

Mathematical Model of Scrap Tire Rubber Pyrolysis in a Non-isothermal Fixed Bed Reactor: Definition of a Chemical Mechanism and Determination of Kinetic Parameters

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Received: 25 May 2017 / Accepted: 11 September 2017 / Published online: 19 September 2017
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Abstract A chemical reaction mechanism is proposed to describe the pyrolysis of scrap tire rubber based on the decomposition of their three main polymer compounds (natural, butadiene and styrene-butadiene rubbers). Samples of each polymer were tested separately using differential scanning calorimetry (DSC) at the same operating conditions (heating rate, temperature and atmosphere). The thermograms clearly show that the polymer decomposition takes place in two or three thermal steps. The comparison with the literature allowed associating these steps with depolymerization reactions. The DSC results also allowed determining the kinetic parameters for each reaction considered in the chemical mechanism proposed in this study. Consequently, these were included in a mathematical model developed for a fixed bed reactor (at laboratory-scale) considering mass and energy balances. The experimental conversion obtained in TGA at operating conditions of pyrolysis using scrap tire rubber as feedstock, were successful confronted with those simulated by the mathematical model obtaining a determination coefficient (R^2) of 0.97. On the other hand, the mathematical model predicts correctly the influence of the temperature in the product yields, being this variable the most statistically significant in the process, being in agreement with ANOVA results (p value < 0.001 at confidence level of 95%) allowing a good prediction of the product yields.

Keywords Thermal degradation · Kinetic reaction model · Reaction mechanism · DSC analysis

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Introduction

Due to their complex chemical structure, scrap tires are a highly pollutant solid waste, representing an economic and environmental problem in the entire world due to difficulties in their treatment and degradation. The main constituents of scrap tires (Although these are constituted by natural and synthetic rubbers), give them a Higher Heating Value (HHV) close to 33 MJ/kg [1], and the possibility to be valorized as fuels. Despite this, scrap tires destination is mainly to be incinerated inappropriately, deposited in open pits or sanitary landfills, or simply abandoned on roads, fields or rivers causing contamination of the soil, water and landscapes, and public health problems. The valorization of its rubber constituents could be performed using different thermochemical treatments such as pyrolysis or gasification, being these, efficient and environmentally friendly technologies. Other possibilities for their valorization have been also studied, such as the co-processing with coal [2], heavy oils [3] or biomass [4] to produce energy, or the use of tires as fuel in clinker furnaces [5].

As in pyrolysis process, the operating temperature varies between 400 and 900 °C where the thermal degradation of carbonaceous materials is performed under inert atmosphere, producing new products with the interesting advantage that allows the reduction of the pollutant emissions when compared with a typical combustion. NO_x and SO_x generation is avoided during pyrolysis due to the reactions that take place in the absence of oxygen [6, 7]. The use of scrap tire rubber in a pyrolysis process to produce fuel is then an excellent alternative to valorize this solid waste.

The pyrolysis process thereby allows the decomposition of volatile organics (mainly rubber chains) to produce gasses (pyrolysis gas), liquids (pyrolysis oil) and a solid product composed of inorganic elements and non-volatile carbon

(mainly carbon black). The mass distribution of the main reaction products depends on the operating conditions used during the process [1]. Several studies [8–10] have demonstrated that tire rubber (TR) pyrolysis can be represented as the sum of the independent decomposition of each component: oil, natural rubber (NR), butadiene rubber (BR) and styrene-butadiene rubber (SBR). Specifically, in the case of SBR, Park and Gloyna [11] suggested that the amount of styrene is not higher than 25 wt%.

The scaling-up of this technology at industrial level must be done by understanding the chemical reactions that occur in the reactor. Therefore, the determination of the reaction pathway and the kinetic parameters for each chemical reaction constitute the basis for the reactor design. To this purpose, kinetic studies of scrap TR have been developed using the most common thermal techniques such as thermogravimetry (TG) and differential thermogravimetry (DTG) using different heating rates (5–900 °C/min) and particle sizes (0.2–3.0 mm) [10, 12, 13]. However, these technologies are not capable of decoupling the rubber decomposition in different reaction steps; in fact, the studies based on TG or DTG only identified two thermal events which are so close together that it is not possible to evaluate them separately [13]. Nonetheless, some authors propose a reaction pathway based on the TR thermal decomposition obtained by TG analysis (TGA), using mathematical criteria to decouple the different decomposition of main TR compounds. For instance, the study performed by Leung and Wang [14] which use the normalized weight-loss ratio and a pyrolysis equation derived by Vachuska and Voboril [15]. Unfortunately, these models are built based on the specific conditions used for the TGA experiments, which does not allow determining a “real” reaction pathway, making the pyrolysis kinetic highly dependent on the heating rates [16]. Besides, the reaction order is commonly chosen as one [17–19] or, in fewer cases between one and two [20, 21] without real criteria, increasing the uncertainty on the definition of the kinetic rates associated to the reaction pathway.

The present study is focused on a modeling of a fixed bed reactor involving the determination of kinetic parameters to predict the TR pyrolysis. For that, a first work is performed using DSC in order to determine a reaction mechanism for degradation based on the decomposition of its three-main polymer compounds constituting it: natural, butadiene and styrene-butadiene rubbers. In this step, each polymer sample was tested separately using DSC at the same operating conditions (heating rate, temperature, atmosphere) identifying two or three different thermal events (exothermic and endothermic peaks) for each of them. The comparison with literature of the temperature associated for each event allowed relating them with the chemical reactions responsible for the polymer degradation. Consequently, the kinetic parameters for each reaction were determined by Bocharadt–Daniels

method using the heat flow obtained by DSC. On a final step, the chemical mechanism and the kinetic parameters associated were included in a mathematical model developed for a fixed bed reactor at laboratory-scale considering mass and energy balances. Finally, the experimental conversion obtained in this reactor at operating conditions of pyrolysis using scrap tire rubber as feedstock, were confronted with those simulated by the mathematical model.

Materials and Methods

Feedstock Characterization

NR sample was supplied by Procauchos S.A., SBR and BR samples were obtained from Mil Cauchos Industry, styrene rubber (SR) was obtained from Metalcrl Company and the scrap TR sample was obtained from crushed scrap tires commercially sold for synthetic carpets maintenance.

The composition analysis of scrap TR sample in its main polymer compounds: NR, SBR and BR was performed using a Pyroprobe pyrolysis unit (CDS 5150 Pyroprobe) coupled to a gas chromatograph equipped with a flame ionization detector (GC/FID) and a HP-5 column (30 m × 0.320 mm in diameter × 0.25 µm). 0.1 mg of each sample (NR, SBR, BR, styrene rubber (SR) and scrap TR) were weighed and placed in the pyroprobe according with the method reported by Lee et al. [9]. The mass composition of scrap TR as a function of its main rubber compounds was previously published by Acosta et al. [1]. In agreement with ASTM D7582 standard norm, each rubber sample was characterized by thermogravimetric analysis (TGA) (2050, TA Instruments) to determine the proximate analysis. Only for scrap TR, an elemental analysis was performed using a LECO equipment (TruSpec Micro model) by ASTM D5373-08 standard norm.

TGA and DSC Analysis

The rubber samples NR, BR, SR, SBR and scrap TR were analyzed using TGA and DSC methodologies. TGA analysis (TA Instruments, 2050) was performed to determine the behavior of each rubber sample during their thermal decomposition under pyrolysis conditions using nitrogen as inert atmosphere (flow rate 56 mL/min, approx. mass 11 mg, heating rate 30 °C/min from 25 to 600 °C). The results were compared with those from the thermal degradation of scrap TR at the same operational conditions.

DSC analysis (TA Instruments, DSC 2920) was performed to determine the kinetic parameters of scrap TR pyrolysis reactions. Approximately 13 mg of each sample were weighed and introduced into DSC equipment operating at a heating rate of 5 °C/min under nitrogen atmosphere and a temperature between 25 and 600 °C.

Determination of Kinetic Parameters

The method used in this study is based on the Bochardt–Daniels method. This method proposed determining the kinetic parameters using the DSC analysis performed at low heating rate (< 10 °C/min). This condition is necessary to decrease the temperature profile in the particle and allowed assuming a temperature equilibrium throughout the whole test sample. Thus, the kinetic study of the thermal decomposition of rubber samples was performed using the heat flow (Fc) reported by DSC tests, as a function of temperature (°C) and time (s).

The area below the “Fc vs. t” curve represents the whole heat released (Q). On the other hand, the partial area under the curve was used to calculate the partial heat released (q) according with the following equations:

$$\int_{t_0}^{t_f} Fc dt = Q \quad (J/g) \quad (1)$$

$$\int_{t_0}^t Fc dt = q \quad (J/g) \quad (2)$$

The relationship of the terms above allows determining the conversion during the thermal decomposition of sample, X_i :

$$X_i = \frac{q}{Q} = \frac{q}{\Delta H} \quad (3)$$

In which ΔH is the heat reaction defined as J/g.

The determination of the conversion rate (dX/dt) corresponds to the decomposition rate. For a reaction following an nth kinetic order in a discontinuous process, this can be described as:

$$C_{i,0} \frac{dX_i}{dt} = k_i \times C_{i,0}^n (1 - X_i)^n \quad (4)$$

In which k_i is the kinetic constant and $C_{i,0}$ corresponds to the initial concentration of compound i in mol/m³ and n is reaction order.

Furthermore, Bochardt–Daniels method considers that the kinetic constant follows an Arrhenius behavior. Therefore, Eq. 4 could be rewritten (as it is shown in Eq. 5), from which its linearization is presented in Eq. 6.

$$\frac{dX}{dt} = k_0 \times \exp\left(\frac{-E_a}{R * T}\right) \times C_{i0}^{n-1} \times (1 - X)^n \quad (5)$$

In this equation, k_0 is the frequency factor, E_a is the activation energy and R is the ideal gas constant.

$$\ln\left(\frac{dX}{dt}\right) = \ln(Z) - \frac{E_a}{R \times T} + n \times \ln(1 - X) \quad (6)$$

From which, $Z = C_{i0}^{n-1} \times k_0$.

Bochardt–Daniels method proposes to divide the curve “Fc vs. t” at least in 20 segments, evenly spaced by time. Besides, the method suggests that the first segment starts at 10% of peak height and the last segment ends at 50% of peak area. At the end, a “data set” including dX/dt, X and temperature is thereby obtained.

Finally, Eq. 6 can be solved with a multiple linear regression of the general form: $z = a + bx + cy$, in which the value consigned in “data set” allows obtaining the kinetic parameters: k_0 , E_a and n .

Description of the Experimental Equipment

The experiments necessary to validate the pyrolysis mathematical model of scrap TR rubber were carried out using a fixed bed reactor at bench-scale scale (Fig. 1). All the equipment is made of stainless steel (316 L). The reactor has 3.5 and 3.9 cm of internal and external diameter, respectively. 50.18 g of scrap TR with a particle size lower than 1.0 mm were placed inside the reactor having a bed volume of 44.3 cm³. The reactor (2) is heated using an electrical tubular furnace (2400 W) which generates a heating rate of approximately 30 °C/min. The system is fed with Nitrogen (UAP grade 5.0, Cryogas) at a constant flow maintaining an inert atmosphere inside the reactor (1). The condensable volatile compounds produced in the reactor are collected in two condensate traps cooled by contact with ice and dry ice, respectively (4 and 5). The pipe (3) between the reaction and cooling zones is maintained at 280 °C approximately, to limit the condensation of heavy hydrocarbons. The gas flow at the outlet is regulated to assure a constant relative pressure of 1 bar(g) in the system (6) and a volumetric flowmeter is placed at the outline of the system to quantify the non-condensable gasses. The product yields (pyrolysis oil and pyrolytic char) were determined by gravimetry, whereas the gas yield was calculated by mass balance once the possible leaks in the unit were minimized. Therefore, a leak test was performed before to each experimental test. In the leak test, the unit was isolated at 4 bar (relative) during 10 h approximately, in which the pressure loss was monitored. Only if the pressure loss during the leak test time was lower than 10%, the leaks were considered negligible and the experimental test could start up.

A factorial experimental design (4×3) were performed varying temperature (400–466–533–600 °C) and gas flow rate (116–155–233 NmL/min) to maximize pyrolysis oil yield. The experimental results were presented in a previous work, and therefore they were not detailed in this document [3]. The choice of these operating conditions was supported

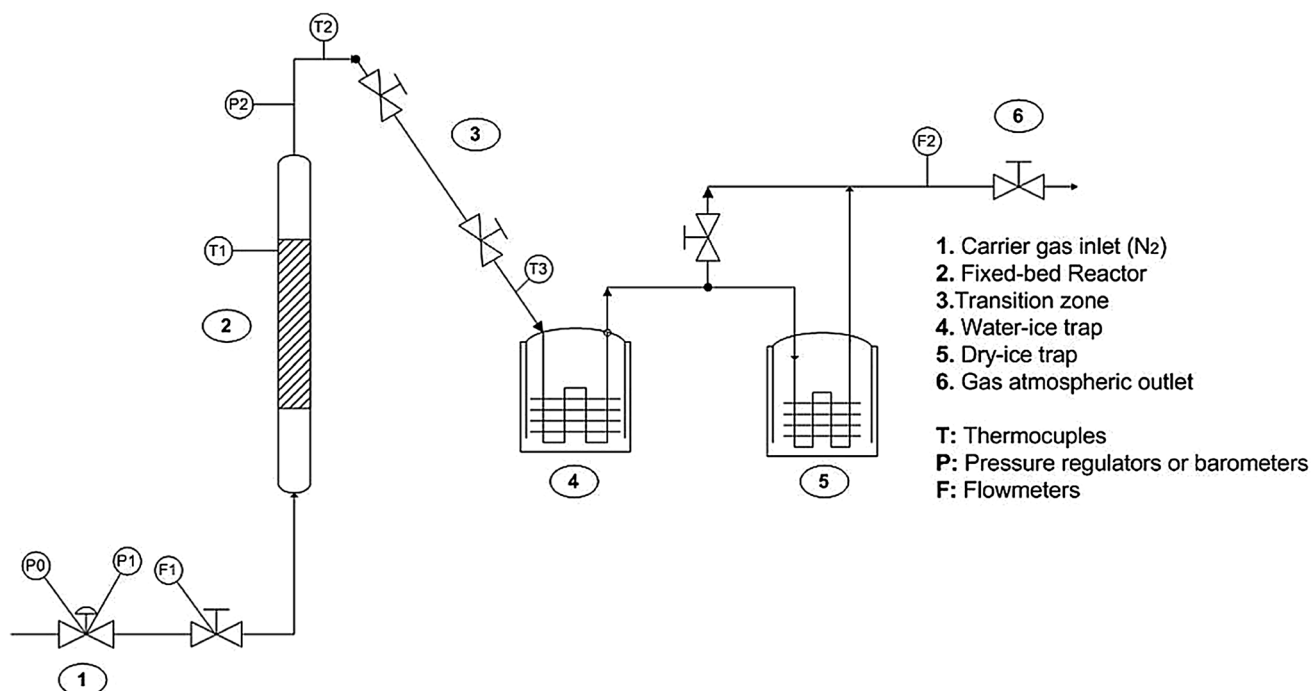


Fig. 1 Experimental unit used for scrap TR pyrolysis tests

in the literature, from which they were considered as the most important parameters for this process [22–24]. For these tests, the reaction time was maintained for 2 h and the particle size was constant and lower than 1.0 mm, due to the results published previously [25] which showed that the influence of particle size and reaction time parameters on pyrolysis oil yield were negligible.

Mathematical Model

The mathematical model proposed in this study is based on the fixed bed reactor (Fig. 1) described below (item 2.5). The assumptions that were considered are:

- The solid product is the sum of char (including ashes) and unreacted rubber
- The gas product corresponds to condensable and non-condensable compounds produced during the reaction.
- The reaction occurs uniformly throughout the bed.
- The gas products pass through the fixed bed without accumulation.
- The particle size is small (< 1.0 mm); the diffusion term is negligible.
- The relation D/L is high (≈ 15), for this reason, a developed flow through the fixed bed was considered.

Two types of mass balances are proposed depending on whether they are gas or solid products. In the case of solid products, the mass balance is depicted by:

$$\left(\frac{dC_S}{dt}\right) = R_S \quad (7)$$

In which S represents the solids present in the reactor, including both the unreacted polymers and char; C_S is the molar concentration of compound (mol/m^3); and R_S describes the molar change due to the chemical reactions of component S ($\text{mol}/\text{m}^3 \text{ s}$).

For the volatile products, the mass balance must be written as:

$$\left(\frac{\partial C_G}{\partial t}\right) + v_z \left(\frac{\partial C_G}{\partial z}\right) = R_G \quad (8)$$

In which G represents the products (liquids and gases) present in the reactor produced by decomposition reactions; C_G is the molar concentration of compound G (mol/m^3); v_z is the linear velocity (m/s) in the z direction and R_G is the molar change due to the chemical reaction of component G ($\text{mol}/\text{m}^3 \text{ s}$).

For the energy balance, Eq. 9 is considered:

$$\bar{C}_p \left[\rho \frac{dT}{dt} + \rho \times v_z \frac{dT}{dz} \right] = (-\Delta H) \left(-\frac{\partial \rho}{\partial t} \right) + Q \quad (9)$$

In which, \bar{C}_p and ρ are the calorific capacity ($\text{J}/\text{kg K}$) and the density (kg/m^3) of reaction mixture, respectively, v_z is the linear velocity (m/s) in the z direction, T is the temperature, ΔH is the enthalpy of reaction and Q is the external

heat given to the system. Therefore, in Eq. 9, the first term corresponds to the variation with the reaction time of temperature in the non-isothermal fixed bed reactor, the second term is associated to the heat transfer by convection, the third term corresponds to the heat change due to the chemical reaction and the last one is associated to the external heat transfer, in this case given by the electrical furnace. It is worth noting that, as the presence of a large amount of nitrogen during the reaction provides a high dilution of the gas produced during the reaction, this specific condition allows supposing that the \bar{C}_p of gas mixture along the reactor is constant.

To simplify the energy balance, it is possible to consider that as the electrical furnace provides a uniform heating along the reactor, then, there is not a significative variation of temperature with z , so the second term can be considered negligible. Besides, the heat transfer to the rubber particle is supposed as a combination of radiation and convection from the surrounding (gas and furnace). Likewise, a thermal equilibrium between the furnace walls and the gas is assumed and thereby, the temperature is the same in both the gas and the walls. Thus, the temperature of the particle surface could be supposed the same as the latter.

The suppression of the second term implies that the variation of temperature observed in the reactor must be associated to heat produced by both chemical reaction and electrical furnace. However, the reaction enthalpy value reported in the literature is lower for all polymers constituting the TR (170, 950 and 160 kJ/kg for pyrolysis of NR, BR and TR, respectively [26, 27]). Associated to the results by Pyle and Zaror [28] who evidenced that the temperature profiles are closed at values of reaction enthalpy of 0 and 210 J/g, it allows to ignore the third term. In conclusion, the energy balance can be simplified, in which the variation of temperature with the reaction time is exclusively given by electrical

furnace. The energy balance is, thereby, considered as constant and equal to the heating rate provided by the electrical furnace.

The equation system formed by the mass and energy balances was constituted by ordinary and partial differential equations which had to be solved simultaneously. The mathematical algorithm was solved in Matlab®, using the solver ODE 113 (variable order method for nonstiff differential equation using Adams–Bashforth–Moulton method for ODE), whereas in the case of OPE it was used the Crank–Nicolson method (commonly used to dynamic modeling of reactors) [29].

Results and Discussion

Rubber Characterization

Table 1 shows the proximate analysis of the different rubber compounds, and the ultimate analysis only for scrap TR. The composition of the four rubbers analyzed is approximately the same showing that those are constituted mainly by volatile matter, while the fixed carbon present can be considered negligible. Likewise, the moisture and ash content are also very low. On the other hand, the values obtained for scrap TR are in the range of the values obtained by other authors [30, 31]. A comparison between the proximate analysis of the rubber compounds of TR, and this last, allows concluding that the fixed carbon present in scrap TR cannot be attributed to the presence of rubber compounds, but it is related to other compounds such as carbon black which, in accordance with Rouse [32], can be approximately 27 wt% of scrap TR (taking into account the composition of scrap tires without the metal reinforcements and fabrics). Therefore, the formation of the different volatile products

Table 1 Proximate analysis for NR, BR, SR, SBR and scrap TR samples and ultimate analysis for scrap TR sample

	Proximate analysis for NR, BR, SR and SBR samples (wt%)				Scrap TR sample composition (wt%) ^a [1]	Ultimate analysis scrap TR sample (wt%)	
	Moisture	Elemental composition	Fixed carbon	Ash		Elemental composition	
NR	0.69	98.00	0.02	1.29	50.05 ± 2.07	C	80.84
BR	0.18	99.50	0.02	0.30	14.72 ± 2.195 ^b	H	7.52
SBR	1.09	98.26	0.00	0.65	1.44 ± 0.125 ^c	S	1.41
SR	0.08	99.09	0.05	0.78		O	2.82
						N	1.41
TR	1.20	65.41	27.31	6.08		Ash	6.00

^aDry basis

^bDetermined by difference

^cSBR composition: 1.07 wt% of BR and 0.35 wt% of SR

(condensable and non-condensable) after pyrolysis treatment can be attributed to the decomposition of the different rubber fraction present in the scrap tire.

Rubber Pyrolysis Study

Figure 2 shows the TGA curve and first derivative of TGA curve, respectively. In accordance with the figure, the scrap TR thermal decomposition starts at 170 °C approx. (a temperature below to that of the rubber compounds), corresponding to the devolatilization of oil, anti degradants, wax, stearic acid and other organic compounds present in the scrap TR [33]. The scrap TR compounds start their decomposition near to 310 °C, approximately. At this temperature, the NR begins its degradation, followed by BR at 340 °C and SR at 360 °C, approximately, according to many authors [34, 35]. The scrap TR decomposition finishes at about 500 °C, in which still 35 wt% of the solid material is preserved even at 600 °C. This behavior differs to that of the rubber compounds, which are completely degraded at this temperature (the solid material remaining is approximately 1 wt%; never higher than 2 wt%).

DSC Kinetic Study

Figure 3 shows the DSC thermograms for NR, BR, SBR and SR. The figure suggests that the rubber decomposition is the result of two or three consecutive steps that can be associated to depolymerization reactions. For all rubber samples, the first step corresponds to exothermic reactions followed immediately by endothermic reactions. Besides this, NR and SBR thermograms showed a third peak at higher temperature produced by an exothermic reaction (peaks at 458.05 and 547.66 °C respectively). For SBR analysis, two

endothermic peaks were observed in the second reaction step at a temperature between 400 and 500 °C due to the thermal degradation of SR and BR present in SBR (peaks at 426.40 and 451.05 °C). These temperatures are confirmed by SR (peak at 417.62 °C) and BR (peak at 450.53 °C) thermograms shown in Fig. 3 (b and d, respectively). Finally, a third reaction step is only presented for NR and SBR thermal degradation. A similar peak was also observed in SBR thermogram at a higher temperature (Fig. 4c). These reaction mechanisms occur at different temperatures depending on the rubber type; Table 2 shows the temperature at the maximal heat flow reached for each rubber studied. According with this table, the thermal decomposition of NR begins before than the other rubber compounds (as also observed in TGA, Fig. 2) followed by thermal degradation of BR and SBR.

Reaction Mechanisms for NR, BR and SR Pyrolysis

The final products obtained during thermal degradation of NR (cis 1,4 polyisoprene) are isoprene and dipentene (D, L limonene, 1-methyl-4-(1-methylethenyl)-cyclohexene) as was confirmed by many authors [34–36]. NR decomposes by random-chain scission with intermolecular hydrogen transfer. Danon et al. [34] suggests an initial scission of β bonds with respect to the double bonds of the main polymer chain, being the β bond energetically more favorable than α bond. The allylic radicals thus formed can propagate or unzip towards the monomer isoprene, or can also undergo an intramolecular cyclization followed by scission yielding mainly dipentene. Other possibility to explain the formation of dipentene includes dimerization of two isoprene monomers which formed a Diels–Alder type recombination reaction. However, the authors highlight that the mathematical model

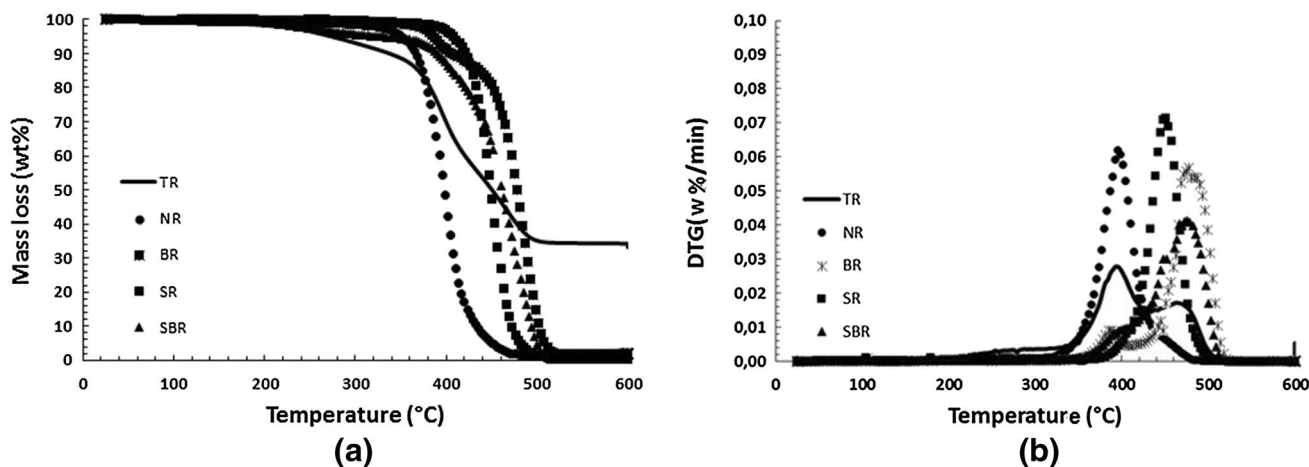


Fig. 2 a TGA and b first derivative of TGA curves of NR, BR, SR, SBR and scrap TR samples during their pyrolysis reaction at N₂ atmosphere and at a heating rate of 30 °C/min

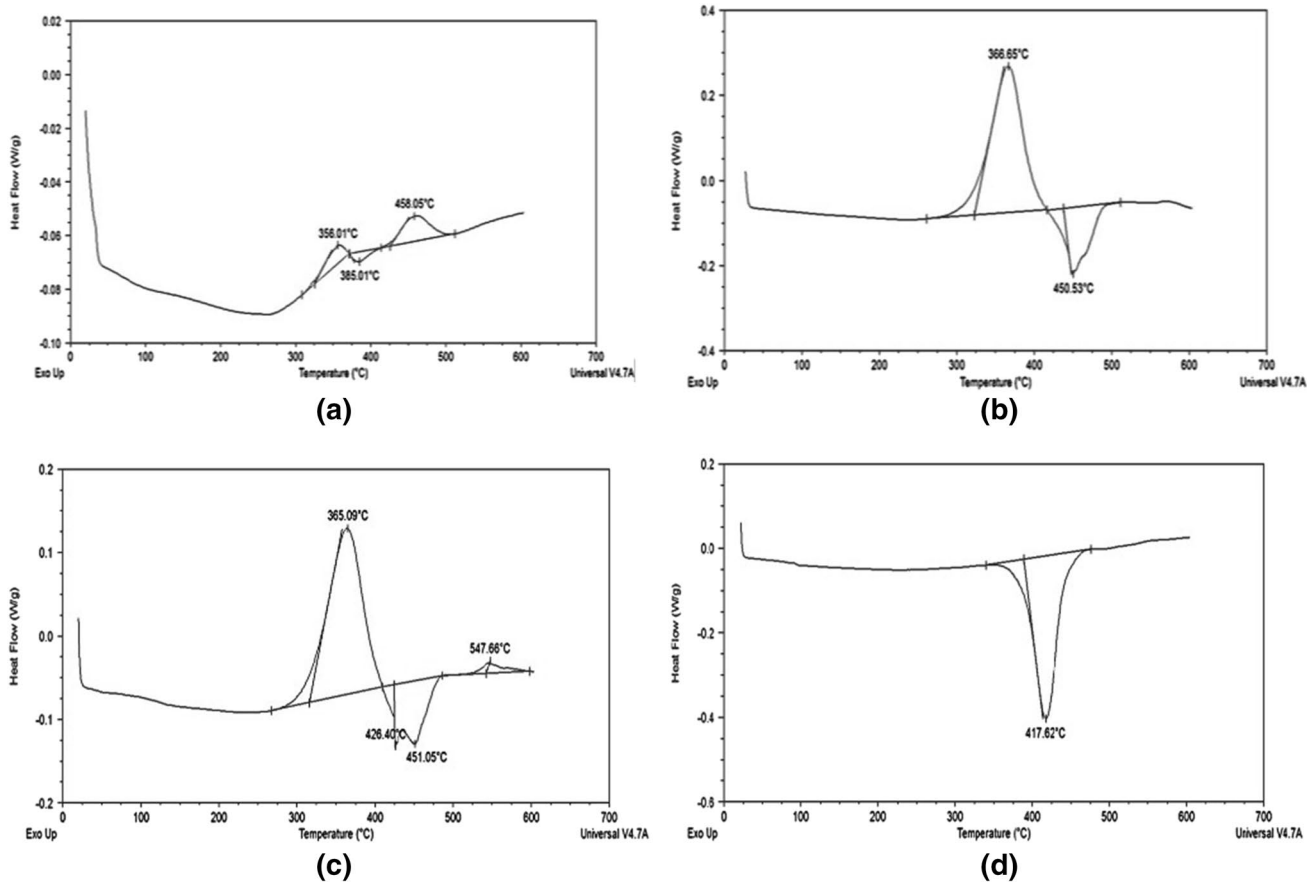


Fig. 3 DSC thermogram for the pyrolysis reaction under N₂ atmosphere at heating rate 5 °C/min of **a** NR, **b** BR, **c** SBR, and **d** SR

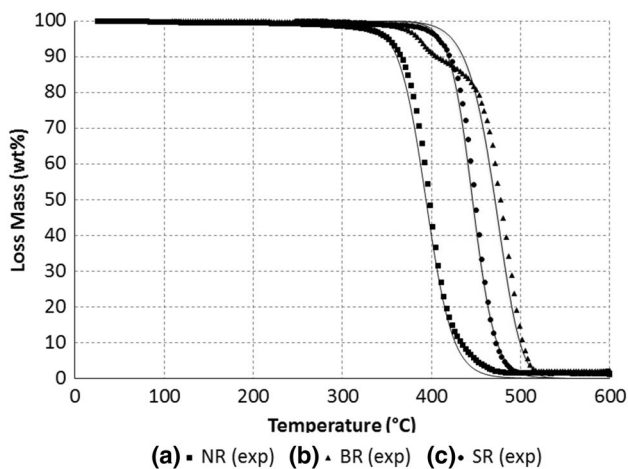


Fig. 4 Mass losses (wt%) as a function of temperature for each rubber compound simulated; **a** NR sim, **b** BR sim and **c** SR sim, and those obtained by TGA (NR TG, BR TG and SR TG)

Table 2 Temperature measured at the maximal heat flow observed in DSC analysis for each rubber

Polymer	Temperature at the maximal heat flow (°C)		
	First step (exothermic reactions)	Second step (endothermic reactions)	Third step (exothermic reactions)
NR	356.17	381.39	458.05
BR	366.65	450.53	
SBR	365.09	428.40–451.05	547.66
SR		417.62	

of dimerization of isoprene by Kar et al. [37] showed diprene as the energetically most favorable product instead of dipentene, concluding that the lack of diprene in the pyrolytic products suggests that dimerization reaction seems unlikely. On the other hand, Danon et al. [34] observed inconsistencies with the possibility of the direct formation of dipentene from polyisoprene after scission of two β bonds, with respect to

the double bonds in the main chain to forms a C10-diradical, which is subsequently isomerized to its cyclic form.

Although reaction pathway is difficult to determine, it is possible to classify the reactions involved in NR pyrolysis into three groups based on DSC data (Table 2): primary pyrolysis reaction (first DSC peak at 356 °C), secondary pyrolysis reaction (secondary DSC peak at 381 °C) and post-cracking reaction of pyrolytic volatiles (three DSC peak at 458 °C). The first could be associated to the formation of intermediate compounds as allylic radicals, which react at higher temperature by isomerization and intramolecular cyclization to produce dipentene and cyclic compounds (liquids); according with proposed by Danon and Görgens [38]. Finally, the cracking reaction is also present at the highest temperature, which can be observed by the increase of gas production.

The degradation of BR is also due by random-chain scission with intermolecular hydrogen transfer producing mainly 4 vinyl-cyclohexene and 1,3 butadiene [35, 39] as the most important cycled compound. The reaction pathway proposed by Choi [39] is like aforementioned for NR, in which the allylic radicals are initially formed, which subsequently react by isomerization and intramolecular cyclization to produce cyclic compounds. However, it is necessary to precise that, according with DSC data (Table 2), the reaction pathway could involve only the two first reaction steps proposed for the degradation of NR.

The thermal decomposition of SBR can be represented as the sum of the isolated decomposition of BR and SR (see Fig. 3b–d). Therefore, to simplify the mathematical model, the SBR was assumed as two separated compounds (BR, SR) that will be degraded. Using this approach, the amount of BR measured in SBR sample (calculated as 1.07 wt% of total mass of scrap TR) was added to the whole composition of BR in scrap TR (Table 1), and the amount of SR measured in SBR (0.35 wt% of total mass of scrap TR) was considered as an independent compound from which its decomposition was taken into account separately. This simplification should not affect the products yields calculated by the model, due to the low amount of SBR in the TR sample (1.42 wt%) which will have negligible influence on the products yields. For

SR decomposition, Peterson and Vyazovkin [40] propose a mechanism based in a thermal scission that produces a dimer, according with the data observed in DSC by an endotherm peak (at 430 °C).

The general reaction mechanism of scrap TR degradation is represented by 6 reactions represented by the Eqs. 10–15, where INR and IBR are the intermediate compounds produced during primary pyrolysis of NR and BR, respectively. LNR, LBR and LSR represent the liquid produced during secondary pyrolysis of NR, BR and primary pyrolysis of SR, respectively. Finally, GNR corresponds to gas produced by post-cracking reaction of NR.

As for NR



As for BR



As for SR



Determination of Kinetic Parameters

Table 3 shows the activation energies, pre-exponential factors and reaction orders calculated using the Bocharđ–Daniels method; the values for each step were compared with those obtained from other studies [20, 21, 41, 42]. The values calculated in this work are near to those reported by the literature, in which the activation energy (E_a) associated

Table 3 Kinetic parameters obtained by DSC data and associated to the general reaction mechanism proposed

Eq. No in the general reaction mechanism	Reaction steps	E_a (kJ/mol)	k_0^*	n
10	Primary pyrolysis reaction for NR	217.33	6.97E+12	1.77
11	Secondary pyrolysis reaction for NR	589.73	3.69E+34	1.90
12	Post-cracking reaction	333.13	9.99E+19	1.32
13	Primary pyrolysis reaction for BR	228.88	4.01E+13	1.25
14	Secondary pyrolysis reaction for BR	295.81	1.07E+17	0.94
15	Pyrolysis reaction for SBR	255.99	3.31E+16	1.43

*The unit of frequency factor depend of reaction order according with Eq. 4

to thermal decomposition of the different rubbers varies between 118 and 254, 125–270, 147–211 and 200–277 kJ/mol for NR, BR, SBR and SR, respectively.

The study performed by Danon et al. [42] using DTG and DTA to follow the devolatilization of different rubbers (NR, BR and SBR) associated to depolymerization/condensation (first weight loss) and degradation reactions (second weight loss). A third weight loss is also observed for SBR that are not observed in this study that authors attributed to the evaporation of additives. The estimated kinetic parameters for each weight loss of different rubbers are near to those obtained in this study for NR (first and second thermal events) and SBR (first thermal event). In the case of BR, the activated energy estimated in this study is far to those obtained by Danon et al. [42], but near to calculated by Seidelt et al. [20] using TG and DTG curves and Conesa and Marcilla [43], for two thermal events. For the apparent reaction orders obtained in this study, the values are in magnitude order of observed for other authors oscillating between 1 and 2 [20, 43].

Experimental Data Obtained from the Pyrolysis Pilot Unit

Table 4 shows the operating conditions, and the solid and liquid yields obtained in each test. The maximal yields obtained were 52.56, 39.50 and 7.93 wt% for solid, liquid and gas, respectively. The yields obtained in the tests are similar to those reported by some researchers [12, 44]. The results were presented in a previous research work and hence they will not be detailed in this document [1].

Table 4 Product yields obtained experimentally from pyrolysis of scrap TR sample in a fixed bed reactor, according with the factorial experimental design

Conditions			Yields (wt%)		
Test	Temperature (°C)	N ₂ flow rate (mL/min at NTP)	Oil	Char	Gas
1	400	116	12.35 ± 0.48	77.56 ± 2.26	10.08 ± 2.75
2	466		22.00 ± 1.68	64.09 ± 2.10	13.90 ± 0.41
3	533		39.94 ± 3.50	39.67 ± 3.88	20.38 ± 0.37
4	600		39.00 ± 1.20	39.90 ± 0.51	21.09 ± 0.68
5	400	155	15.22 ± 0.82	77.52 ± 1.04	7.25 ± 0.21
6	466		25.08 ± 1.97	62.05 ± 0.37	12.86 ± 1.59
7	533		37.17 ± 2.87	47.69 ± 3.05	15.14 ± 0.18
8	600		41.96 ± 0.33	38.05 ± 0.16	19.98 ± 0.17
9	400	233.3	21.60 ± 5.02	70.12 ± 3.45	8.27 ± 1.56
10	466		24.57 ± 0.31	62.52 ± 1.27	13.49 ± 0.96
11	533		38.14 ± 3.93	46.60 ± 4.64	15.25 ± 0.70
12	600		42.60 ± 1.20	37.79 ± 0.58	19.60 ± 0.61

Mathematical Model

The mass balances proposed in this study to describe the thermal decomposition of each rubber (NR, BR and SR) can be written using the Eqs. 7–9. The production rates were described according with the general reaction mechanism for the decomposition of scrap TR proposed in this study (see Eqs. 10–15), while the kinetic parameters were obtained by DSC (Table 3). The equation system involving the mass balance for each compound and the energy balance are shown in Table 5.

A first comparison was performed to determine if the proposed model represents correctly the thermal degradation of each rubber compound constituting the scrap TR. Figure 4 presents the loss mass curves obtained experimentally by TGA and compares with those predicted by the model, in which the mass balances for NR, BR and SR correspond to a discontinuous reactor (Eqs. 16, 17 and 18). As it can be observed, the thermal decomposition of NR, BR and SR is in agreement with the results observed in DSC and TGA; the first rubber compound that reacts is NR followed by BR and SR (Table 2). The results show that the model predicts quite accurately the decomposition of all rubbers, although there is a slight difference in the initial temperature of the thermal decomposition of BR between experimental and simulated values (difference of 10–20 °C, approx.). The determination (R^2) obtained were 0.97 for the three models (NR, BR and SR in Fig. 4).

Figure 5 shows a qualitative comparison of the influence of the different operational variables (as temperature and gas flow rate) on the liquid and gas yields experimentally obtained (Table 4), and those calculated for the fixed bed reactor showed in Fig. 1 in the same conditions. For the simulated data, it should be noted that the whole liquid products using to compare with the experimental data, corresponded to the sum of the partial concentrations obtained by Eqs. 21, 22 and 23 in Table 5.

In Fig. 5, the experimental data are presented in mass fraction (%wt) whereas simulated data are in molar fraction (mol%), therefore, only the trends of each variable can be comparable. It is evident that the influence of temperature (at a constant N₂ flow rate) on the product yields is represented relatively correct, especially for the liquid fractions. In addition, for the influence of the N₂ flow rate (at constant temperature), the product yield predicted by the model seems to be not affected by this variable which is opposite to the behavior observed experimentally.

An ANOVA was performed on simulated data obtained by the fixed bed reactor model, using the forward selection function present in the Statgraphics software. This function allows adjusting a polynomial model using multiple regression analysis in which only the most significant variables and the interaction between them are included. Equations 26 and

Table 5 Mass and energy balances for TR pyrolysis in a non-isothermal fixed bed reactor

Mass balances (mol/m ³ s)		
Eq.	Compound	
(16)	NR	$\left(\frac{dC_{NR}}{dt}\right) = -k_1 C_{NR}^{1.77}$
(17)	BR	$\left(\frac{dC_{BR}}{dt}\right) = -k_4 C_{BR}^{1.25}$
(18)	SBR	$\left(\frac{dC_{SBR}}{dt}\right) = -k_6 C_{SBR}^{1.43}$
(19)	Intermediate in NR pyrolysis (INR)	$\left(\frac{dC_{INR}}{dt}\right) = k_1 C_{NR}^{1.77} - k_2 C_{INR}^{1.9} - k_3 C_{INR}^{1.32}$
(20)	Intermediate in BR pyrolysis (IBR)	$\left(\frac{dC_{IBR}}{dt}\right) = k_4 C_{BR}^{1.25} - k_5 C_{IBR}^{0.94}$
(21)	Liquids from NR (LNR)	$\left(\frac{\partial C_{LNR}}{\partial t}\right) + v_z \left(\frac{\partial C_{LNR}}{\partial z}\right) = k_2 C_{INR}^{1.9}$
(22)	Liquids from BR (LBR)	$\left(\frac{\partial C_{LBR}}{\partial t}\right) + v_z \left(\frac{\partial C_{LBR}}{\partial z}\right) = k_5 C_{IBR}^{0.94}$
(23)	Liquids from SBR (LSBR)	$\left(\frac{\partial C_{LSBR}}{\partial t}\right) + v_z \left(\frac{\partial C_{LSBR}}{\partial z}\right) = k_6 C_{SBR}^{1.43}$
(24)	Gases from NR (GNR)	$\left(\frac{\partial C_{GNR}}{\partial t}\right) + v_z \left(\frac{\partial C_{GNR}}{\partial z}\right) = k_3 C_{INR}^{1.32}$
Energy balance (°C/s)		
(25)		$\frac{dT}{dt} = 0, 5$

27 represent the regression model with the best adjustment for the liquid and gas yields, respectively. Table 6 shows the ANOVA obtained for each polynomial model and Table 7 shows the p-value and t-statistic for each significant variable. The results show that the temperature is the most significant variable in the process at 95% of confidence level, according with those observed in previous studies performed using the same type of experimental unit and feedstocks [3, 27]. In addition, ANOVA showed that these models represent at 89.27% and 73.38% the variability of simulated data (R^2).

$$\%Yield_{Liq.}(wt\%) = -58.0203 + 0.155375 \times T[^\circ C] \quad (26)$$

$$\%Yield_{Gas.}(wt\%) = -98.6202 + 0.284598 \times T[^\circ C] \quad (27)$$

The low influence of the gas flow rate in the simulated product yield could be explained considering the restrictions included in the model. The reaction mechanism proposed in this study considers the production of gas only for the NR decomposition (see Eq. 12); however, the difference between simulated and experimental data for the gas yield is more important at high temperature, where the secondary cracking reaction takes place during the thermal decomposition process, causing a decrease in the liquid yield and producing gas [45, 46]. This suggests that the model proposed in this study could be completed including additional steps associated with this type of cracking reactions in the reaction mechanism. Furthermore, the gas velocity associated with the convective term in the mass balance was assumed constant during all the time that the reaction occurs. This supposition is not exactly because the gas velocity could

be decreasing during the reaction, due to the changing in the bed porosity as consequence of the solid decomposition. Even so, this imprecision in the model could not be important since the statistical analysis of the experimental data presented by Acosta et al. [1] in previous studies (which were performed with the same experimental unit and feedstocks), showed that there is not a statistically significant influence of the gas flow rate on the product yields.

Figure 6 illustrates the concentration profiles simulated for all the species present in the pyrolysis of scrap TR (which corresponds to the sum of the three rubber compounds simulated NR, BR and SR) at 600 °C and 155 Nm³/min for the first 20 min of the reaction in the fixed bed reactor showed in Fig. 1. The concentration profiles show that the pyrolysis takes place very fast. The scrap TR sample begins its thermal degradation after 11 min of reaction, however, the maximal liquid production (which corresponds to the sum of all the liquid compounds described in Eqs. 21–23 in Table 5) is obtained only after 18 min of reaction due to the total consumption of the intermediate compounds. The concentration of the end products (liquid and gas) in Fig. 6 corresponds to the values accumulated.

Conclusions

Proximate analysis of all rubber samples (NR, BR, SBR, SR and TR) and the pyrolysis test performed using TGA allowed determining that the pyrolytic solid residue obtained

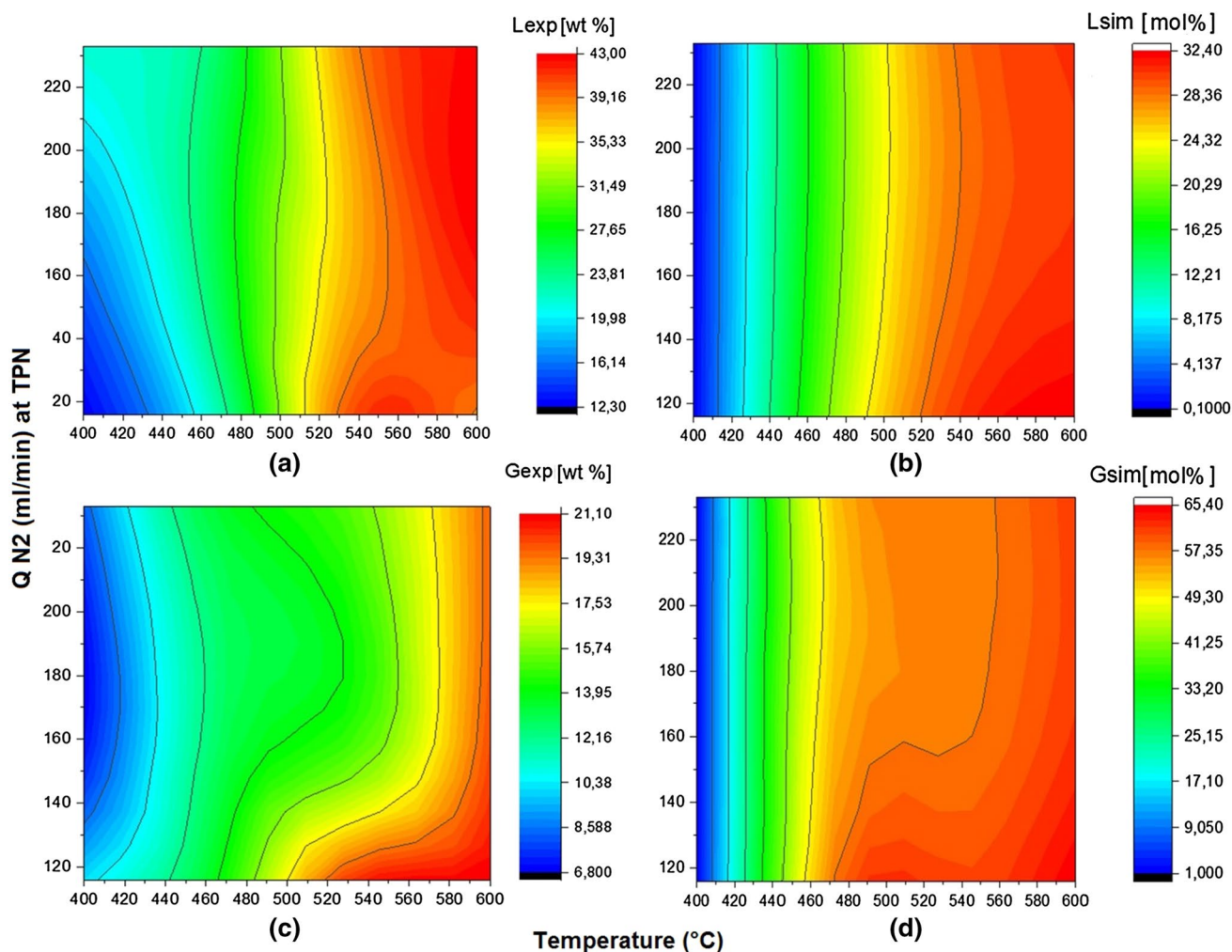


Fig. 5 a Liquid and c gas experimental yield (wt%); and b liquid and d gas simulated yield (mol%) as a function of temperature (T; °C) and gas flow rate (Q; ml/min—at TPN)

Table 6 ANOVA analysis of simulated data for the mathematical model of scrap TR pyrolysis in a fixed bed reactor

Product	Source	Sq. sum	Df	Mean Sq	F value	p value
Liquid Equation (19)	Model	1611.06	1	1611.06	83.22	0.0000
	Residuals	193.593	10	19.3593		
	Total (corr.)	1804.65	11			
Gas Equation (20)	Model	5405.2	1	5405.2	27.57	0.0004
	Residuals	1960.81	10	196.081		
	Total (corr.)	7366.0	11			

Table 7 p-Value and t-statistic for temperature as significant variable according with ANOVA

Product	Source	Mean	Std error	t-statistic	p value
Liquid Eq. (26)	Constant	-58.0203	8.60609	-6.74178	0.0001
	Temperature (°C)	0.155375	0.0170322	9.12243	0.0000
Gas Eq. (27)	Constant	-98.6202	27.3891	-3.60071	0.0048
	Temperature (°C)	0.284598	0.0542055	5.25035	0.0004

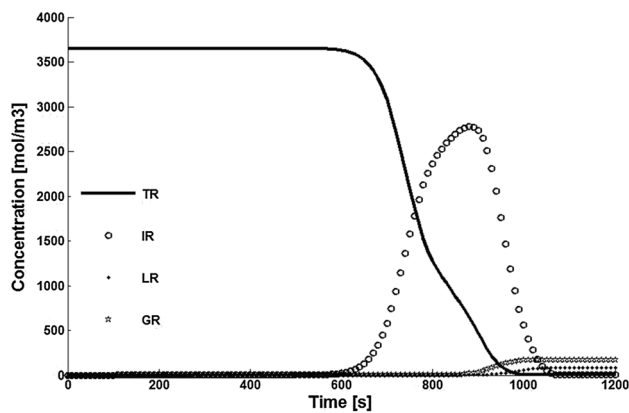


Fig. 6 Concentration profiles simulated for scrap TR in the pyrolysis (corresponds to the sum of the three rubber compounds simulated NR, BR and SR), ITR (corresponds to the sum of all intermediate compounds described in Eqs. 9–14), LTR (corresponds to the sum of all liquid compounds described in Eqs. 9–14) and GTR (corresponds to the sum of all gas compounds described in Eqs. 9–14)

after the pyrolysis of scrap TR sample corresponds mainly to carbon black that was not transformed during the process. Therefore, the pyrolytic oil and gasses yields come exclusively from the rubber compounds of scrap TR.

The general reaction mechanism proposed in this study is constituted by six reaction steps; three associated to a primary pyrolysis (exothermic), two, a secondary pyrolysis (endothermic) and one to a post-cracking reaction (exothermic, it was observed for NR and SBR), as the result of two or three main steps suggested in DSC analysis. The kinetic parameters associated with the general reaction mechanism are in agreement with the literature for the first reaction step (cyclization-crosslinking reactions).

A first comparison between the loss mass curves obtained experimentally by TGA and those predicted by the model showed that the model predicts quite accurately the decomposition of all rubbers (R^2 evaluated in 0.97), although there is a slight difference in the initial temperature of the thermal decomposition of BR between experimental and simulated values.

A qualitative comparison of the influence of temperature and gas flow rate on the liquid and gas yields experimentally obtained, and those calculated by the model for the fixed bed reactor at the same conditions, showed a strong influence of temperature on the product yields (which agrees with ANOVA; t -value < 0.001 at confidence level of 95%) whereas they seem not to be affected by the N_2 flow rate, which is opposite to the behaviour observed experimentally.

According with the model for the fixed bed reactor proposed in this study at 600 °C, the scrap TR begins its thermal degradation after 11 min of reaction obtaining a maximal liquid production at a reaction time of 18 min, where occurs the total consumption of the intermediate compounds.

Acknowledgements The authors are grateful to *Vicerrectoría de Investigación y Extensión* from Universidad Industrial de Santander for research funding (Grant number 5457). Y. Cely is grateful to *Colciencias* for the Young Researcher scholarship.

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