Maximization of the oil and aromatics yields obtained from pyrolysis of scrap tire rubber

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Abstract

This research study reveals the results of the experimental study of the scrap tire rubber pyrolysis in a fixed bed tubular reactor for the maximization of pyrolytic oil and aromatic compounds of high industrial value present in the oil (benzene, toluene, xylenes, alkylbenzenes and cymenes). An experimental 4x3 design was performed using as dependent factors: temperature and nitrogen flow. A maximum oil yield of 42.6 wt% was obtained at an operating temperature of 600 °C and a nitrogen volumetric flow of 233 Nml/min. As for the main compounds of the oil, a maximum yield of aromatics was found at 466 °C and a nitrogen volumetric flow of 155 Nml/min. ANOVA showed that temperature is the most influential variable on the oil yield, while the nitrogen volumetric flow did not present any statistical significance on it. On contrary, in the case of aromatic yield, ANOVA showed that both the temperature and the nitrogen volumetric flow had an influence on it. On average, an oil fraction with a density of 850.8 kg/m^3 was obtained, its calorific value was higher than 42.12 MJ/kg, and its acidity of 0.789 mg KOH/g.

1. Introduction

Since the 1990s, different operating variables have been studied to evaluate their influence on the production of pyrolytic oil during the pyrolysis of scrap tire rubber (STR). Different variables such as pressure, temperature, heating rate, particle size, gas volumetric flow and reaction time have been evaluated. However, due to the STR pyrolysis is an endothermic process [1–4], the temperature has a significant effect on the oil yield and its composition contrary on other variables as pressure, heating rate and particle size [5–9].

Many research studies [10], [11], [12] performed in a fixed bed tubular reactor showed that the liquid yield increases as the operating temperature increases until obtaining a maximum value. Besides, in the case of Fernandez *et al.* [11], they observed that as temperature increase as the gas and pyrolytic oil yields increase and the solid yield decreases. González *et al.* [12] observed that once the maximum pyrolytic oil yield is reached, this decreases constantly with the temperature as a consequence of the cracking reactions promoting at a higher operating temperature and thereby, favoring the production of gas despite liquids compounds. For all studies, the temperature was observed as the most influential operating variable allowing to obtain a maximum pyrolytic oil yield was close to 50-55 wt%.

The pyrolytic oil yield can increase even more reducing and control the cracking reactions. To make it, the inclusion of an inert carrier on the pyrolysis process has been studied. Thus, a new operating variable, the gas flow, must be considered because it has a direct influence on the surface velocity and residence time of the volatile compounds produced during the pyrolysis process. It is known that larger flows allow evacuating fastly the vapors out of the reaction zone and, thereby, minimize secondary reactions [12]. Martínez *et al.* [13] mentioned that several authors have concluded that high residence times might favor some secondary reactions, such as cracking and polymerization, which affect the distribution and composition of char, pyrolytic oil, and gas.

Therefore, although many authors [12–15] claimed that the composition of the pyrolytic oil can also be influenced by the residence time of the volatile compounds in the reactor, there are not the complete studies have been carried out to evaluate this parameter and its interaction with the operating temperature. The previous studies [14, 16] show that the pyrolytic oil of STR is constituted by a mixture of aromatic hydrocarbons, olefin, and paraffin, sulfur and nitrogen compounds. Of these compounds, there are some with a higher additional value as BTX aromatics (*i.e.* benzene, toluene, xylenes), cymenes and unsaturated cyclic hydrocarbons as limonene. The firsts used at industrial level in applications as plastics chemical synthesis, synthetic rubbers, paints, pigments,

explosives, pesticides, detergents and perfumes and as solvents; and the last ones used in the manufacture of flavors, fragrances, cleaning agents, degreasing agents and they are used as solvent and in a variety of household applications [17, 18].

It is worth noting that, although the STR pyrolysis has been widely studied in recent times [19–23], those were focused mainly on pyrolytic oil production or activated carbon, and very few of them aimed to the production of valuable compounds in the oil such as aromatics. The results of these previous researchers on STR pyrolysis show a maximum concentration of benzene, toluene, and xylenes in pyrolytic oil of 1, 1 and 4 wt %, respectively [20, 24–26]. Therefore, this research study is focused on the determination of the optimal operating conditions to obtain the maximum oil yield and aromatics yield, as a starting point for its valorization. The experimental study was performed by a design of experiments (DoE) 4x3 and using the response surface methodology. Two important variables were studied: temperature and nitrogen volumetric flow (residence time)**.** The range of temperatures and residence times were established according to the results found in previous research studies for STR pyrolysis in fixed bed reactors [10–12].

2. Materials and Methods

2.1. Description of the pilot unit

The pilot pyrolysis unit used in the development of the experimental tests is detailed in Fig 1. The system consists of four zones: the gas inlet (1), a heating zone in which the pyrolysis reaction is performed (2), a condensation zone (3) and a gas collection and outlet zone (4).

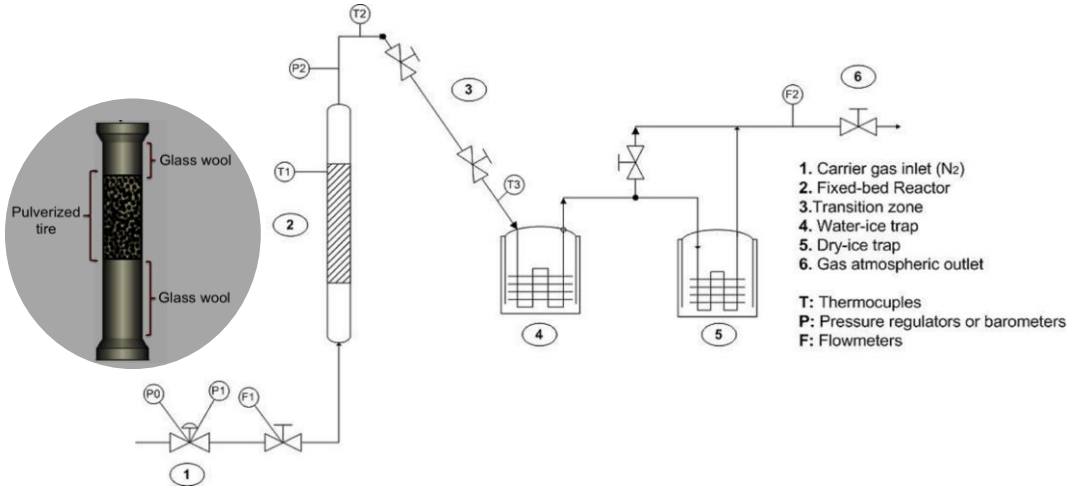


Fig. 1 The pyrolysis system at laboratory-scale: (1) the gas supply section, (2) the reaction section with a fixed bed reactor, (3) the cooling zone, and (4) the gas evacuation zone.

The carrier gas (Nitrogen UAP grade 5.0, Cryogas) (1) is fed at the bottom of the reactor (2) at constant flowmeter operating in the 40-500 mL/min range (at TPN). The reactor is a vertical tubular reactor made of 316 L stainless steel (54 cm length; 3.5 and 3.9 cm internal and external diameters, respectively); the crushed STR (particle diameter <1 mm) is placed inside it. The tubular reactor has two grids, one inlet, and one outlet to prevent the entrainment of solid material. This was heated by a tubular furnace equipped with an electric resistance with a maximum power of 2400W to 220V which allows a heating rate of approximately 30 °C/min. The tubular furnace has a thermocouple that measures the reactor wall temperature.

The reactor was charged before pyrolysis tests as shown in Fig. 1, using glass wool in the lower zone, and STR in the highest zone. This configuration was chosen to minimize the residence time of the volatile compounds produced during the reaction and ensure their condensation only in the cooling trap. The mass of STR was calculated according to the bulk density of the material to obtain a length of the fixed bed of 20 cm.

The gas produced leaves at the top of the reactor toward a cooling zone (3), this zone has a heating cord which avoids the condensation in the tubing and their return to the reactor. Subsequently, they are directed to the gas cooling system, composed of two cooling traps made of stainless steel, hermetically sealed. The first trap is cooled with ice and the second with dry ice. In the cooling traps, the pyrolytic oil is recovered from the condensation of the volatile compounds present in the gas. The non-condensable gas passes through a mass flowmeter before being

evacuated into the atmosphere (4). The gas flowmeter (Cole-Parmer, range 0-1280 ml/min at TPN) at the outlet was regulated to assure a relative pressure of 100 kPa in the system.

2.2. Raw material

The raw material used in this study was obtained from a crushing plant in the city of Medellín - Colombia. The particle size was selected according to the results obtained in a previous study [7]. The STR sample of this study is composed of 50 wt% of natural rubber (NR), 14.72 wt% of butadiene rubber (BR) and 1.44 wt% styrene-butadiene rubber (SBR) [7], which according to literature, corresponds to a truck tire [27, 28].

2.3. Experimental development

The response surface method was used to maximize the pyrolytic oil and aromatics yields. Two multifactorial design of experiment (DoE) (4x3) was performed using as independent variables: temperature *(T)* and nitrogen volumetric flow (Q_{N_2}). The set of tests considered a range of operating conditions indicated as good conditions to produce liquid according to the experimental studies performed by other authors aforementioned. Thus, the temperature was evaluated in four levels (400 – 600ºC) and nitrogen volumetric flow in 3 levels (116 – 233 ml/min at TPN). Takin into account that the gas residence time is influenced by the nitrogen volumetric flow according to literature [14, 28], the analysis was also done using the residence times. The gas residence time was calculated following Equation (1). The range of Q_{N_2} allowed residence times between 10 and 28 s.

$$\boldsymbol{\tau = \left(1 - P_p\right)\left(\frac{A_{reactor} * h}{Q_{N_2}}\right)} \qquad (1)$$

Where: $\tau = \text{Residence Time [s]}$, $P_p = \text{Porosity of fixed bed } (\rho_{bulk}/\rho_{real})$,
$A_{reactor} = \text{Cross} - \text{sectional area of the reactor [cm}^2\text{]}$, $h = \text{Bed height[cm]}$,
$Q_{N_2} = \text{Nitrogen volumetric flow at the temperature and pressure of the reactor [ml/min]}$

To STR samples, with a range of particle size varied between 0.85 and 1mm, their real and bulk densities measured were 511.9 and 347.7 kg/m^3, respectively.

A total of twelve tests for each experimental plan were performed (P1.0-P12.0) with their respective duplicates. The tests were carried out at a constant pressure of 1 bar (g) and a reaction time of 2h [7]. During each test, the volumetric flow, pressure, and temperature of the reaction mixture and synthesis gases were recorded each 2 min. The range of operating conditions used in this DoE is presented in Table 1.

Table 1. The range of operating conditions used in two multifactorial designs of experiments 4x3 performed in this study.

Variable 1: Temperature (°C)	Variable 2: Q_{N_2} (ml/min at TPN)	Response variable 1 (wt %)	Response variable 2 (wt %)
400	116		
466	155	Pyrolytic oil yield	Aromatic compounds yield
533	233		
600			

For each test, the initial and final weight of the solid sample, wool and traps plates of the cooling zone were recorded in order to calculate the products yields according to Equation (2). The mass of pyrolytic oil and char were determined by gravimetry, whereas the mass of the gas was calculated by mass balance once the possible leaks in the pyrolysis system were minimized. Therefore, a leak test was performed before each test isolating de pyrolysis system with nitrogen at 300 kPa (relative) for 10h, approximately, in which the pressure loss was monitored. The leaks were considered negligible and the experimental test could begin only if the pressure loss during the leak test time was lower than 10%.

$$\boldsymbol{Product\ yield\ [wt\%] = \frac{\text{Mass of product}}{\text{Initial mass of the STR sample}} * 100} \qquad (2)$$

An ANOVA was performed to determine the significance and influence of the variables in the pyrolytic oil and aromatic yield using Statgraphics Centurion Software. On the other hand, according to different authors [28, 29], it was found that the major compound in the pyrolytic oil is limonene, therefore it is decided to quantify this compound as well. The yields of both aromatics compounds and limonene were calculated, based on the concentration of them in the pyrolytic oil, and also the pyrolytic oil yield obtained at each operating condition, according to Equation 3 [30].

$$\boldsymbol{Compound\ yield}\ [wt\%] = \textbf{Mass fraction of compound} * \textbf{Oil yield}\ [\ \textbf{wt}\%] \quad (3)$$

2.4. Characterization of pyrolytic oil

The pyrolytic oil was characterized by determination of High heating value (HHV), real density and acidity. The HHV determination was done in a calorimetric pump Parr 6200 following the ASTM D-4809 and ASTM D-5865 standards [31, 32]. The real density was determined by gravimetry using a pycnometer of 1 mL. The acidity was measured by an acid-base titration with sodium hydroxide according to the standard UNE-EN ISO 660 [33].
The chemical characterization of the pyrolytic oil was first performed by GC/MS (7890A Agilent Technologies). The compounds that could not be identified by GC/MS were identified by GC/FID using standards. In both cases, an HP-5 column (29.5 m x 0.320 mm x 0.25 μm) was used. The method was programmed as follow: the GC oven temperature was programmed from 50°C (2 min) to 290°C at 5°C/min and held at 290°C for 2 min. The injector and detector temperatures were 250 and 280°C, respectively. The injection split ratio was fixed at 1:100. For the analysis, the oil samples were filtered and diluted to 20 wt% in n-pentane.
Once the retention times of different compounds were determined, the quantification was performed using an external standard technique (n-heptane). The relative response factors (RRF) of the compounds were calculated having the concept of the effective carbon number (ECN) reported by Katrizky et al. [34] and Scanlon & Willis [35]. The ECN was calculated from the heteroatoms and functional groups according to the contributions of each heteroatom reported by Scalon & Willis [35]. The response factors were then calculated with Equation 4 [34, 35], using as standard material n-heptane, and obtaining RRF of 0.91 for benzene, 0.92 for toluene, 0.93 for ethylbenzene and xylenes, 0.94 for cymenes and 0.95 for limonene.

$$RRF = \frac{(\text{MW of compound})(\text{ECN of standard})}{(\text{MW of standard})(\text{ECN of compound})} \quad (4)$$

3. Results and discussion

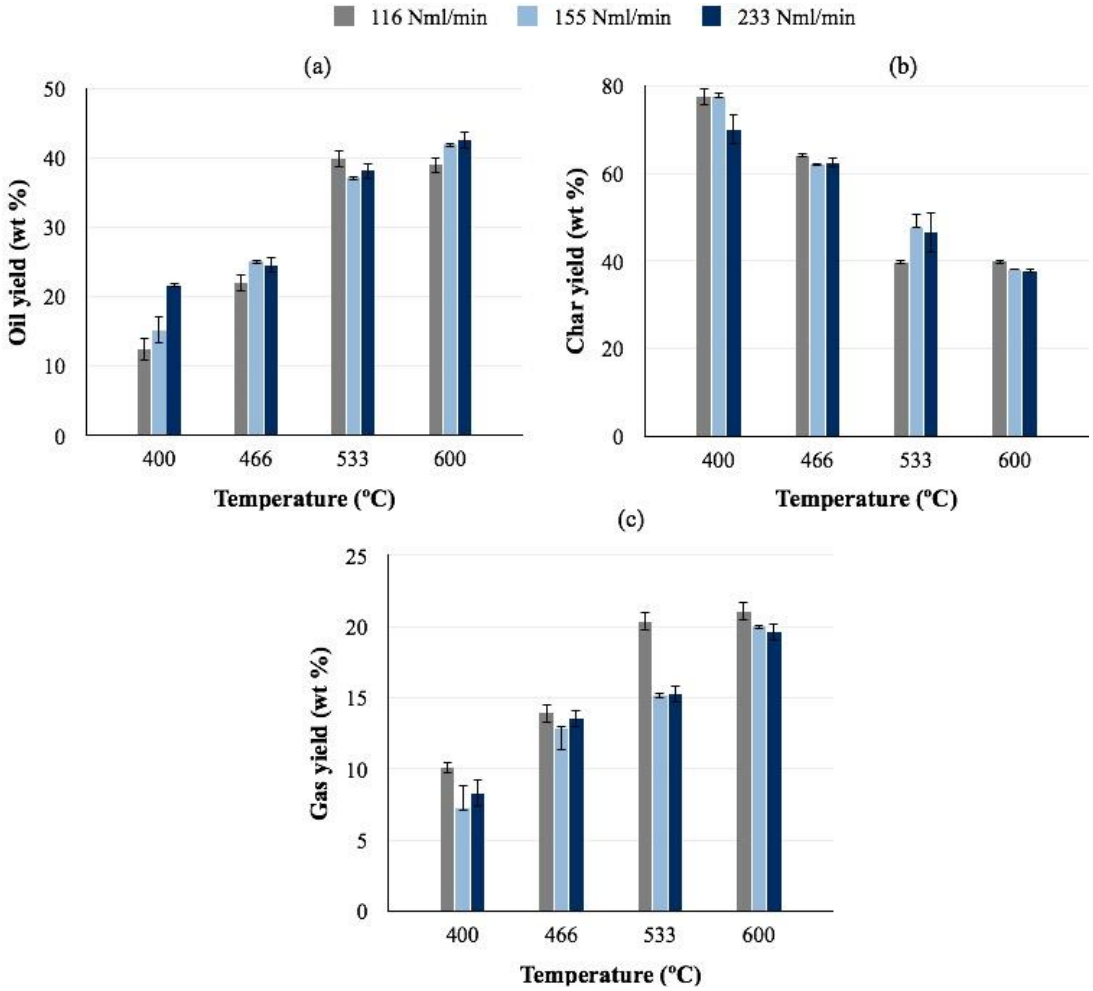
3.1 Products Yields

The product yields (pyrolytic oil, gas, and char) for all experimental tests are shown in Table 2. The reported values correspond to the average between two tests made for each point, all standard deviations being lower than 5 wt%. It is seen that the highest pyrolytic oil yield (42.60 wt%) was obtained at 600 °C using a nitrogen volumetric flow of 233 ml/min at TPN. Regarding the oil yields obtained by different authors, some variations on the temperature of maximum oil yield are observed. For instance, Berrueco *et al.* [36] obtained the maximum oil yield (42.8 wt%) at 700 ºC, a value very close to that observed in this study. Islam *et al.*[14] obtained a maximum of oil yield (49.13 wt%) at 475 ºC, and De Marco Rodriguez *et al.* [37] obtained a maximum oil yield of 38.5 wt% at 700 ºC. The differences in the values observed could be influenced by variables, non-analyzed in this study, which could promote (or not) the secondary reactions, such as the tire type, its composition, its particle size and the reactor dimensions [38]. Specifically, in the case of a secondary reaction, the authors mention that high temperatures are not suitable since at these conditions the cracking and polymerization reactions of the volatile compounds are favored, producing non-condensable gases and solid carbon polycondensates [38].

Fig. 2 shows the trend found for the yield of each product at different temperatures and nitrogen volumetric flow. In each product, it can be observed with slight differences when the nitrogen flow is varied, while marked differences can be found with the increase in temperature. This trend is due to the STR pyrolysis is an endothermic process, and the temperature has an important effect on the distribution and product composition, which is why it becomes the most influential and studied variable by different authors [2, 28].

Table 2. Yields obtained at different operating conditions of the DoE.

Test	T (°C)	Q_{N_2} (ml/min at TPN)	τ (s)	Yield (wt%)		
				Oil	Char	Gas
P1.0	400	116	28.27	12,35±0,48	77,56±2,26	10,08±2,75
P2.0	466	116	25.74	22,00±1,68	64,09±2,10	13,90±0,41
P3.0	533	116	23.60	39,94±3,50	39,67±3,88	20,38±0,37
P4.0	600	116	21.79	39,00±1,20	39,90±0,51	21,09±0,68
P5.0	400	155	21.16	15,22±0,82	77,52±1,04	7,25±0,21
P6.0	466	155	19.27	25,08±1,97	62,05±0,37	12,86±1,59
P7.0	533	155	17.67	37,17±2,87	47,69±3,05	15,14±0,18
P8.0	600	155	16.31	41,96±0,33	38,05±0,16	19,98±0,17
P9.0	400	233	14.07	21,60±5,02	70,12±3,45	8,27±1,56
P10.0	466	233	12.82	24,57±0,31	62,52±1,27	13,49±0,96
P11.0	533	233	11.75	38,14±3,93	46,60±4,64	15,25±0,70
P12.0	600	233	10.85	**42,60±1,20**	37,79±0,58	19,60±0,61



* Gas volumetric flow is given in Nml/min corresponding to standard operating conditions (*i.e.* at TPN).

Fig. 2 Yields at different conditions of temperatures and nitrogen volumetric flow: (a) Pyrolytic oil yield, (b) Char yield and (c) Gas yield.

Specifically, it was found that the pyrolytic oil and gas yields increase as the temperature increases, while the char yield decreases. Some authors reported that the increase in temperature allows an increase in the pyrolytic oil yield, due to the decomposition of the natural rubber, butadiene rubber, and styrene-butadiene rubber in lower molecular weight compounds [26, 39]. It is worth noting that the lower pyrolytic oil yield is obtained in most of the tests performed at lowest nitrogen volumetric flow. On the other hand, the results show that at the same temperature the increase in nitrogen flow leads to marked increases in oil yield, and slight decreases in char and gas yields. According to Islam *et al.* [14], a lower nitrogen volumetric flow (inert gas) means a longer residence time of the volatiles in the hot zone, favoring the secondary reactions causing a decrease of the pyrolytic oil. This trend is also found in this study, in which at a maximum residence time (400 ° C and 116 ml/min at TPN), the lowest pyrolytic oil yields and higher char yields are obtained whereas, at a minimum gas residence time (600 ºC and 233 ml/min at TPN), the maximum pyrolytic oil yield and minimum gas yield were obtained. Although the gas yield increases with the temperature, mainly due to the effect of the temperature that favors the cracking reactions, a possible effect of the nitrogen volumetric flow could also be presented. Regarding Fig. 2 for each temperature, a seeming decrease of gas yield can be observed when increasing the nitrogen volumetric flow (which means a decrease in residence time), and this effect is more noticeable between 116 and 155 ml/min at TPN. This means that, as other authors have mentioned, as the residence time of the volatiles in the reaction zone decreases, as the gas yield decreases too and the oil yield increases [14].

In addition, at 533 °C, a deviation of the trend of the char yield when the nitrogen volumetric flow was increased. On the other hand, at this temperature, it can be seen that the gas yield presents a noticeable decrease in higher nitrogen volumetric flows. This can be explained by possible polymerization reactions taking place at the same time of cracking reaction.

3.2 Analysis of Varianza (ANOVA) for the oil yield

To determine the significance and influence of each variable in the pyrolytic oil yield an ANOVA was performed using Statgraphics Centurion software. For the analysis, the dependent variables and their possible interactions were considered. The summary of ANOVA with a confidence level to 95% using multiple linear regression models to fit the experimental data is shown in Table 3. According to the analysis, the model has a good fit with an R-squared statistic explaining near to 91% of the variation in the responses. Besides, the standard error of the estimate shows that the standard deviation of the residuals is approx. 3.5.

Table 3. ANOVA; Sum of squares type III for pyrolytic oil yield with all factors and their interaction.

Source	Sum of squares	DF	Middle Square	*F*-Value	*p*-Value
T	90.0938	1	90.0938	7.04	0.0162
$\boldsymbol{Q}_{N_2}$	13.2439	1	13.2439	1.03	0.3226
T*$\boldsymbol{Q}_{N_2}$	24.2664	1	24.2664	1.90	0.1855
T^2	33.5121	1	33.5121	2.62	0.1231
$(\boldsymbol{Q}_{N_2})^2$	0.828008	1	0.828008	0.06	0.8021
Residue	230.455	18	12.8031		
Total (corrected)	2706.61	23			

R-square = 91.4855 %
R-square (adjusted by DF) = 89.1203 %
Standard error of estimate = 3.57814
Absolute mean error = 2.28756
Durbin-Watson statistic = 2.71009 (P=0.8823)

Furthermore, it is observed that the most influential variable was the temperature (*p*-value of 0.0162) whereas the change on the nitrogen volumetric flow and the interactions between this operating variable and the temperature are not significant on pyrolytic oil yield. This result is in agreement with various previous investigations, which concluded that the temperature is the most important parameter having an influence on the yield and composition of pyrolytic oil due to the endothermic reactions involved in STR pyrolysis process [26, 38]. On the other hand,

the general trend observed for pyrolysis oil yield at different gas volumetric flow rates agreed with the results observed in other studies using waste biomass as a feedstock [40].

The highest *p*-value was 0.8021, which corresponds to $(Q_{N_2})^2$ interaction. Since the p-value is greater than 0.05, that term is not statistically significant at a confidence level of 95.0%. Therefore, a new analysis was performed by removing $(Q_{N_2})^2$ variable and finding a new model in which the highest *p*-value was 0.0802, corresponding to Q_{N_2} variable. Since the *p*-value is greater than or equal to 0.05, that term is not statistically significant with a confidence level of 95.0%, therefore it is considered to eliminate Q_{N_2} from the model. In this case, the R-Square calculated for the last analysis was 93.25%; that is greater than the previous analysis. According to this analysis, the effect of variable Q_{N_2} on the oil yield can be definitively discarded. Although Q_{N_2} does not have a significant individual effect, it could have an effect when it interacts with the other variable, for thus a new analysis of variance by eliminating Q_{N_2} is performed to discard this interaction.

The new analysis shows that the variables *T*, (T*Q_{N_2}) and T^2 have a statistically significant effect (*p*-value ≤0.05). The results of this last analysis performed is shown in the Table 4.

To improve the fitting of experimental data and predict pyrolytic oil yield as a function of temperature and nitrogen volumetric flow, a mathematical model adjustment was proposed, using the effects that were obtained as significant on the response.

Table 4. Analysis of variance ANOVA Sum of squares type III for oil yield eliminating $\boldsymbol{Q_{N_2}}$ and ($\boldsymbol{Q_{N_2}}$)$^{\boldsymbol{2}}$ of the model.

Source	**Sum of squares**	***DF***	***Middle Square***	***F-Value***	***p-Value***
T	222.364	1	222.364	19.85	0.0003
T*Q_{N_2}	76.6613	1	76.6613	6.84	0.0175
T^2	109.352	1	109.352	9.76	0.0059
Residue	2.43469	1	2.43469		
Total (corrected)	201.687	18	11.2048		
R-Squared = 93.2477 %					
R-Squared (adjusted by DF= 91.3721 %					
Standard Error of estimate = 3.34736					
Absolute mean error = 2.2381					
Durbin-Watson Statistic = 2.53107 (P=0.7739)					
The mean error (ME)					
The mean error rate (MPE)					

The model thus obtained to describe the oil yield as a function of temperature *(T)* and nitrogen volumetric flow (Q_{N_2}) is presented in Equation 5.

$$\text{Oil yield (wt\%)} = 0.3909\,T + 0.0000495\,T * Q_{N_2} - 0.000266\,T^2 - 101.71 \qquad (5)$$

Using the experimental results and the proposed model (Equation 5), was elaborated the surface response (Fig. 3-(a)). These show the combined influence of the two variables (temperature and nitrogen volumetric flow) on the pyrolytic oil yield. According to Fig. 3-(a), the highest pyrolytic oil yields are obtained at temperatures between 530 – 600 ºC.

Furthermore, it is observed that the pyrolytic oil yield changes considerably with the temperature, being this variable the most influential as aforementioned. On the contrary, the nitrogen volumetric flow has a higher influence at a lower temperature than at higher one, in which the effect on pyrolytic oil yield is slight. In other words, at lower and higher temperatures, the pyrolytic oil yield increases when the volumetric gas flow rate increases too (indicating that it decreases with gas residence time). This phenomenon can be explained by the presence of cracking reactions that are favored at higher gas residence times [36, 41].

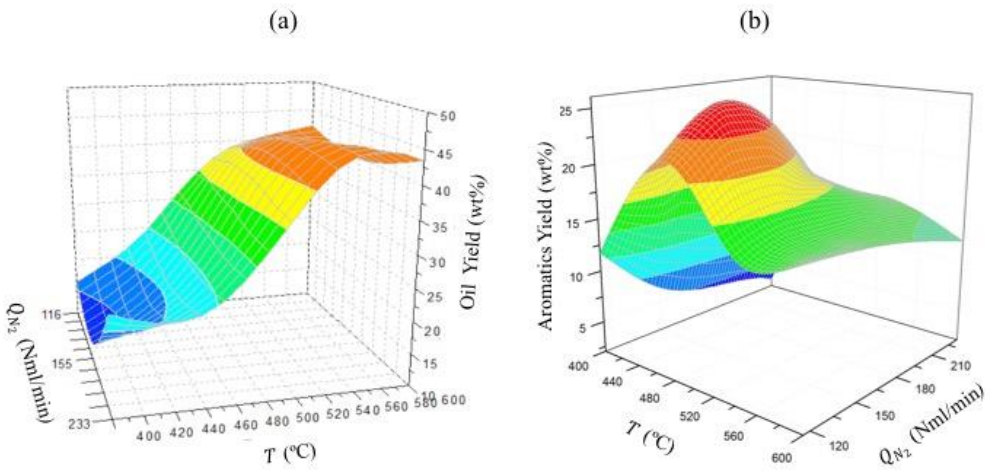


Fig. 3 The surface response to the effect of *T* and $\boldsymbol{Q_{N_2}}$ on: (a) pyrolytic oil yield and (b) Aromatics yield.

3.3 Characterization of pyrolytic oil

The pyrolytic oils densities and HHV obtained in each test in the experimental plan do not show changes in the different conditions of temperature and nitrogen volumetric. The average pyrolytic oil density was 0.85 ± 0.01 g/ml, the value that is in agreement with those reported by some authors [42]. On the other hand, the density of this pyrolytic oil is close to the commercial diesel fuel range (about 0.845 g/ml) [42], and a little higher than gasoline (about 0.7 g/ml) [43].

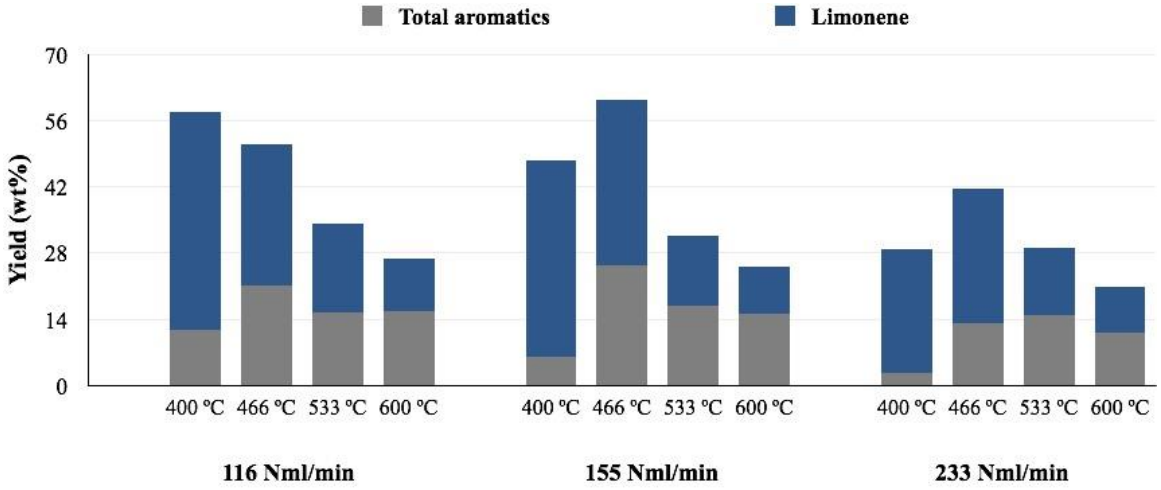
The average value of HHV obtained was 42.12 ± 1.20 MJ/kg, value agrees with other authors [7, 14]. This value is slightly lower than the one of the commercial diesel (43-46 MJ/kg) and close to the one of the commercial gasoline (42-44 MJ/kg). However, it is higher than that observed for coal (29-36.8 MJ/kg) and for oil obtained from different biomasses (25-32 MJ/kg) [5, 40, 42].

On the other hand, the acidity showed different values with changes in *T* and $\boldsymbol{Q_{N_2}}$. The pyrolytic oil presents an acidity between 0.39 and 1.57 mg KOH/g. Only the values of acidity for the pyrolytic oil obtained at 466°C are closed to the permissible limit for fuel oils (0.3 mg KOH/g) [44]. According to Benallal *et al.* [45] in the pyrolysis reaction at low temperatures, the olefins and diolefinic hydrocarbons are the predominant compounds in the pyrolysis oil, which may be the cause of its high acidity. The reactions such as aromatic cyclization and dehydrogenation of olefins and diolefins in the reactor can also decrease the acidity [45].

The concentration of single ring aromatic compounds (BTX, alkylbenzenes, and cymene) and limonene in pyrolytic was characterized and the yield of this compounds was calculated. The compound found in the highest proportion in all samples analyzed in this study was limonene (10 – 50 wt%) whereas the aromatic compounds are in few proportions (11 – 25 wt%).

The results obtained for the aromatic and limonene yields are shown in Fig.4. Comparing aromatics yields (Fig. 4) with the results of pyrolytic oil yield (Table 2 and Fig. 2), we found that even if the oil yield increases as the temperature increases, the aromatic yield (including BTX compounds) seems to rise a maximum at 466 °C and still is constant at higher temperatures. An exception is seen for a nitrogen volumetric flow of 233 Nml/min at TPN, in which the maximum is reached at 533 °C followed by a decrease at higher temperatures.

The experimental data show that the highest yield of both, total aromatics and limonene, was obtained at 466 °C and 155 Nml/min at TPN. This behavior can be explained according to the studies performed by Pakdel *et al.* [19, 46] and Cunliffe *et al.* [20] about the formation of aromatic compounds from limonene and the presence of other reactions as cracking or polymerization, which are favored at a higher temperature and low nitrogen volumetric flow conditions.



* Gas volumetric flow is given in Nml/min corresponding to standard operating conditions (*i.e.* at TPN).

Fig. 4 The yield of aromatics compounds and limonene at each operating condition of the DoE.

3.4 Analysis of Varianza (ANOVA) for the aromatics yield

An ANOVA analysis by Square Sum Type III with a confidence level of 95% was performed. This analysis allows to know the contribution of each variable and eliminating the effects of the other factors. Table 5 shows the results obtained in this analysis for aromatics yield. Since the p-values of the two variables are 0.05, these factors have a statistically significant effect on aromatic yield with a 95.0% confidence level.

Table 5. Analysis of Variance for Aromatic Yield - Sum of Squares Type III

Variable	Sum of squares	DF	Mean Square	*F*-Value	*p*-Value
T	100,162	3	33,3875	59,04	0,0000
Q_{N_2}	7,17452	2	3,58726	6,34	0,0082
Residues	10,1784	18	0,565469		
Total (Corrected)	117,515	23			

Once the effects of each of the variables were known, a linear multiple regression was performed. For this, the two variables and their possible interactions were taken into account and a backward elimination was used to establish the most adjusted model. Based on all the possible interactions, those variables that were not statistically significant (p-value ≥ 0,05) were eliminated. The variable Q_{N_2} and the interaction ($T^* Q_{N_2}$) are not significant on pyrolytic oil yield and they were deleted of the model. Table 6 shows the results of fitting a multiple linear regression models to describe the aromatics yield with only the variables that showed p-value ≤ 0,05.
Since the p-values of all the variables are ≤ 0,05 there is a statistically significant relationship between the variables with a confidence level of 95.0%. In addition, the p-value of the model is ≤ 0,05, that term is statistically significant with a confidence level of 95.0%. Consequently, the variables presented in Table 6 are the most significant and the final variables of the model.

The final model selected to describe the relation between aromatic yield and the variables selected with a statistical significance is shown in Equation 6.

$$\text{Aromatic Yield (wt\%)} = 0{,}245574\,T - 0{,}000221624\,(T^2) - 0{,}0000272774\,\left(Q_{N_2}\right)^2 - 60{,}893 \quad (6)$$

Taking into account the analysis of experimental data presented before, the adjusted model evidences the influence of operating variables as temperature and nitrogen volumetric flow (gas residence time) on aromatic yield, differing than the ones found for the pyrolytic oil yield.

Table 6. Multiple linear regression for aromatics yield with all factors and their interactions.

Variable	Estimated	Standard Error	*p*-Value
Constant	-60,893	8,91238	0,0000
T	0,245574	0,0362315	0,0000
T^2	-0,000221624	0,0000361672	0,0000
$(Q_{N_2})^2$	-0,0000272774	0,00000928923	0,0082

Source	Sum of squares	DF	Mean Square	*F*-Value	*p*-Value
Model	105,113	3	35,0377	56,50	0,0000
Residue	12,4025	20	0,620124		
Total (Corrected)	117,515	23			

R^2 = 89,45 %
R^2 (Adjusted) = 87,863 %
Standard Error of the estimated = 0,78748
Average absolute error = 0,516667
Durbin-Watson = 2,22719 (P=0,6415)

In order to graphically evaluate the most favorable operating conditions for the maximization of aromatics yield, the response surface was done using the experimental results and the proposed model (Equation 5). The Fig. 3-(b) shows the combined influence of the two variables (temperature and nitrogen volumetric flow) on the aromatic yield. According to the figures, the most favorable conditions for the maximum yield are temperatures between 450 - 490 °C and nitrogen volumetric flows between 130 and 180 Nml/min at TPN, being the highest point at 466 °C and 155 Nml/min at TPN (residence time 19,27 s). Note that the temperature is the most influential variable on aromatic yield in the operating range that was analyzed. On the other hand, the residence time has a most important effect at a lower temperature than a higher temperature, in which it has not an influence on aromatic oil.

4. Conclusions

The results showed that the operating conditions for the maximum oil yield differ from those conditions to obtain the maximum aromatic yield. The temperature has a strong influence on the production of pyrolytic oil while the volumetric nitrogen flow (residence time) does not show such a strong influence on the range studied. According to the optimization results, the highest pyrolytic oil yields can be obtained at temperatures between 530 - 600 ºC, and the nitrogen volumetric flow has a higher influence at a lower temperature than at higher temperature.

On the other hand, the aromatics yield is influenced by both the temperature and the residence time. The most favorable conditions for the maximum yield are temperatures between 450 - 490 °C and nitrogen volumetric flows between 130 and 180 Nml/min at TPN (medium residences times).

From the physicochemical characterization of the pyrolytic oil, it can be stated that both: nitrogen volumetric flow and the temperature do not affect significantly the density or HHV. However, the acidity does vary, this because the acidity depends mainly on the composition of the pyrolytic oil. The lowest acidity is obtained at a temperature of 466 °C and nitrogen volumetric flow of 155 Nml/min at TPN, conditions in which the highest yield of total aromatics was obtained.

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