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Investigation of hot char catalytic role in the pyrolysis of waste tires in a two-step process

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Abstract

This study pursues the valorization of waste tires by pyrolysis using a different approach for tire parts, specifically, the tire tread rubber (TTR) and side wall rubber (SWR). TTR was used to produce a hot char with the purpose of using it in situ cracking catalyst. SWR was valorized by pyrolysis and in line catalytic reforming over TTR derived hot char in a two fixed bed reactor system. This work aims to improve the quality of pyrolysis products using TTR derived hot char as an inexpensive catalyst. The thermal decomposition behavior and products characteristics were tested by means of TG-FTIR, GC, GC-MS, nitrogen adsorption and SEM. Under reforming temperature of 500-550 °C, a high yield of valuable single ring aromatics (concentration in the oil of 50 %) was obtained. The yield of gas can reach 10.5 wt.% after pyrolysis reforming step, which just only 3.0 wt.% with pyrolysis step. The yield of undesirable byproducts as PAHs and carbon deposits was also limited. This strategy represents a novel and feasible alternative to traditional waste tire catalytic pyrolysis processes using expensive catalysts as zeolite.

Keywords: waste tire; hot char; in line reforming; product upgrading.

1. Introduction

With the significant increase in automobile transportation, the waste tire generation has continuously increased in the last decades. It has been reported that the annual global

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62 production of waste tire is about 1.7 million tons[1]. Waste tires have been regarded as “black
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64 pollution” due to their low recycling efficiency and the environmental problems associated
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66 with their improper handling. Many waste treatments were proposed for the waste tire
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68 disposing and recycling, i.e. incineration, landfill, retread, gasification and pyrolysis.
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70 Incineration is a very common disposal method for solid waste, but it produces more
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72 secondary pollution, especially dioxins in the case of waste tires [2]. Landfill has been
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74 gradually abandoned due to lots of land taken up and accidental fire risk. Retreading is
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76 suitable for tire that can be used one more time. Although these valorization routes play a
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78 certain role in disposal of waste tire, there are still some pollution generated and potential
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80 hazard existed[1].
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84 In recent decades, waste tire pyrolysis treatments have been studied extensively because its
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86 environmental advantages. A considerable development of pyrolysis technologies was
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88 reached, amongst them, fixed beds[3], fluidized beds[4], spouted beds[5] and rotary kiln[6,7]
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90 are the most common reactor designs. In addition, different strategies have been proposed for
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92 the improvement of process performance or products quality as is the case of vacuum
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94 pyrolysis[8], microwave assisted pyrolysis[9], hydrogenative pyrolysis[10], co-
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96 pyrolysis[11,12] and catalytic pyrolysis[13,14].
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99 Liquid oil or tire pyrolysis oil (PO) is main product obtained from waste tire pyrolysis, its
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101 high heating value and composition could promote its use as replacement for conventional
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103 fuels or further separation for high value chemicals (limonene, toluene and xylene)[15].
104
105 Pyrolysis char is a carbon-rich solid which composition and quality greatly influence tire
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107 pyrolysis economic feasibility. Tire char can be reutilized as carbon black[16] or upgraded to
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109 produce activated carbons especially suitable for the adsorption of heavy metals and other
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111 pollutants from water[17]. The yield of gases from tire pyrolysis is far less than those of PO
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113 and char. The most frequent use for the gas is to supply the heat required by the process[18].
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Urged by the necessity of improving the quality of waste tire pyrolysis products, catalytic pyrolysis is gaining increasing attention. In this framework a wide variety of catalysts have been reported in the literature for this process, i.e., HZSM-5[19], HY[20], Al₂O₃[21], Na₂CO₃[22] and blast-furnace slag[6]. It is to note that the incorporation of catalyst to tire pyrolysis could greatly influence the quality and yield of oil, gas and char. The yield of gas is significantly increased after catalytic pyrolysis, especially operating with acid catalysts. Interestingly, high yields of valuable light olefins (ethylene, propylene and butenes) was reported[20]. In the same line, an improvement of PO composition was also pursued in catalytic pyrolysis, with the cracking of heavy oil fraction and the production of high added value chemicals, especially BTX[23], and the reduction of sulfur content[24] as main objectives. However, the role played by the catalyst and its influence on oil quality and composition need further examination and analysis[13]. Furthermore, the catalyst selection in waste valorization processes faces several challenges: (1) features as high activity, selectivity and stability are required. (2) the price of the catalyst must be low in order to guarantee the economy of the process. (3) it is also a problem to be solved how to recycle the used catalyst. In this regard, the utilization of waste derived char represents a cheap and feasible alternative for the full-scale development of waste tire catalytic pyrolysis. In fact, the activity of biomass and waste pyrolysis char for the cracking of gasification tars has been reported in the literature[25]. Some experiences in the utilization of waste derived chars for the cracking of pyrolysis volatiles have been reported[26]. The whole tire rubber was often used for derived char preparation. However, according to the different composition lies in the different part of tire, the tire rubber can be divided into tire tread rubber (TTR) and side wall rubber (SWR) [27]. TTR has high ash content (inorganic compounds), and SWR contains high volatiles matter content but low ash. The derived char of TTR has better surface area and potential catalytic activity than that of SWR. So, the TTR could be considered to prepare derived hot

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180 char as inexpensive catalyst used in the pyrolysis process. Few reports investigate to use the
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182 TTR derived hot char as catalyst in pyrolysis.
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185 In this work, a new economic method was developed for the improvement of the tire pyrolysis
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187 products quality. The tire was separated into TTR and SWR, and the derived TTR hot char
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189 was prepared. The reforming of the pyrolysis volatile using the hot char as catalyst was
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191 investigated. A wide experimental design was carried out, analyzing main process conditions
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193 (hot char preparation temperature, pyrolysis temperature, reforming temperature, hot char/side
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195 wall (HC/SWR) ratio and residence time) on product yields and their composition.
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197 2 Materials and Methods

198 2.1 Materials.

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200 The waste tire (Maxxis 510) used in this study was obtained from a garage of Xi'an, China.
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202 Particle size of the pyrolysis feedstock influences the heat transfer and efficiency of pyrolysis
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204 reaction rate. Generally, the smaller the particles are, the better heat transfer, but it also offers
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206 higher pressure drop to carrier gas and grinding cost. The particle size for pyrolysis is
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208 reported to range between 0.4 mm and 2.0 mm [28]. The basic composition of tire includes
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210 rubber and fillers including carbon black, steel, sulfur, zinc oxide, processing oil and
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212 vulcanization accelerators. However, the composition of SWR and TTR are actually different.
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214 Accordingly, SWR and TTR were separated and cut into small pieces (~ 2.0 mm). Proximate
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216 analysis, ultimate analysis and higher heating value (HHV) analysis were used to characterize
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218 SWR and TTR. The characteristics of SWR and TTR as received are reported in Table 1.
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222

223 Table 1. Property of waste tire used in this study

	Proximate analysis (wt%, ar)				Ultimate analysis (wt%, ar)					HHV (MJ/kg)
	M	V	A	FC	N	C	H	S	O ^a	
SWR	0.53	68.59	2.99	27.89	0.48	80.51	7.06	1.59	7.37	37.74
TTR	0.9	63.74	12.96	22.39	0.42	65.93	5.98	1.65	13.06	34.73

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231 ^a By difference.

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The two raw materials showed quite different properties. As can be seen from Table 1, the components of SWR and TTR are mainly different at ash content. The TTR contained much higher ash content (12.96 %) than that of SWR (2.99 %). In addition, the volatile content of SWR (68.59 %) is higher than that of TTR (63.74 %), which were quite similar with literature (i.e. 69.88 % vs. 65.70 %) reported[27]. The fixed carbon content of SWR (27.89 %) was also higher than that of TTR (22.39 %). The ultimate analysis indicates that C/H ratios for SWR and TTR were 11.40 % and 11.03 %, respectively. The TTR has more oxygen than SWR, almost double. The high heat value (HHV) investigated that SWR (37.74 MJ/kg) had a higher calorific value than TTR (34.73 MJ/kg).

2.2 Pyrolysis Experimental equipment and procedure

Pyrolysis experiments were conducted in a tubular electric furnace with two fixed beds operating in line, as shown in Figure 1.

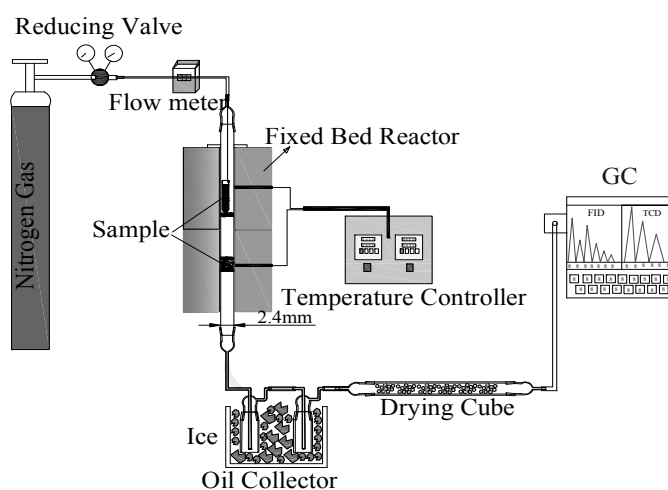


Figure 1. The schematic representation of pyrolysis and in line reforming unit.

In this study, two types of pyrolysis experiments were carried out. On the one hand, SWR (3.5 g) was pyrolyzed without TTR hot char in-line reforming for 1 hour in the upper section of the furnace at different temperature under atmospheric operating pressure. The pyrolysis volatiles were carried by 40 mL/min of nitrogen flow. On the other hand, pyrolysis and hot char in situ reforming runs, SWR (3.5 g) and TTR (different weight) were respectively placed

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on upper and lower section furnace. First, hot char was prepared by pyrolysis of TTR sample using lower section furnace for 1.0 h with 100 mL/min of nitrogen flow at different temperatures. Then, SWR was pyrolyzed and pyrolysis volatiles were carried by 40 mL/min of nitrogen flow to the lower hot char bed for their catalytic transformation. To make pyrolysis volatile evenly distributed, four-layer quartz wool was used in pyrolysis reforming experiment, which were placed under and above of SWR and TTR respectively. In each run, prior pyrolysis reactions, nitrogen was fed in a constant flow rate of 100 mL/min and keep 20 minutes to ensure an inert atmosphere. After purged with nitrogen, the reactor was heated from room temperature to designated temperature at a heating rate of 30 °C/min, and then keep 1.0 h to ensure raw material complete pyrolysis, finally cooled down to room temperature. All pyrolysis products were collected for subsequent analysis. Char and PO were recovered from the reactor and condenser, respectively and weighted; gas product was collected in a gas tedlar bag and its yield was calculated by GC analysis using and external reference.

In order to determine suitable operating conditions and understand their influence on process performance a wide experimental work was carried out. The influence of hot char preparation temperature over its catalytic activity was analyzed between 550 and 800 °C. The temperature effect was studied following two different strategies: i) Analyze its role over the reforming step (between 450 and 600 °C) but with a fixed pyrolysis temperature (600 °C) and ii) Study the combined effect of temperature in both reaction steps in the 450 to 600 °C range. Besides, the influence of HC/SWR ratio (between 0 and 1) and residence time (between 0 and 27.2s) was studied. The residence time of SWR pyrolysis volatile can be calculated by the formula. The corresponding residence time of different proportion is reported in Table 2.

$$T = \frac{60\pi r^2 H}{v} \quad (1)$$

T—residence time, s;
 r—the radius of the reaction tube, mm;
 H—the height difference of TTR in reaction tube, m;
 v—the flow rate of carrier gas, mL/min.

Table 2. The corresponding residence time of different proportion

Material Proportion	Height difference (cm)	Residence time (s)	
		40 mL/min	80mL/min
0	0	0	
0.30	1.2	8.1	
0.324	1.3	8.8	
0.50	2.0	13.6	6.8
0.75	3.0	20.3	
1.00	4.0	27.2	

2.3 Product Analysis

Proximate and ultimate analyses of SWR and TTR were tested in an automatic proximate analyzer (FO410C, Yamato, China) and elemental analyzer (Vario ELIII, Germany), respectively. The high heating value (HHV) of the samples was determined by an oxygen bomb calorimetry (SDC 5015, Sundy, China).

Thermal decomposition behaviors and functional groups of SWR and TTR were investigated by TG-FTIR analysis. The transfer line between the TG (EXSTAR 6000 TG/DTA 6300, Japan) and FTIR (IRAffinity-1S, Japan) apparatus was made of polytetrafluoroethylene with an internal diameter of 2 mm and length of 1.5 m. The gas generated in TG was analyzed by FTIR carried by nitrogen (75 mL/min). The temperature of the line was maintained at 200 °C. In each run, approximately 12 mg of the sample was placed in an alumina crucible. The sample was heated from ambient temperature to 900 °C at a heating rate of 30 °C/min under the nitrogen atmosphere (75 mL/min). Simultaneously the weight loss data and functional groups were recorded online.

Physical properties of pyrolysis chars were determined by physical adsorption-desorption instrument (JW-BK200B, China), which can evaluate the surface area and pore size distribution (micro-pore, mesopore and macro-pore) by resolving the nitrogen adsorption-

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417 desorption isotherms at 77 K. Multipoint BET (Brunauer-Emme TTR-Teller) was used to
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419 determine the specific surface area (S_{BET}), BJH (Barre TTR-Joyner-Halenda) method was
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421 utilized to calculate the mesoporous volumes[29]. Before the test, the samples (0.3 g) were
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423 outgassed at 300 °C for 3.0 h under vacuum atmosphere for removing moisture and impurities.
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425 The gaseous products were analyzed off-line by gas chromatography (GC) (Techcomp GC-
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427 7900) to quantify the concentrations of H₂, N₂, CH₄, CO, CO₂, C₂H₄, C₂H₆, C₃H₆ and C₃H₈.
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429 The GC was equipped with a flame ionization detector (FID) and a thermal conductivity
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431 detector (TCD). Argon was used as carrier gas. The yield of pyrolysis gas was determined by
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433 external standard method with a standard gas.
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436 The chemical composition of PO was determined by GC-MS (Agilent 7000B, America).
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438 SWR pyrolysis oils and pyrolysis reforming oils are mixed with dichloromethane (CH₂Cl₂) in
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440 a ratio of 1:50, and then, mixtures are heated for evaporation and the chromatographic peaks
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442 were identified according to the NIST library. The experiment started at 40 °C and the
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444 temperature was held there for 3 min, and then set to 280°C with heating rates of 4 °C/min. In
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446 addition, final temperature was kept for 5 min. Helium was used as the carrier gas with the
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448 flow rate of 30 mL/min, and the split ratio was 50:1. The injector temperature was 220 °C and
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450 sample dosage of 1 uL. The mass spectra were obtained from m/z 50~500.
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452 **3. Results and discussion**

453 **3.1 TG-FTIR analysis**

454
455 Thermo-gravimetric (TG) and derivative thermo-gravimetric (DTG) curves of SWR and TTR
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457 at a constant heating rate of 30 °C/min under nitrogen atmosphere (75 mL/min) from room
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459 temperature to 900 °C are shown in Figure 2. As observed in Figure 2, the weight loss curves
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461 of both TTR and SWR are similar. Thermal decomposition started at 230 °C and almost
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463 finished at 600 °C. The solid residue yield at 600 °C was of 33.67 % for SWR and of 37.76 %
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465 in the case of TTR, with this difference being associated with their different composition. It
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can be easily observed different degradation steps in the DTG curve of TTR and SWR. A significant weight loss peak at 462 °C (1.983 mg/min) with 46.398% weight loss rate on the DTG curve of TTR. Two sharp weight loss peaks on the DTG curve of SWR, which appeared at 408.20 °C (2.008 mg/min) with 21.703 % weight loss rate and 480 °C (2.039 mg/min) with 56.602 % weight loss rate respectively. According to previous literature the DTG peaks correspond to natural rubber (NR), styrene butadiene rubber (SBR) and butadiene rubber (BR) in raising temperature order[30].

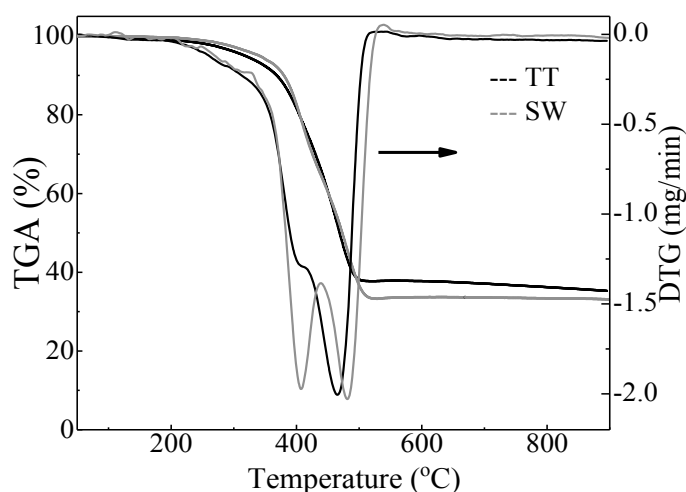


Figure 2. TG and DTG curves of SWR and TTR obtained at 30 °C/min.

The volatile generated in the thermo-gravimetric progress were transported to the infrared spectrometer through the gas transmission tube. The infrared spectrometer obtained the infrared spectrum diagram through real-time tracking and recording. The FTIR diagrams of SWR (a) and TTR (b) were shown Figure 3, respectively. The FTIR curves are really different due to their chemical structure. The FTIR curves of SWR and TTR proved that waste tire composition complex, SWR has a pure and simple composition than TTR.

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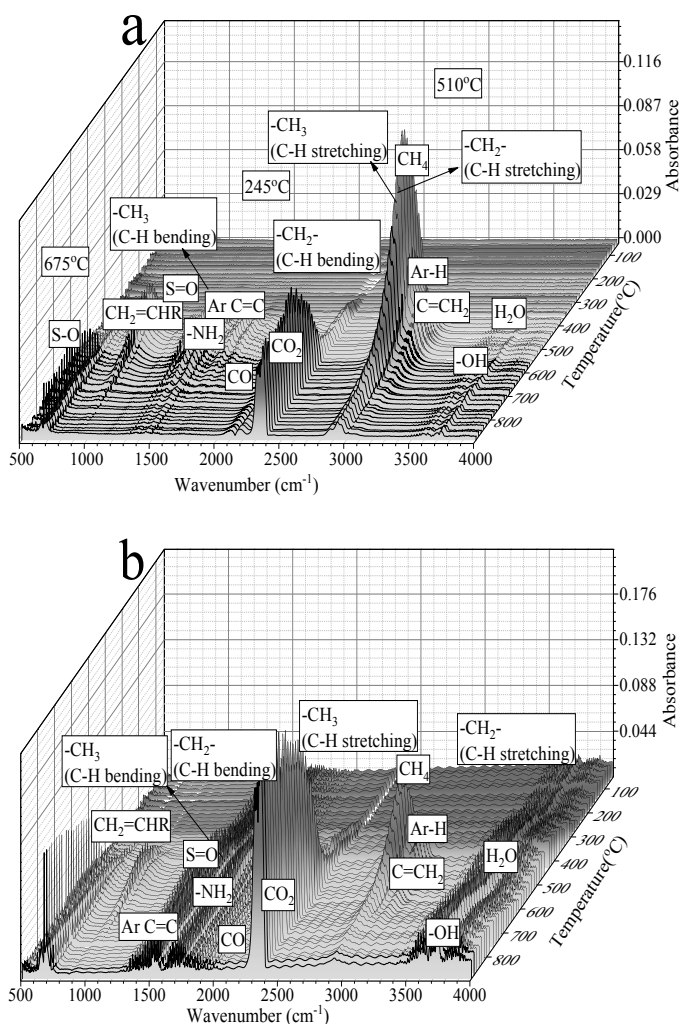


Figure 3. FT-IR curves of SWR (a) and TTR (b) at 30 °C/min.

The peaks were shown with all samples between 2800 and 3000 cm^{-1} are due to the alkanes (- CH_3 , - CH_2 and C-H) presence. All samples had sharp peak around 3020 to 3100 cm^{-1} , 1620 to 1670 cm^{-1} , which indicates the alkenes ($\text{C}=\text{CH}_2$ and $\text{C}=\text{CH}$)[31]. It is to note that SWR has more alkanes than TTR. Three weak peaks were noticed between 3000 and 3100 cm^{-1} in both samples. These peaks denote the aromatic hydrocarbons presence in SWR and TTR. Alcohols have the same hydroxyl group with phenols, and the vibration frequencies of O-H and C-O are their characteristic absorption. The peak of O-H usually situated at between 3200 and 3670 cm^{-1} , which can be found in all the figures. Two peaks were noticed around 1050 cm^{-1} and 1200 cm^{-1} in both samples. According to these characteristic peaks, alcohol and phenols are present in pyrolysis volatiles derived from SWR and TTR. The strong peak between 1680

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593 and 1750 cm^{-1} at conjugated mode due to C=O inductive effect denotes aldehydes or ketones
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595 presence in all the samples. Two different peaks were shown at different bands between 2720
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597 and 2820 cm^{-1} , which further determined aldehydes presence in pyrolysis volatile. In both
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599 pyrolysis volatile of SWR and TTR, the peaks were noticed at between 1650 and 1690 cm^{-1} ,
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601 between 1420 and 1400 cm^{-1} , which indicate amide presence[32]. The weak peak at between
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603 1300 and 1400 cm^{-1} was assigned to sulfur dioxide (SO_2) in volatile. Two significant peaks
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605 were shown at between 670 and 810 cm^{-1} (S-O stretching vibration), between 1340 and 1385
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607 cm^{-1} ($-\text{SO}_2-$ asymmetric stretching vibration), which indicate sulfonic acid presence in
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609 pyrolysis product. Briefly, the strong peak, between 2200 and 2400 cm^{-1} , indicates CO_2
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611 present in product. Two weak peaks next to CO_2 peak at between 2050 and 2200 cm^{-1} prove
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613 CO present in pyrolysis product. The elements from functional groups are consistent with the
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615 results of element analysis.
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619 The FTIR curves revealed that TTR was easily pyrolyzed than SWR due to TTR including
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621 more easy composition, such as amide and sulfur organic. The evolution of CO_2 and CO from
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623 the SWR and TTR samples started at about 245 $^\circ\text{C}$. With the temperature increasing, the CO_2
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625 and CO were gradually rose and formed a high intensity peak due to the decomposition of
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627 more stable ether. The CO_2 intensity peak for SWR were about 700 $^\circ\text{C}$ lower than that of
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629 TTR about 730 $^\circ\text{C}$, because TTR have more oxygen than SWR.
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633 The release of CH_4 from both samples started at about 340 $^\circ\text{C}$ and the CH_4 intensity peaks at
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635 about 500 $^\circ\text{C}$. The release of CH_4 was mainly from decomposition of rubber. The CH_4
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637 significant peak for SWR about 500 $^\circ\text{C}$ is higher than that of TTR. The appearance of sulfonic
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639 acid from both samples was about 330 $^\circ\text{C}$. The peak areas of sulfonic acid in TTR are higher
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641 than those in SWR since TTR has more sulfur than SWR.
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3.2 Effect of hot char preparation temperature on in line reforming of pyrolysis volatile

The influence hot char preparation temperature has on its catalytic performance has been studied between 550 and 800 °C. The pyrolysis and reforming steps were carried out at 550 °C. The results obtained in the pyrolysis step (without in line reforming) have been reported in order to assess the role played by the hot chars prepared at different temperatures.

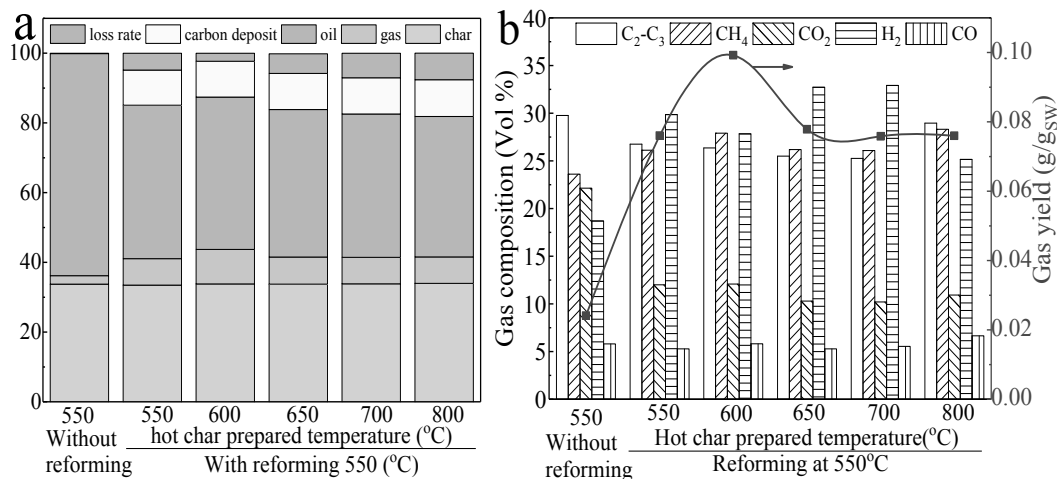


Figure 4. Influence of hot char prepared temperature on product distribution (a) and gas composition (b) in the in line reforming (550 °C) of pyrolysis volatiles (550 °C). HC/SWR ratio 0.5.

As observed in Figure 4 the utilization of TTR derived hot char as catalyst has a remarkable impact on product distribution (4a) and gas product composition (4b) for all the hot char preparation temperatures. As the result of long time pyrolysis, SWR could be completely pyrolyzed. The final yields of chars derived from SWR are almost unchanged. The gas yield of 2.4 wt.% obtained in the pyrolysis step at 550 °C was increased to around 7.5 wt.% after reforming for all the studied hot chars with the exception of that produced at 600 °C that showed a higher cracking activity and produced a higher gas yield (9.93 wt.%). Pyrolytic char tends to agglomerate at high temperature stage, agglomeration causes the decrease in specific surface area, which is one of the main reasons for smaller specific surface area of char. The bond agglomeration decreases and specific surface area increase of char derived at 800 °C and prepared long time. The specific surface area of char is one of the main reasons for cracking

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711 reaction. The larger the specific surface area (see Table 4), the more yield of gas is produced.
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713 At 600 °C, the pores at surface of char for catalytic are more so that more gas yields produced,
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715 but from 600-800 °C the gas yields decreased due to agglomeration and more carbon deposit
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717 covering the active sites. Thus, the gas yields decrease from 600 °C to 800 °C. Since the
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719 specific surface area of char prepared at 800 °C is close to that of char prepared at 550 °C, the
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721 yield of gas produced by reforming of both is almost identical. The yield of oil varied from
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723 63.71 to 40.29 wt.% before and after hot char reforming. In addition, a remarkable
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725 carbonaceous material deposition over char surface was observed, its value was around 10.24
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727 wt.% independently of the char used. The results investigate that hot char have a significant
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729 encouragement on pyrolysis volatile reforming. And the increase of gas production at
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731 expenses of PO. According to FT-IR data (see Figure 3), small molecules firstly emits from
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733 the surface, followed by medium and large molecules. At first, small molecules are reformed
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735 on the lower char surface to produce smaller molecules of H₂ and carbon, which will block
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737 the active pore site of the hot char. Another part of molecular would be cracked on the surface
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739 of hot char to produce smaller molecules of volatile matter and carbon deposition on the
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741 surface of char. Thus, before and after catalytic reforming, the specific surface area of char
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743 changes greatly. This is also the reason of more yield of H₂ in the start and then falls down.
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745 The yield of CO₂ is just the opposite, which drops first and then rises.
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749 Gas yield and its composition of the pyrolysis step are compared with those after reforming at
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751 550 °C using hot chars prepared at different temperatures in Figure 4b. This figure clearly
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753 reveals a significant modification of gas composition in the reforming step. The most relevant
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755 effect of pyrolysis volatiles reforming is the increase of H₂ concentration, from 18.7 % in
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757 pyrolysis step to values in the 25.2 to 32.9 % range for different hot chars. In addition, the
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759 concentration of CH₄ showed a clear increase. In spite of the fact that C₂-C₃ hydrocarbons
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761 concentration slightly decreased after reforming, their yield markedly increased as the overall
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771 gas yield is three times higher. From the previously mentioned results it can be concluded that
772 the hot char prepared at different temperatures are suitable for the cracking of tire pyrolysis
773 volatiles, being the differences observed in product yields and gas composition limited.
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777 778 3.3 Effect of temperature on pyrolysis and in line reforming process

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780 In this section the influence of temperature was analyzed with two different types of
781 experiments: i) reforming temperature was varied between 450 and 600 °C with the pyrolysis
782 step being performed at 600 °C, ii) the temperature of both pyrolysis and in line reforming
783 was varied simultaneously in the 450 to 600 °C range. It should be noted that the hot char in
784 these runs was prepared at 600 °C and the HC/SWR ratio of 0.5.
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791 Figure 5a and 5b show the results obtained varying pyrolysis reforming temperature
792 simultaneously. From figure 5a, with the increase of pyrolysis temperature, the yield and
793 composition of gas has limited increase, only a limited dependence on pyrolysis temperature.
794 However, the yield of gas obtained from pyrolysis reforming step can reach 10.5 wt.% at 600
795 °C, much higher than that on pyrolysis step. From these results it can be concluded that
796 temperature has a much lower effect on pyrolysis step results than that on reforming step.
797
798 This trend was previously reported in the literature in pyrolysis studies performed under slow
799 heating rates[15,33], however, the effect of temperature is generally much relevant under fast
800 pyrolysis conditions[34]. This result was associated with the fact that tire reach almost
801 completely degraded high temperatures under slow heating rates, being the influence of
802 varying final temperature limited. In the same line pyrolysis temperature varied only slightly
803 gas and PO compositions.
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817 Due to the fact that pyrolysis step showed a limited effect on volatile stream composition, the
818 results obtained when the pyrolysis and reforming steps were varied simultaneously (Fig 5a
819 and 5b) are similar to those obtained in the runs in which reforming temperature was modified
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829 (Figure. 5c and 5d). In fact, in these experiments can be concluded that optimum conditions
830 were in the 500 to 550 °C range as long as the higher yield of valuable single ring aromatics
831 were in the 500 to 550 °C range as long as the higher yield of valuable single ring aromatics
832 was obtained. However, higher yield of gas and high value chemicals were obtained in 600 °C.
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834 The gas and PO composition and yield modification in the reforming step clearly reveal the
835 hot char positive role played by TTR derived char. Thus, in the gas fraction an important
836 increase in the H₂ and CH₄ was reported. In the PO a significant formation of single ring
837 aromatics was observed, while an important reduction of olefinic hydrocarbons was obtained.
838 This indicates that in the reforming step the PO cracking reactions are associated with the
839 increase of CH₄ and light hydrocarbons yield in the gas product. The modification of PO
840 composition was mainly due to Diels-Alder condensation together with dehydrogenation of
841 alkanes to alkenes reactions, followed by cyclization and aromatization[35]. It is to note that
842 the latter reactions provoked a H₂ that justify its high yield in reforming products. The extent
843 of these reactions was enhanced at high reforming temperature, moreover the aromatic ring
844 condensation reactions were specially promoted which gave way to a remarkable increase of
845 the PAHs yield[36]. It is to note that the previous described reaction mechanism for the
846 cracking of tire pyrolysis volatiles is similar to that observed in the literature in the catalytic
847 pyrolysis over different acid catalysts[20].
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865 Figure 5c shows a remarkable effect of low-temperature reforming on product distribution,
866 that is, the increase of temperature promoted PO cracking reactions to produce gases and the
867 formation of solid residue over char was also enhanced. Thus, in the pyrolysis step a gas yield
868 of 3 wt.% was obtained, with the gas mainly made up of light hydrocarbons (C1-C3) and CO₂,
869 being lower the H₂ and CO contents (see Figure 5d). Cracking reactions are endothermic, and
870 the higher the temperature is, the more favorable the cracking reaction is. After reforming step,
871 the gas yield increased and also H₂ and CH₄ concentrations with this trend being more acute
872 as reforming temperature was raised. In spite of the fact that C2-C3 fraction concentration
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decreased with temperature, its yield remarkably increased due to the whole gas product yield growth. The results donate that low-temperature reforming make a certain positive influence on pyrolysis volatile. However, the same temperature reforming could make a bigger difference in the product distributions than low-temperature reforming.

The commented modification in the gas composition was directly related with the evolution of PO yield and composition with reforming temperature. This modification was evidenced in the results of GC-MS analyses from the PO obtained in the pyrolysis step and that after reforming, see Figure 6. In fact, even the visual observation of these pyrolysis oils reveals significant differences. Thus, the PO obtained in the pyrolysis step, is a heavy, tawny brown liquid. This oil would easily divide into two layers, heavy oil on bottom and light oil on top. This phenomenon was described in the literature[15]. However, the PO produced in the reforming step was a lighter black liquid. In fact, the GC-MS analyses of the pyrolysis and reforming POs reveal a higher presence of heavy compound in pyrolysis step oil than that in reforming one. In Figure 6a, a very sharp peak indicates the presence of D-limonene, this peak represents the 29.5 % of whole area. The high content of this compound in waste tire thermal pyrolysis oil, especially under fast pyrolysis conditions, has been widely reported[18,37]. However, the chromatogram corresponding to the PO obtained in the reforming process clearly shows large peaks of light compounds. Table 3 shows the detailed composition of PO produced under different reaction conditions. As observed, the reforming of pyrolysis volatiles favored the conversion of alkenes and cycloalkenes into aromatic hydrocarbons, with a remarkable yield of single ring aromatics. It is to note that the optimum reforming temperature to produce valuable single ring aromatics was 550 °C with a concentration in the PO of 47.08 %, a further increase of temperature to 600 °C reduced its concentration to 45.34 % while enhances the concentration of PAHs such as naphthalenes, indenenes, phenanthrene and azulene. Moreover, the increase of reforming temperature

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promoted the cracking of aliphatic acids and other oxygenates with a remarkable decrease in their yields. It should be noted that the heteroatomic compounds in the PO, such as nitrogen, sulfur and oxygen compounds, were associated with the tire additives, processing additives and vulcanization agents degradation[38].

Comparing with the results, the yield of gas obtained with pyrolysis step is lesser than that from varying pyrolysis reforming temperature simultaneously. Even at 450 °C reforming, the total gas yield is higher than that with pyrolysis step, but is far less than that with the same temperature reforming. The GC-MS analysis indicates that more high value chemicals in PO obtained from same temperature reforming than that of low-temperature reforming. The results donate that low temperature reforming make a certain positive influence on pyrolysis volatile. However, the same temperature reforming could make a bigger difference than low temperature reforming.

In fact, the interest of several tire catalytic pyrolysis studies in the literature is centered in the productions of BTX using zeolites as HZMS-5[39,40], HY[23,39], H β [41] and USY[42]. This result is of great relevance due to the unexpressive nature of tire derived char in relation to more expensive zeolites and the high selectivity to light aromatics especially when the reforming step was performed between 500 and 550 °C. In fact, the single ring aromatics yields are of the same order of the aforementioned studies with different zeolites. Lesser Oxygenates, more indenenes and naphthalenes included in oil obtained from reforming oil.

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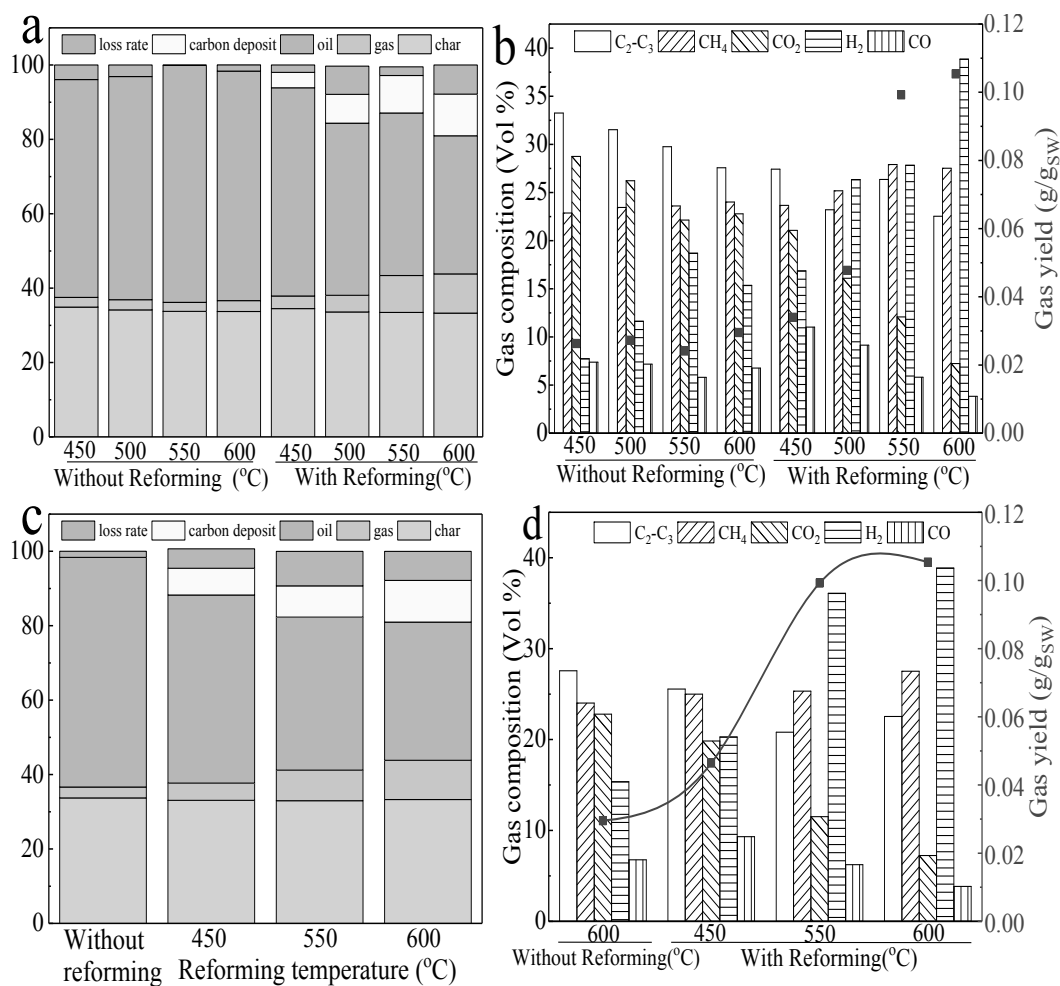
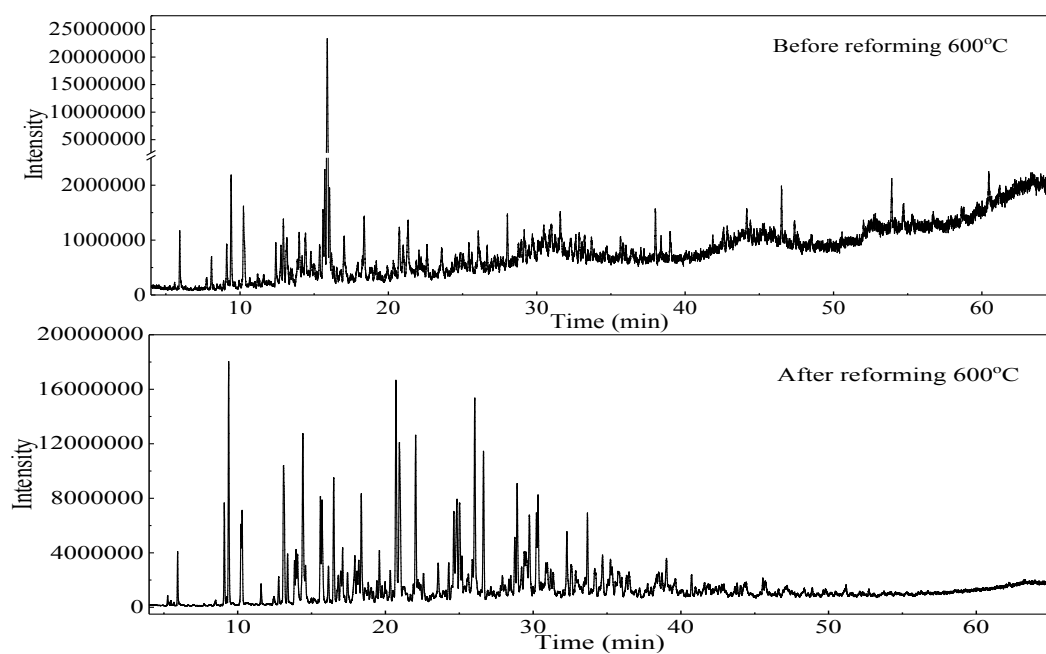


Figure 5. Influence on product yields (a) and gas composition (b) from without reforming and reforming with same temperature. Effect of reforming temperature on product yields (c) and gas composition (d). Char prepared at 600 °C, HC/SWR ratio 0.5.



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Figure 6. GC-MS analyses performed to the PO obtained in the pyrolysis step at 600 °C and after being reformed at 600 °C over a char prepared at 600 °C. HC/SW ratio 0.5.

Table 3. The composition of the PO obtained in different pyrolysis and pyrolysis-reforming experiments.

Compounds	Without reforming				With reforming							
	450- N/A- 40	500- N/A - 40	550- N/A - 40	600- N/A - 40	450- 40	500- 40	550- 40	600- 40	600- 40	600- 40	600- 40	600- 80
Single ring aromatics	18.95	18.33	20.24	16.13	38.45	50.66	47.07	42.47	47.08	41.98	45.34	
Biphenyl	-	-	0.55	0.78	1.34	1.38	1.87	3.79	2.31	0.88	2.94	
Fluorene-phenanthrene	-	-	-	-	0.72	0.72	0.71	3.49	0.98	0.6	2.01	
Thiazole	-	-	-	1.21	1.40	1.55	1.79	1.28	1.86	1.28	1.25	
Quinoline	0.93	0.92	0.95	0.90	1.14	0.90	0.78	0.49	0.73	0.96	0.43	
Aliphatic acids	3.18	2.49	2.7	1.84	2.56	3.73	1.55	-	1.06	4.06	-	
Indenes	2.49	2.97	2.41	2.74	3.10	6.19	14.17	17.8	15.94	4.77	16.39	
Naphthalenes	2.33	0.79	1.27	1.96	5.65	7.29	16.98	23.19	19.61	4.11	24.45	
Azulene	-	-	-	-	-	0.51	1.38	3.42	1.36	0.40	2.56	
Alkenes	10.73	7.6	8.45	7.53	3.91	3.74	0.58	1.24	1.26	1.02	1.48	
Cycloalkanes	1.84	2.83	3.57	2.84	1.09	0.49	-	-	-	1.27	-	
Alkanes	1.11	0.83	1.42	1.20	7.84	6.11	3.86	-	2.86	5.88	0.62	
Cycloalkenes	39.49	38.82	37.82	38.94	17.05	7.76	0.84	-	0.78	23.11	-	
Thiophene	-	-	-	-	0.50	-	-	0.54	0.60	0.39	0.49	
Nitriles	-	-	-	-	1.11	0.49	0.80	0.97	0.95	0.52	1.01	
Oxygenates	12.73	10.3	11.28	9.79	7.33	5.85	1.12	0.69	1.45	8.05	0.53	

450-450-40 means Pyrolysis temperature (°C) -reforming temperature (°C) -nitrogen flow rate (mL/min), N/A presents without reforming process.

-means not detected

3.4 Effect of hot char/SWR ratio and residence time on in line reforming of pyrolysis volatile

In this section the influence the amount of char in the reforming reactor has on product yields and their composition was analyzed. These experiments were performed at 600 °C both in the pyrolysis and reforming reactors, in addition the hot char in the reforming step was also prepared at 600 °C. Figure 7 shows the product distribution and gas composition obtained with different HC/SWR ratios in the reforming step. It should be clarified that the experiment corresponding to HC/SWR = 0 correspond to the results obtained in the pyrolysis step. As observed in Figure 7a, the increase of the HC/SWR ratio promoted cracking reactions which greatly increase gas yield. Thus, a gas of 2.9 wt.% was obtained in the pyrolysis step and this value progressively increased up to 25.3 wt.% for a HC/SWR ratio of 1. The gas composition

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1124 was influenced by the modification of HC/SWR ratio. Figure 7b clearly shows an increase in
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1126 the concentration of CH₄ and H₂. In spite of the fact that C₂-C₃ slightly decreased their
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1128 concentration with HC/SWR increase, its yields also remarkably increased considering the
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1130 evolution of whole gaseous fraction yield.
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1133 However, this HC/SWR ratio should be carefully adjusted as long as it also provoked an
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1135 increase in carbon deposition and therefore a reduction in the PO yield. In fact, the PO yield
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1137 was of only 18.6 wt.% for a HC/SWR ratio of 1. Thus, the increase in HC/SWR ratio not only
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1139 promotes cracking reactions to yields gases but also the reactions associated with the
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1141 formation of coke or carbonaceous deposits over hot char. In fact, the increase of carbon
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1143 deposit yield was closely related to aromatization and dehydrogenation reactions on the char
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1145 surface. Aromatic compounds and alkenes are prone to be involved in reaction pathways
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1147 leading to coke deposition, as they take part in hydrogen transfer and cyclisation reactions.
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1149 Accordingly, the extent of these reactions increases as HC/SWR ratio was higher, and more
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1151 coke was therefore deposited on the char bed.
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1154 According to the afore mentioned results, HC/SWR ratio should take values in the 0.5 range
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1156 in order to promote the improvement PO composition but at the same time avoid over
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1158 cracking and excessive condensation reactions to ensure a high PO yield.
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1160 The influence of HC/SWR in the in line catalytic pyrolysis of waste tires has been studied
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1162 using different cracking catalysts. It could be remarked that the results reported in these
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1164 studies were qualitatively similar to those of the present paper[39,42,43], i.e., the increase of
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1166 the HC/SWR reinforced the catalyst cracking with an increase of the gas yield and a reduction
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1168 of that of PO.
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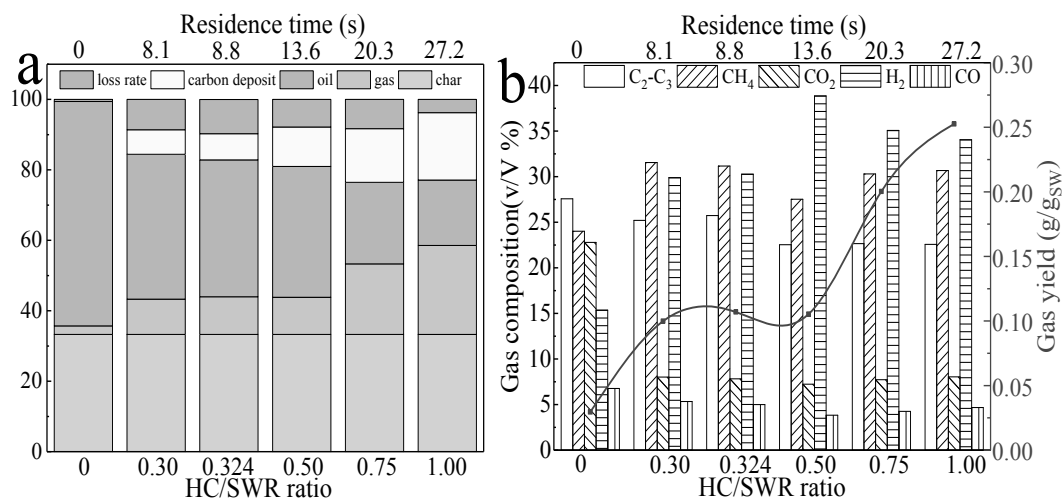


Figure 7. Influence of HC/SWR ratio and corresponding residence time on product distribution (a) and gas composition (b) in the in line reforming of pyrolysis volatiles.

Pyrolysis and reforming temperature 600 °C and char prepared at 600 °C.

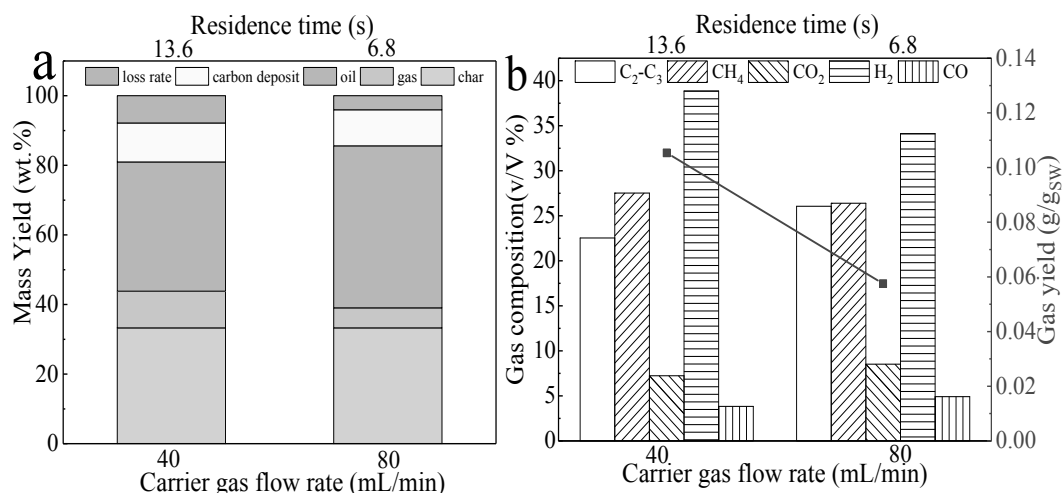


Figure 8. Influence of residence time on product distribution (a) and gas composition (b) in the in line reforming of tire pyrolysis volatiles. Pyrolysis and reforming temperature 600 °C, char prepared at 600 °C, HC/SW ratio 0.5.

In order to evaluate the influence that residence time has in the pyrolysis and in line reforming process the inert gas flow rate was varied between 40 and 80 mL/min (see Figure 8). Both pyrolysis and reforming temperature were of 600 °C, moreover, the TTR derived hot char was also prepared at 600 °C and the HC/SWR ratio was of 0.5. It is to note that the reduction of gas flow rate not only increased the residence time of tire pyrolysis volatiles in the reforming reactor but also increased their partial pressure. These conditions reinforce the catalytic role

of TTR derived hot char leading to higher extent of cracking reactions. Thus, the gas yield increased from 5.8 to 10.5 wt.% when the inert gas flow rate was reduced from 80 to 40 mL/min. In the same line the PO yield decreased from 46.6 to 37.1 % and that of carbon deposit increase from 10.4 to 11.2 % with the gas flow rate reduction.

As a result of the higher activity of the hot char operating with low gas flow rate, the concentration of CH₄ and H₂ increased, that of C₂-C₄ slightly decreased while those CO and CO₂ remained almost constant. Therefore, gas flow rate reduction showed a similar qualitative effect to that observed when the HC/SWR ratio was increased.

3.5 Characterization of the char used in the reforming step

The previously reported experimental results revealed a relevant catalytic role of TTR derived hot char in the transformation of tire pyrolysis volatiles. At the same time, a remarkable carbon deposition over the char was observed, especially when the reforming step was carried out at high temperatures. In this section the properties of the TTR hot chars prepared at different temperatures and the modification of their properties throughout the in line reforming are evaluated. Thus, the BET surface area, pore structure and SEM of char used before and after reforming were tested. The Table 4 summarizes the surface characteristics of the chars obtained at different temperatures before and after their utilization in the reforming step. The evolution of surface area with preparation temperature shows a minimum at 700 °C of 59.1 m²/g, however the values obtained at the maximum and minimum preparation temperatures, 550 and 800 °C, are both around 80 m²/g. The average pore diameters of all char are between 20 and 30 nm, which suggested the prevailing presence of mesopores. Although a reduced presence of micropores was also observed in some samples.

As observed in Table 4 the chars after the reforming step increased their surface area, in addition, the pore volume was higher after their utilization. These results reveal that the carbonaceous material deposited during the reforming step is of porous nature and enhances

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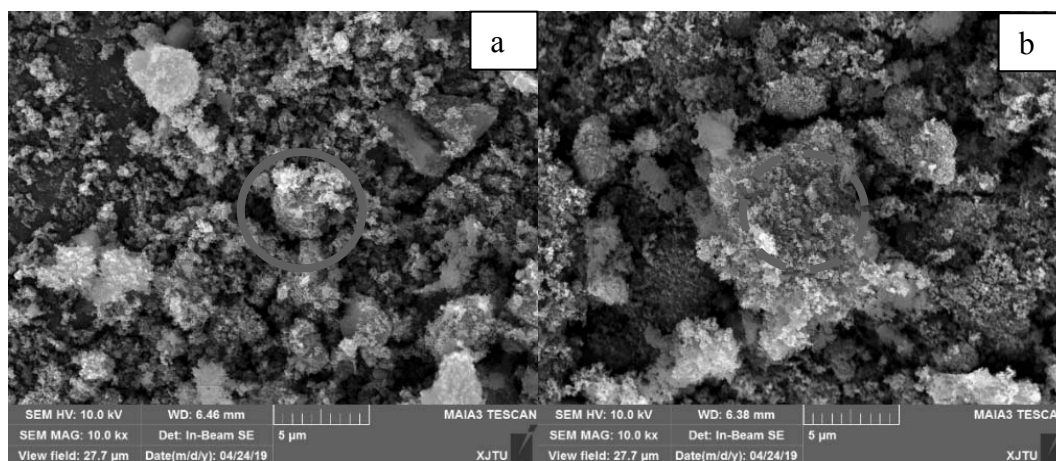
the surface area of the catalysts instead of blocking the original porous structure of the char. This may be due to the fact that the carbonaceous material deposits occur as small particles, SEM also confirmed this point (see Figure 9 a, b). In fact, in Figure 9 reveals that more flocs existed on the char after reforming than before.

Table 4. Comparison of char structure before and after reforming.

Char	S_{BET} (m^2/g)	V_{tot} (cm^3/g)	D_p (nm)	V_{mec} (m^3/g)	V_{mic} (m^3/g)	Meso-porous ratio (%)
Before reforming						
B-550	80.7	0.505	25.0	0.505	--	100
B-600	67.9	0.371	21.9	0.346	0.0249	93.29
B-650	64.1	0.504	31.4	0.504	--	100
B-700	59.2	0.453	30.6	0.431	0.0223	95.08
B-800	79.9	0.428	20.9	0.396	0.0314	92.66
After reforming						
A-550	96.7	0.651	26.9	0.651	--	100
A-600	96.1	0.598	24.9	0.598	--	100
A-650	96.0	0.649	26.5	0.611	0.0379	94.16
A-700	90.6	0.632	27.9	0.596	0.0354	94.40
A-800	84.0	0.467	22.2	0.434	0.0324	93.06

--Means micro-porous not tested

Figure 9. SEM and images of B-600 (a) and A-600 (b)



4. Conclusion

The pyrolysis of side wall waste tire followed by the in line reforming of its derived volatiles over tire tread pyrolysis char was studied in an experimental unit made up of two fixed bed reactors. This process represents a novel and attractive alternative to conventional strategies and catalysts commonly applied waste tire catalytic pyrolysis. Interestingly, this material

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1360 showed a remarkable cracking activity and high selectivity. The reforming over TTR hot char
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1362 showed a high selectivity to yield light compounds, especially the yields of valuable single
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1364 ring aromatics and syngas. The yield of single ring aromatics varied from 38.45 to 50.66%
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1366 after reforming and nearly twice as much as that in pyrolysis step. The optimum results in
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1368 terms of single ring aromatics selectivity were obtained in the 500 to 550 °C range, a further
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1370 increase in temperature promoted secondary reactions (over cracking and condensation) and
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1372 an excessive yield of undesired products as PAHs and solid residue. The yield of gas varied
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1374 from 3.0 to 10.5 wt. % before and after reforming with 40 mL/min nitrogen flow rate at 600°C.
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1376 In the same line HC/SWR ratio (0.5) and gas flow rate (40 mL/min) must be carefully
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1378 adjusted in order to get relatively better products. However, the hot char production
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1380 temperature showed a limited effect on its performance of the reforming process which can be
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1382 related with their similar features.
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