.80%    | 0.39%    | 0.47%    | 1-Cycloheptene, 1,4-dimethyl-3-(2-methyl-1-propene-1-yl)-4-vinyl-|
| 41     | 23.8       | 1.11%    | 1.14%    | 0.44%    | Bicyclo[5.2.0]nonane, 4-methylene-2,8,8-trimethyl-2-vinyl-|
| 42     | 24.0       | 0.27%    | 0.27%    | 0.34%    | Cyclohexane, 1-ethenyl-1-methyl-2,4-bis(1-methylethenyl)-, [1S-(1α,2β,4β)]-|
| 43     | 24.2       | 0.87%    | 0.82%    | 0.38%    | Cyclohexane, 1-ethenyl-1-methyl-2-(1-methylethenyl)-4-(1-methylethylidene)-|
| 44     | 26.2       | 0.30%    | 0.32%    | 0.21%    | Hexadecane       |
| 45     | 26.346     | 2.17%    | 2.68%    | 3.87%    | Quinoline, 1,2-dihydro-2,2,4-trimethyl-|
| 46     | 28.9       | 0.29%    | 0.22%    | 0.25%    | Octadecane       |
| 47     | 30.245     | 0.01%    | 0.02%    | 0.02%    | β-D-Glucopyranose, 1,6-anhydro-|
| 48     | 30.5       | 0.19%    | 0.35%    | 0.40%    | (E,E,E)-3,7,11,15-Tetramethylhexadeca-1,3,6,10,14-pentaene|
| 49     | 30.7       | 0.02%    | 0.07%    | 0.05%    | 1,5,5-Trimethyl-6-(3-methyl-buta-1,3-dienyl)-cyclohexene|
| 50     | 31.0       | 0.33%    | 0.88%    | 1.25%    | Cyclohexane, 1-ethenyl-1-methyl-2-(1-methylethenyl)-4-(1-methylethylidene)-|
ramp and using (50 mL/min) N₂ as the carrier gas in a thermobalance (Netzsch, model STA 409 PC).

**Micropyrolysis Assays (Py-GC/MS):** The Fig. 2 (a–f) summarizes the experimental protocol for performing analytical pyrolysis experiments. Moreover, a detailed explanation on the experimental design and equipment’s conditions/protocols is provided below.

In a typical experiment, around 1 ± 0.1 mg of waste tire were weighted in an AD 6000 Ultra MicroBalance (Perkin Elmer, ±10⁻⁶ mg) and placed in the pyrolysis reactor (Fig. 2d), supported by glass wool. Fast pyrolysis experiments for waste tires, with and without catalysts, were carried out in a CDS 5200 pyroprobe (CDS Analytical). The quartz tube reactor (25 mm length and 1.9 mm ID) was inserted inside a probe and electrically heated using a resistively heating Pt filament (Fig. 2e). For the catalytic pyrolysis, a fixed catalyst-to-tire mass ratio of 4:1 was used. In this case, the tire and the catalyst were separated by glass wool to perform the experiment in an ex-situ regime. All the experiments were done under a constant flow of He (pure 99.996%, Iconsa, Chile) of 20 mL min⁻¹ to transport the volatiles to the analysis area (GC/MS) (Fig. 2f). The heating rate was varied according to the reaction temperature (400 and 450 °C), considering a residence time of 12 s, and the kinetically-controlled regime was confirmed by the dimensionless numbers of Biot, \( \text{Py}^I \) and \( \text{Py}^II \) (See Eqs. ((1)–(3)).

\[
\text{Bi} = h \cdot R/\lambda
\]  

\[
\text{Py}^I = \lambda / (k \cdot \rho \cdot C_p \cdot R^2)
\]  

\[
\text{Py}^II = h / (k \cdot \rho \cdot C_p \cdot R)
\]

Here \( \lambda \) is the thermal conductivity (Wm⁻¹K⁻¹), \( R \) is the characteristic length (m), \( h \) is the heat transfer coefficient (Wm⁻²K⁻¹), \( \rho \) is the mass density of the WT (kgm⁻³), \( C_p \) is the specific heat Jkg⁻¹K⁻¹ and \( k \) is the apparent kinetic constant for the solid conversion (s⁻¹).

Before entering the GC, the volatiles passed by a Sorbent Tube, packed with 20:35 mesh Tenax-TA (pre column Perkin Elmer), which was kept at 280 °C to release the volatiles through a heated transfer line (CDS Analytical) to the gas chromatograph (Clarus, 690, Perkin Elmer) (Fig. 2f). Then the volatiles were separated in an Elite 1701 column (30 m × 0.25 mm × 0.25 μm) using He as carrier gas at 15 mL min⁻¹ and using a heating ramp from 45 to 280 °C at 2.5 °C min⁻¹. The chromatograph is equipped with a quadrupole mass...
detector (SQ8S, Perkin Elmer) working in electron ionization mode. The compounds were ionized and the resulting mass spectra were compared with the standard spectra database from the NIST library in a m/z range of 30–600 Da. Because the amount of tire was strictly controlled, the relative peak area \( R_A \) (Eq. (4)) was used as a measured of the products selectivity.

\[
R_A = \frac{n}{\sum_i (A_{peak_i})}
\]

\( R_A \) is the relative peak area, \( A_{peak_i} \) peak area for the \( i \)th compound and \( n \) is the total number of identified compounds.

**Ethics Statement**

Provided dataset do not involve human subjects nor experiments with animals. Furthermore, it represents original data gathered by the research team thus it does not imply the collection of information from social media or any other public database.

**Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

**CRediT Author Statement**

**Beatriz Smith Azócar:** Conceptualization, Methodology, Writing – original draft; **Paula Osorio Vargas:** Data curation, Writing – original draft; **Cristian Campos:** Investigation, Formal analysis; **Francisco Medina:** Methodology, Investigation; **Luis E. Arteaga-Pérez:** Conceptualization, Supervision, Writing – review & editing.

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