

Article

Decomposition of Used Tyre Rubber by Pyrolysis: Enhancement of the Physical Properties of the Liquid Fraction Using a Hydrogen Stream

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Abstract: The disposal of discarded tyres represents an environmental challenge for solid waste management entities. The need to reduce solid waste in urban areas along with the depletion of natural resources have made it necessary to reincorporate used materials into productive processes, giving value to what is considered waste, and minimizing the requirement of natural resources. In this study, pyrolysis was selected to thermally decompose used ground waste vulcanized rubber from automobile tyres. This rubber was exposed to the pyrolytic process in an indirectly heated batch reactor at three different temperatures. Three fractions (i.e., gas, liquid and solid) were obtained during the process. The effect of a hydrogen stream on the properties of the liquid fraction was analysed and characterized following the American Society for Testing and Materials procedures (ASTM) for the pyrolysis of liquid fuels. A multifactorial statistical analysis was used to evaluate the experimental data and thermographs of the process were recorded. Differences in thermographs suggest a different degradation pathway for the rubber exposed to 600 °C compared to the rubber exposed to lower temperatures. Temperatures in the range of 450 to 500 °C favored the production of carbon black regardless of the use of a hydrogen stream. In contrast, high temperatures favored the production of liquid and gas fractions. The highest production of liquid fraction was obtained at 550 °C, where 37% of the rubber was turned into liquid. Results also showed that a constant flow of hydrogen improves the appearance of the pyrolysis liquid. Furthermore, the hydrogen atmosphere reduces the sulphur content, water and sediments; and increases the values for the heat of combustion and the liquid fraction.

Keywords: pyrolysis; tyre rubber; valorization of waste; liquid fuels

1. Introduction

In 2015, the European tyre and rubber manufacturers association estimated that the annual production of tyres are approximately 1.5 billion with an estimate of generation of used tyres of approximately 17 million tonnes worldwide [1]. The main three components of a passenger car's tyres, the most common type of vehicle worldwide, are: metal (21.5 wt %), textile (5.5%) and vulcanized rubber (78 wt %) [2]. From these three fractions, the textile and metal fractions can be separated by mechanical methods and recycled without technical limitations. On the other hand, due to their physicochemical properties, the vulcanized rubber fraction of used tyres represents a challenge for the solid waste industry [3]. The most common rubbers used in the manufacture of tyres are *cis*-polybutadiene rubber (CBR), isobutylene-isoprene copolymer rubber (i.e., butyl rubber (BR)) and styrene-butadiene copolymer rubber (SBR) [4]. These synthetic rubber compounds comprised of

cross-linked long-chain polymers with sulphur atoms which made the elastomers chemically stable and, therefore, limited their degradability [5]. Furthermore, the low density and elasticity of the rubber made it difficult to recycle and subsequently dispose of the material as it cannot be compacted. In addition to the synthetic rubber, the rubber fraction of tyres usually contains natural rubber, carbon black plasticizers, lubricants, antioxidants and inorganic materials such as calcium carbonate and silica, which add greater complexity to the sustainable waste management of the used tyres [4]. Some of the uses of waste rubber from cars involve: energy recovery in kilns, as material for sport fields and playgrounds, tyre retreading and foundation material for the construction of civil structures such as embankments and pavements [6].

Due to the complexity associated with the reuse or recycling of used rubber, interest in energy and fuel generation using thermochemical conversion technologies is increasing [3]. Pyrolysis is a thermochemical alternative to treating vulcanized rubber for the recovery of valuable products. Pyrolysis involves the decomposition of the rubber at high temperatures in the absence of an oxygen-rich atmosphere [7]. In pyrolysis, the main products are: a solid fraction, usually carbon black; a liquid fraction comprised of light oil and tar; and a gas fraction. Different studies have used pyrolysis on synthetic rubber and focused mainly on the identification of the products and by-products produced at different temperatures [4,8–11]. During the pyrolysis of vulcanized rubber, the yield of the different fractions varied with temperature due to the evaporation rate of the different compounds. Low temperatures, in the range of 300–400 °C, have been associated with an increase of heavy oil fractions (i.e., tar) and, therefore, higher temperatures have been preferred for the process, making it energy intensive. Studies involving the pyrolysis of synthetic rubber with a range of temperature between 400 and 600 °C have shown that increasing temperature favored the production of gas fractions. However, the effect of temperature in the liquid yield varied within studies, indicating that other factors such as reactor configuration, amount of feed materials and atmosphere play an important role. For instance, Kaminski [8] and Laresgoiti [11] found an increase of the liquid fraction with temperature in the ranges of 500–600 °C and 300–500 °C respectively, while Ayding [9] and Berruoco [12] observed the increase in the range of 400–500 °C. All authors observed a plateau in the production of liquid fractions at higher temperatures. In contrast, Alvarez et al. [10] and Cunliffe [13] observed a decrease of the pyrolysis liquid yield when the process is carried out at similar temperatures in the range of 425–575 °C.

Another variable that plays an important role in pyrolysis is the atmosphere. Some of the common atmospheres used in pyrolysis include steam [8], nitrogen [9,10,13,14] and helium [15,16] which replace the air and thus the atmospheric oxygen. Theoretically, the injection of gases or vapor in the pyrolysis process affects the process in different ways. Inert gases help to decrease the excessive formation of oxides commonly produced during combustion. Inert gases also reduce the partial pressure of different compounds, limiting reactions where aromatics are condensed, and moderate the production of carbon black. In practice, however, the effect of the pyrolysis atmosphere is not always directly observed. For instance, Kamistry [8] studied the pyrolysis of synthetic tyre rubber in a fluidized-bed reactor using nitrogen and steam. The use of different inert atmospheres did not affect the yield or quality of the carbon black and other products obtained. Similarly, Gonzalez [17] suggested no influence of the nitrogen on the composition or yield of the pyrolysis products, except the potential effect of high flow rates of nitrogen-removing products from the reactor (reaction zone) that might lead to minimizing secondary reactions such as cracking and char formation. In contrast, Choi [18] reported a lower content of sulphur in the pyrolysis performed with nitrogen when compared to products obtained using pyrolysis product gas as reactor atmosphere. Despite the important role of the pyrolysis atmosphere, the majority of studies of waste tyres have not reported data related to the use of different inert gases during the process and, therefore, the effect of the atmosphere in the yield of the pyrolysis fractions or in the composition of these fractions has not been extensively studied. This paper presents, for the first time, a study of pyrolysis of vulcanized styrene-butadiene-rubber, using a non-inert atmosphere. In this work, the tyre's rubber was subjected to pyrolysis at two different

atmospheres (i.e., with and without hydrogen stream) at four different temperatures. The liquid fraction was characterized as pyrolysis liquid fuels and the effect of temperature and hydrogen stream on the physicochemical properties of the pyrolysis liquid was analyzed. This work offers an alternative to improve the properties and stability of pyrolytic liquid fuels by using a reactive non-oxidative atmosphere.

2. Materials and Methods

Vulcanized rubber was extracted from cars' used tyres and the textile and metal fraction was removed mechanically. The rubber was grinded and different particle sizes were separated using a sequence of sieves. The fraction of rubber collected between Tyler mesh 14 and 16 with a particle size on the range of 1.0 to 1.4 mm was selected for further characterization and pyrolysis experiments. The selected size is in agreement with literature that suggests that, in pyrolysis, particle size of materials below 5 mm has no influence on the reaction rates, as the temperature gradients inside the particle are not significant [17,19]. Table 1 displays the physical characterization of the bulk grinded rubber used for the pyrolysis experiments.

Table 1. Bulk properties of ground vulcanized rubber, Tyler mesh 14–16 from waste tyres.

Physical Property	Value
Compressibility	20.08%
Aerated bulk density	0.386 g/mL
Apparent bulk density	0.405 g/mL
Packed bulk density	0.483 g/mL
Average density	0.434 g/mL
Porosity	6.58%

The pyrolysis was carried out in a stainless steel batch reactor with an internal diameter of 3 cm and length of 23 cm. The reactor was heated externally using a heating system with an automatic temperature controller (Figure 1). The internal temperature of the reactor was measured using a digital thermocouple thermometer (Hanna HI-93551N) and the reaction was carried out at four different temperatures ranging from 450 °C to 600 °C. Hydrogen was used to displace the oxygen from the reactor. Two atmospheres were tested, one with an initial injection of hydrogen and another with a constant flowrate of hydrogen passing through the experimental apparatus. Gases produced during pyrolysis passed through a condenser where the condensable organic vapors were collected (i.e., pyrolysis oils), and the light gas fraction passed through a column of deionized water, akin to a liquid trap, to visually observe the formation of the gas fraction and trap any dissolved gases.

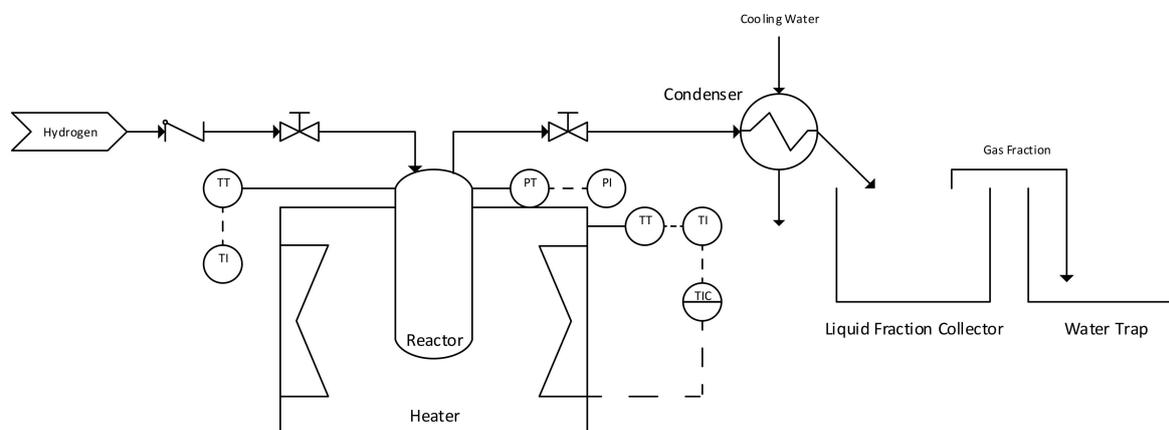


Figure 1. Pyrolysis set up.

For each experiment, 120 g of ground rubber with a particle size on the range of 1.0 to 1.4 mm was introduced into the reactor. For all experiments, hydrogen gas flowed for one minute through the set up at a rate of 100 mL/min. For experiments with a constant injection of hydrogen, the volumetric flow rate was set at a rate of 6.5 mL/min and was kept constant during the reaction. Previous experiments with higher hydrogen flow rates resulted in a significant decrease of the liquid fraction due to a short retention time of the gas stream in the condenser. The reactor was inserted into the external heating system which was previously pre-heated to the selected experimental temperature. The reaction time was set to 90 min in which the majority of the liquid fraction was produced. Previous experiments indicated that longer reaction times did not improve the liquid yield and the solid fraction was already carbonized after 70 min. Once the reaction was finalized, the reactor was removed from the external heater and left to cool to ambient room temperature. The solid and liquid fractions were collected, weighed and stored in darkness for further analysis. The liquid fraction composition, as per the American Society for Testing and Materials procedures (ASTM) procedures for characterizing liquid fuel, is shown in Table 2. The experimental data was statistically analyzed using confirmatory data analysis with a level of significance of 0.05.

Table 2. American Society for Testing and Materials procedures (ASTM) analysis performed on the liquid fraction obtained from the pyrolysis of vulcanized rubber from waste tyres.

Property	Method
Mass Liquid Fraction	Mass Balance
pH	ANSI ¹ / ASTM E 70
Specific Gravity	ANSI / ASTM D 287
API ² Gravity	ANSI / ASTM D 287
Kinematic Viscosity	ANSI / ASTM D 446
Saybolt Viscosity	ANSI / ASTM D 446
Sulphur Content	ANSI / ASTM D 129
Gross Heat of Combustion	ANSI / ASTM D 240
Water and Sediments	ANSI / ASTM D 96
Ash Content	ANSI / ASTM D 482
Flash Point	ANSI / ASTM D 56,92

¹ American National Standards Institute; ² American Petroleum Institute.

3. Results and Discussion

3.1. Thermographs

The thermographs from inside the reactor (Figure 2) show an initial increase of temperature followed by a plateau. In all of the experimental test runs, the internal temperature inside the reactor increased to a maximum value. Subsequently, the temperature inside the reactor was variable and finalized with a constant increase of the temperature at the end of the process. During the first part of the reaction, a period of constant temperature occurred in all of the experiments. For experiments carried out at 600 °C, the isothermal stage occurred at 94 °C between minutes 3 and 5. For experiments carried out at 450 °C, the isothermal stage was observed at 90 °C between 5.5 and 9.5 min. Other studies have also referred to this first period of the process (i.e., $T < 200$ °C) as a stage of minimal mass change where the main process is an elimination of the moisture contained by the rubber [4].

The reactions carried out with and without a flow of hydrogen displayed analogous thermographs (continuous versus dotted lines in Figure 2). However, after the maximum temperature was reached, reactions carried out with a constant flow of hydrogen (continuous lines) displayed more temperature variations than the experiments without hydrogen (dotted lines). This second stage was characterized by the major production of a liquid fraction, indicating that, at this stage, the majority of the production of condensable compounds occurred. In the last stage of the reaction, after 50 min, the differences between the experiments with and without hydrogen were more evident. For the experiments

performed at an external temperature of 400 °C, temperatures inside the reactor were higher in the presence of a hydrogen stream, with a maximum difference of temperature of 30 °C at 67 min. In contrast, experiments carried out at 600 °C displayed higher internal temperatures in the absence of hydrogen, with a maximum difference of temperature of 40 °C at 76 min. Results suggested that at this final stage the majority of the volatile compounds were released and the predominant process was a heating process. In terms of yield, the major production of the liquid phase occurred after 16 min for the experiments carried out at 600 °C (blue lines) and after 26 min for the experiments performed at 450 °C. Regarding the decomposition of different types of rubber present in the raw material, the pyrolysis thermogravimetric analysis of tyres and their components performed by Williams and Besler [15] suggested that SBR decomposed mainly at high temperatures, natural rubber (NR) at lower temperatures whilst BR can be decomposed at both higher and lower temperatures. This suggested that during the first stage of the reaction, the main byproducts formed were produced by the decomposition of NR and BR while the compound formed during the second stage, mainly liquid fraction, were produced by the thermal decomposition of SBR and in low-proportion BR. Thermographs for all the experimental temperatures are shown in supplementary information in Figures S1 and S2.

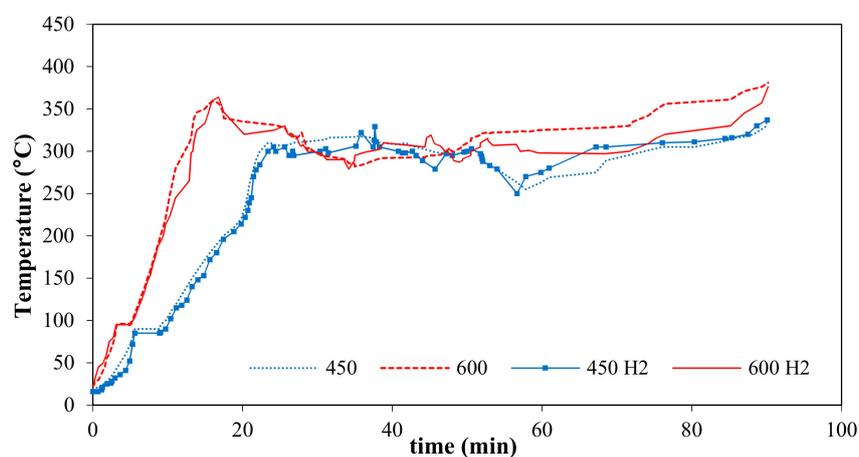


Figure 2. Thermographs measured inside of the reactor with and without flow of hydrogen.

3.2. Production of Pyrolytic Products.

For the experiments without a constant flow of hydrogen, the time of the initial production of gases varied with the experimental temperature. For the experiment carried out at 450 °C, the constant production of gases started after approximately 20 min with an internal temperature of the reactor of 220 °C. On the other hand, the maximum generation of gases with the external temperature of 600 °C occurred after 10 min with an internal temperature of the reactor of 250 °C. This result suggests similar degradation pathways regardless of the external temperature. Lah's study [20] suggested that during the pyrolysis of the tyre's rubber the major release of organic vapors occurred in the range of temperature of 200–500 °C, where also the major mass loss happens. In this range, volatiles present in rubbers (e.g., oil, plasticizer and additives) decomposed at around 300–350 °C, which explains the abundant formation of gas in the reactor [20]. In the present study, the formation of gases attributed to volatile organic vapors occurred at lower temperatures in the range of 220–250 °C. Similarly, Choi [21] and Seidelt [16] proposed that between 300–450 °C the decomposition of NR and BR rubber components are more likely to occur; and the decomposition of SBR are usually reported to occur in the range of 400–500 °C [16]. Herein, the decomposition of NR, BR and SBR also occurred at lower temperatures, as discussed previously, and in accordance with other studies that have also demonstrated degradation of those types of synthetic rubbers at lower temperatures [11].

In terms of composition of the fractions produced during the pyrolysis of vulcanized rubber, studies have found that the composition of the different fractions is mainly a mixture of aromatic, cyclic and aliphatic hydrocarbons [4]. The main aliphatic and naphthene compounds found in the liquid fraction of pyrolysis of SBR are pentenes, hexenes, 4-ethenylcyclohexene and other C₈ and C₉ aliphatic compounds. Additionally, the SBR's co-monomer, 1,3-butadiene, is decomposed producing reactive components such as 4-ethenylcyclohexene that participate in secondary and tertiary reactions during the pyrolysis [8]. The amount of aliphatic compounds usually increases slowly with temperature. Thus, similar proportions of aliphatic compounds can be obtained at different temperatures. In contrast, the amount of aromatic compounds increase considerably with a rise of temperature [8]. The main aromatic compound in the liquid fraction is styrene followed by ethylbenzene, benzene, toluene and xylenes (BTX), and in a lower proportion, methylstyrenes. benzothiazoles and thiophenes, used during vulcanization of the rubber, are also commonly found in the liquid fraction. For the gas fraction, studies have found that the main products are 1,3-butadiene with a small percentage (lower than 0.5%) of methane, carbon monoxide, carbon dioxide, hydrogen sulphide, methane, ethane, propene, and *n*-Butane. The solid fraction, also referred to as pyrolytic char, contains mainly carbon black and, in a minor proportion, carbonized rubber polymer, non-volatile hydrocarbons and residual portions of rubber additives such as zinc, sulphur, clays and silica [7].

Regardless of the use of hydrogen during the pyrolysis, low temperatures (i.e., 450 °C) resulted in the high production of carbon black (Figure 3). Similarly, the solid fraction decreased with an increase in temperature until 550 °C. Further increases in temperature resulted in an increase of 4% in the production of solids. In contrast, high temperatures favored the production of the liquid fraction. Only 10% of the initial material resulted in a liquid fraction for pyrolysis performed at external temperature of 450 °C. On the other hand, the highest amount of liquid fraction (37 wt %) was obtained at 550 °C with a constant hydrogen flow. Pyrolysis carried out at 600 °C, with and without hydrogen, led to the higher production of the gas fraction and a reduction of the liquid fraction compared to samples obtained at 550 °C. In agreement with these results, other studies using inert atmospheres have also reported an increase of the liquid fraction with temperature and a reduction or stabilization of the liquid yield at temperatures higher than 600 °C [7,8].

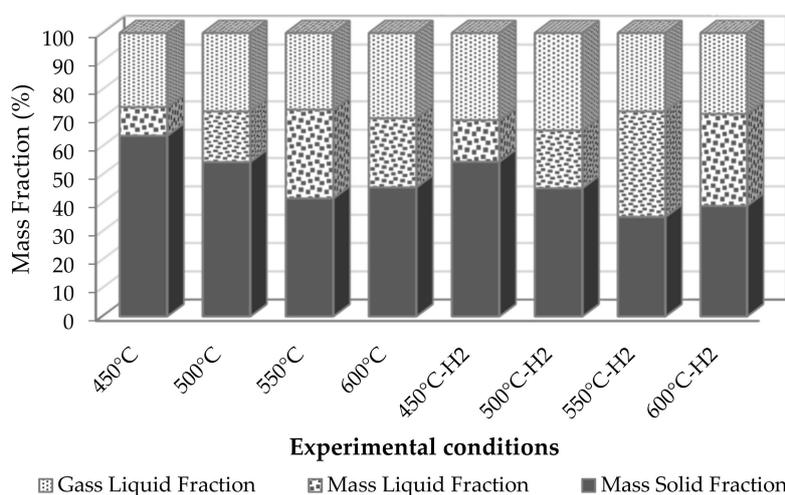


Figure 3. Gas, liquid and solid mass fractions obtained after pyrolysis was completed.

The role that hydrogen plays in the process is still under investigation. As a reactive gas, hydrogen can interact with the chemical species inside the reactor and stabilize the hydrocarbon chains, limiting the re-polymerization process and enhancing the production of liquid and gas fractions. On the other hand, studies with inert gases such as nitrogen have been associated with the presence of nitrogen-containing compounds in the use of additives during the manufacture of the synthetic rubber for tyres rather than the

use of nitrogen gas during the pyrolysis. Some of nitrogen-containing compounds commonly found are quinoline, *N*-(1-methylethyl)-*N'*-phenyl-; 1,4-Benzenediamine, *N*-(1,3-dimethylbutyl)-*N'*-phenyl-; Phenol, 2,6-di(*t*-butyl)-4-(cyclohexanylidene)-amino;(6-isopropyl-3,4-bis(methylamino)-2,4,6-cycloheptatrienyldene) malononitrile; *N*-(1,3-dimethylbutyl)-*N'*-phenyl-, and 1,4-Benzenediamine [4].

3.3. Effect of Pyrolysis Condition on the Pyrolytic Liquid Fuel

The statistical analysis showed that properties such as flash point, ash content and water and sediments were not affected by changes in the experimental temperature and, therefore, no significant differences in these parameters were found. Similarly, the statistical analysis showed that the injection of constant hydrogen did not affect the pH, flash point and ash content of the liquid fractions collected. In contrast, the rest of the properties analyzed, including yield of the liquid fraction, viscosity, American Petroleum Institute (API) gravity, sulphur content and heat of combustion were affected either by the experimental temperature, the presence of a hydrogen, and/or by the interaction between these variables.

For all the experiments, the collected liquid fractions were translucent with no visible presence of suspended material. Samples displayed different tones of colors from a light copper color to brown. Table 3 show the geometrical average values that resulted from the physicochemical characterization of the samples. Samples obtained with a constant flow of hydrogen displayed lower values of water and sediments, sulphur content and higher values of the heat of combustion. The densities of the liquid fractions were in the range of 0.83–0.88 g/cm³ which are similar to the density values required for diesel, and in accordance with the ASTM standard values of 0.84 ± 0.05 g/mL [22]. Kinematic viscosities were in the range of 1.59–3.07 cSt while the standard for diesel is 2.62 cSt. Values of the flash point for the samples were considerably lower, in the range of 31.0–35.5 °C compared to the standard value for diesel of 60 °C. The latest result suggests the presence of a higher fraction of volatile vapors in the pyrolytic liquid compared to commercial diesel. The heat of combustion values were in the range of 45.95–48.67 MJ/kg which are higher than diesel standard values of 10,995 cal/g. In general, samples obtained with a constant flow of hydrogen displayed lower values of water and sediments, sulphur content and higher values of the heat of combustion.

Table 3. Geometrical average values that resulted from the physicochemical characterization of the pyrolysis liquid sample.

Experimental	Liquid Fraction	pH	Density	API Gravity	Kinematic Viscosity	Saybolt Viscosity
Conditions	% mass		g/mL	°API	cSt	Seconds
450 °C without H2	10.14	8.81	0.83	38.7	1.59	31.4
500 °C without H2	17.91	9.01	0.85	35.6	1.88	32.3
550 °C without H2	31.09	8.84	0.88	30.2	2.77	35.2
600 °C without H2	24.57	9.12	0.86	33.6	2.65	34.8
450 °C with H2	14.59	8.74	0.86	33.1	2.35	33.9
500 °C with H2	20.47	8.50	0.85	34.4	2.41	34.1
550 °C with H2	37.25	8.26	0.87	31.4	2.48	34.3
600 °C with H2	32.56	8.10	0.88	29.6	3.07	36.2
Experimental	Sulphur Content	Heat of Combustion	Heat of Combustion	Flash Point	Water and Sediments	Ash Content
Conditions	% mass	cal/g	MJ/kg	°C	% mass	% mass
450 °C without H2	1.09	11,625.0	48.67	32.0	0.90	0.10
500 °C without H2	1.06	11,283.5	47.24	32.5	0.75	0.04
550 °C without H2	0.89	11,324.5	47.41	30.5	0.75	0.04
600 °C without H2	1.07	11,214.5	46.95	35.5	0.35	0.04
450 °C with H2	0.87	10,975.0	45.95	34.5	0.55	0.04
500 °C with H2	0.78	11,479.0	48.06	30.5	0.40	0.04
550 °C with H2	0.67	11,307.0	47.34	31.0	0.25	0.08
600 °C with H2	0.80	11,449.0	47.93	31.0	0.30	0.03

As shown in Figure 4, the yield of the liquid fraction for the experiments without a hydrogen stream (dotted bars) was in the range of 10% and 31% and 15% to 37% for experiments carried out with

hydrogen (gray bars). These results are in accordance with liquid yields obtained with packed bed reactors working in batch mode [4,23]. Other reactor configurations, such as fluidized bed or conical spouted bed reactors, displayed greater liquid yields up to 55% [24]. In terms of pyrolytic atmosphere, the injection of hydrogen increased the liquid fraction for all of the experimental temperatures used. The highest yield for the liquid fraction was found at 550 °C followed by 600 °C, where the injection of hydrogen increased production by 18.5% and 32.7%, respectively.

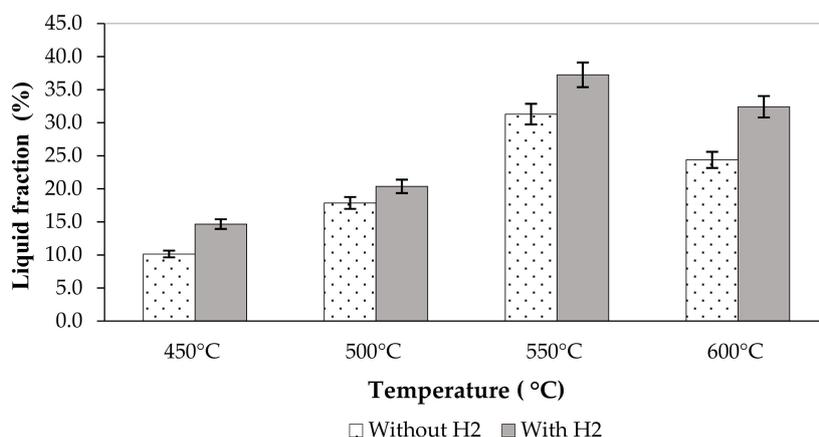


Figure 4. Mass fraction of the liquid fractions obtained at different temperatures with and without a constant flow of hydrogen.

Sulphur-containing compounds are derived from the decomposition of vulcanisation agents and accelerator materials [25]. During pyrolysis, reactions of the formation and consumption of sulphur compounds takes place and those reactions can be temperature-dependent [26]. In this study, the values of the sulphur in the liquid fraction obtained without a hydrogen stream are similar to the sulphur content found in other studies of pyrolysis of tyre rubber at the final temperature of 500 °C in a nitrogen atmosphere [21]. High temperatures in the reactor and the constant flow of hydrogen led to a desulphurization process. Figure 5 shows the values of the total sulphur content without a hydrogen stream (dotted bars) and with hydrogen (gray bars) at different temperatures. The increase of the external temperature in the reactor, up to 550 °C, resulted in lower sulphur content. A further increase of temperature resulted in higher values of sulphur content. The injection of a constant flow of hydrogen reduced the total sulphur content by 20–30% without the assistance of any catalyst and produced more stable products with lighter colors. Although different percentages of desulfurization were observed at different temperatures, no trend was established as the values fluctuated between temperatures. For example, the maximum sulphur reduction was obtained at 500 °C, while similar values of sulphur reduction were obtained at 450 °C and 550 °C. Analogous to liquid phase hydrogenative pyrolysis, the hydrogen acts as a proton donor where radicals formed at high temperatures are hydrogenated and saturated, minimizing coking and repolymerization reactions [26]. Likewise, sulphur compounds are good hydrogen acceptors, and thus it is likely that the desulfurization process of the pyrolysis liquid fraction occurred by increasing the amount of hydrogen sulfide. Further desulfurization can be limited by the presence of sulfur-polycyclic-aromatic hydrocarbons, such as thiophenes, dibenzothiophene and their derivatives, which are more stable and difficult to degrade thermally [27]. Nevertheless, partial desulfurization was obtained at relatively high temperatures, without the aid of a catalyst and at atmospheric pressure, by contrast with the desulfurization of petroleum-derived feedstocks, which is performed under high hydrogen pressures in the range of 30–130 atm on the surface of a catalyst, such as cobalt-molybdenum or nickel molybdenum supported on alumina, at temperatures between 300 and 400 °C [27]. Other desulfurization mechanisms have been studied for the pyrolysis of tyre rubber based on the addition of additive mixtures such as sodium carbonate, zeolite, and lime [28] and sodium hydroxide, calcium hydroxide

and lime [9] with considerable reduction of the sulphur content between 34% and 83%, with minor effects on the yield of the different fractions.

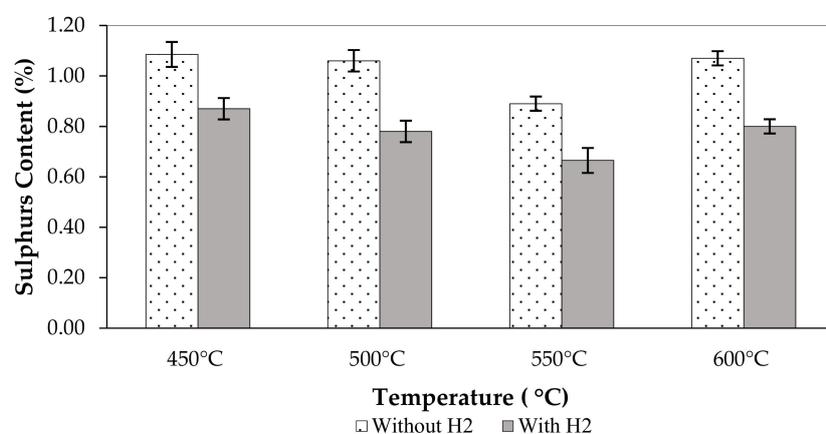


Figure 5. Sulphur content of the liquid fractions obtained at different temperatures with and without a constant flow of hydrogen.

In terms of the heat of combustion, the statistical analysis showed that this parameter is affected by the experimental temperature and hydrogen flow; however, no trend or correlation was found between the experimental variables and the heat of combustion. Figure 6 displays the values of the total content of sulphur without a hydrogen stream (dotted bars) and with hydrogen (gray bars) at different temperatures. The liquid fraction with the highest heat of combustion (11,600 cal/g) was obtained at 450 °C without hydrogen flow. These samples also had the highest sulphur content indicating a potential increase of the heat of combustion due to the presence of organosulphur compounds. In contrast, for the experiments performed at higher temperatures, the flow of hydrogen resulted in higher heats of combustion. The values obtained for these samples match the heat of combustion of other fuels such as gasoline (47.31 MJ/kg), diesel (44.79 MJ/kg) and sunflower biodiesel (40.61 MJ/kg).

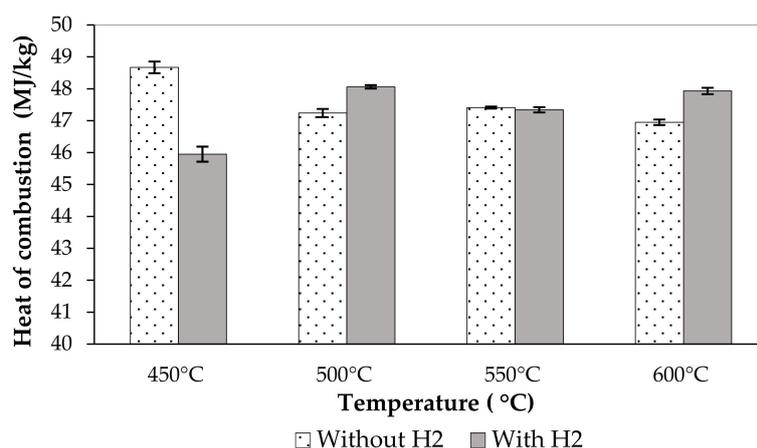


Figure 6. Heat of combustion of liquid fractions obtained at different temperatures with and without a constant flow of hydrogen.

The results obtained herein offer a new insight into the potential of using different pyrolytic atmospheres, which has not been well discussed. The use of a constant hydrogen stream, a reactive non-oxidative atmosphere, resulted in an improvement of some physicochemical properties of the liquid fraction. To extend knowledge in this area, a future research direction involves the analytical chemical characterization of the liquid fraction to identify differences in composition

and in the pathway of the desulfurization process. Furthermore, safety measures need to be taken into consideration when using hydrogen, a reactive atmosphere, in thermal processes. A number of hydrogen's properties make it safe and environmentally friendly. For example, hydrogen is not toxic, its combustion byproducts are water and, due to its low density, it dissipates rapidly, thereby minimizing the risk of accumulation. However, hydrogen has a wide range of flammable concentrations in air and lower ignition energy than other fuels such as natural gas or gasoline which increase the risk of explosion. Hence, adequate ventilation and leak detection are an important consideration in the design of a pyrolysis process with hydrogen as the pyrolytic atmosphere. In addition, due to hydrogen's small atomic radius and reactivity, some materials are not suitable for use with hydrogen as they may become brittle when directly exposed to it or they may allow leaks due to material porosity. Consequently, the specification of the system (i.e., materials of construction, valves and instrumentation) has to comply with the technical regulations and standards for the safe use and storage of hydrogen.

4. Conclusions

Pyrolysis was used to degrade ground waste vulcanized rubber from used automobile tyres. Three fractions, gas, liquid and solid, were obtained during the process and the effect of a hydrogen stream and temperature on the properties of the liquid fraction was analyzed. Thermographs of the internal temperature of the reactor displayed three zones of the process: an initial stage where water and moisture is eliminated and the gas fraction predominated; a second stage where the majority of the decomposition reactions occurred; and a final stage where the heating process of the remaining material occurred. A multifactorial statistical analysis showed that the yield of the liquid fraction, viscosity, API gravity, sulphur content and heat of combustion were affected either by the experimental temperature, the presence of hydrogen, and/or by the interaction between these variables, while other physicochemical properties were independent of the experimental variables. Low temperature favored the production of carbon black regardless of the use of a hydrogen stream. In contrast, high temperatures favored the production of liquid and gas fractions. The highest production of liquid fraction was obtained at 550 °C where 37% of the rubber was turned into liquid. Results also showed that a constant flow of hydrogen improves the appearance and properties of the pyrolysis liquid. Furthermore, the hydrogen atmosphere increases the values of the heat of combustion and the liquid fraction reduces the content of water and sediments and content of sulphurs without the use of any catalytic or additive material.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2076-3298/5/6/72/s1>, Figure S1: Thermographs measured inside the reactor at different temperatures without a constant hydrogen flow, Figure S2: Thermographs measured inside the reactor at different temperatures with a constant hydrogen flow.

Author Contributions: A.R.-C. and Y.F.M.-C. conceived and designed the experiments; A.R.-C. and Y.F.M.-C. performed the experiments; A.R.-C, Y.F.M.-C. and P.S. analyzed the data; A.R.-C. and P.S. wrote the paper.

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