

THERMAL CONVERSION OF SCRAP TYRES

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Abstract

Slow pyrolysis of scrap tyres has been carried out in a batch reactor and the results yields, composition of gas and liquid fraction and solid residue have been discussed. Batch operation in the 400-570°C range gives way to a yield 1.4 - 11.1 wt. % of gases, 6.4-50.0 wt.% liquid fraction, with a maximum yield of limonene of 9.0 wt% at 450°C and 6.1 - 46.3 wt.% of solid residue (char). The volatile fraction is a complex mixture of hydrocarbons, from methane to compounds of high molecular weight. From non-hydrogen component there are present carbon monoxide and carbon dioxide. Isoprene and benzene with temperature and yield of aromatic C₇-C₁₀ fraction decreases. The high yield of limonene are the advantages of batch technology.

Keywords : Scrap tyres, thermal conversion, pyrolysis, bath reactor.

1. Introduction

Scrap tyres have been designated as a priority waste stream by the European Commission and, as such are subject to recycling target and recommendations regarding environmentally acceptable treatment and disposal methods. It is estimated that Europe produces about 250 million scrap car and truck tyres each year, representing about 3 million tonnes by weight of tyre. The worldwide generation of scrap tyres is estimated at 1000 mil. tyres /y ^[1].

Tyres are composed of vulkanised rubber in addition to the rubberised fabric with reinforcing textile cords, steel or fabric belts and steelwire reinforcing beads. A number of different natural and synthetic rubbers and rubber formulation are used to produce tyres. Other components in the tyre include : carbon black, which is used to strengthen the rubber and aid abrasion resistance; extender oil, which is a mixture of aromatic hydrocarbons and serves to soften the rubber and improve workability; sulphur which is used to cross-link the polymer chains within the rubber and also to harden and prevent excessive deformation at elevated temperatures; an accelerator, typically an organo-sulphur compound, added as a catalyst for the vulcanisation process; zinc oxide and stearic acid used to control the vulcanisation process and to enhance the physical properties of the rubber. Carbon nanotubes are taking rubbery behavior to new extremes. A novel rubberlike material made from long, tangled strands of single-, double-, and triple-walled carbon nanotubes (CNTs) maintains its viscoelasticity at temperatures as low as -196°C and as high as 1000°C in an oxygen-free environment. Most rubbery materials, in contrast, turn brittle in the cold and degrade when things heat up. Because of its temperature-invariant viscoelasticity, the CNT-based material could find use in vehicles that travel to the cold reaches of interstellar space. It could also be used inside high-vacuum furnaces , where it could take the heat without running the risk of reacting with oxygen ^[14].

An alternative technology for the thermal treatment of tyres is pyrolysis which is the thermal degradation of the tyre in an inert atmosphere. Pyrolysis of the tyres has been established for many years but is currently receiving renewed attention. The process produces an oil, char and gas product, all of which have the potential for use. The recovery of oil can be as high as 58 wt. % of tyre rubber and has a high calorific value, of the order 42 MJ/kg. It can be used as a fuel, chemical feedstock or can be added to petroleum refinery feedstocks. The char can be used as a solid fuel, or can be upgraded for use as activated carbon or carbon black. The yield of char from the process is of the order of 35-38 wt. % of tyre rubber. The derived gas has a sufficiently high calorific value to provide the energy requirements for the pyrolysis process. In addition the steel reinforcement can be easily separated from the friable char and recycled back into the steel industry.

A number of commercial pyrolysis units have been developed. For example, in the Slovak Republic Deep Scavenger Steam Cracking Process or Steam Cracking Activation Process (DSSC/SCA) operate a flow pyrolysis system to process shredded scrap tyres with a planned capacity of 15.000 tonnes per year [2]. The DSSC/SCA process has been developed by DRON-sklady, Mliečany, Slovakia [3]. Advantages of DSSC/SCA process : new effective technology of thermal cracking of used tyres with steam activation; full exploitation process of rubber waste and used tyres; total material conversion of rubber scrap and used tyres; own energy supplies and high potential in the nearest future. Coalite Tyres Services operate a batch pyrolysis system to process shredded scrap tyres with planned capacity of 90 000 tonnes per year [4]. In addition, other commercial or demonstration units for tyres pyrolysis are available worldwide which are based on different designs. For example, vacuum pyrolysis of tyres has been used in Canada for the production of high-value chemicals, such as limonene, in the derived pyrolysis oil [5]. Other commercial plants in operation are located in South Korea and Taiwan [6].

The behaviour and chemical analysis of tyre pyrolysis was studied [1] and reported that tyre oil is a complex mixture of organic compounds of 5-20 carbon with a higher proportion of aromatics. The percentage of aromatics, aliphatic, nitrogenated, sulphur (benzothiazol) compounds were also determined in the tyre pyrolysis oil at various operating temperatures of the pyrolysis process.

In recent years some experimental studies revealed that the use of tyre pyrolysis oil derived from waste automobile tyres can be used as an alternative fuel in diesel engines. Despite the operative and expensive approach, the best possible utilisation of tyre pyrolysis oil is still to be determined. Tyre pyrolysis oil characteristics strongly depend on the pyrolysis process characteristics, process temperature and nature of waste automobile tyres used. The viscosity and sulphur content of crude tyre pyrolysis oil are the two parameters which influence the engine performance and emissions. High viscosity of the fuel will lead to problems in the long run include carbon deposit, oil ring sticking, etc. Crude tyre pyrolysis oil contains char, sand and alkali metals. Wear problems will arise both in the injection equipment and in several other engine parts, such as valves, valve seats, piston rings and liners. In addition, exhaust emissions may be impaired by these solid particles. Though the experimental results have no remarks about the emission of oxides of sulphur, the higher sulphur content will definitely affect the use of crude tyre pyrolysis oil as an alternate fuel in diesel engines. Crude tyre pyrolysis oil contains tar and polymers in the form of gummy materials. The presence of polymers, tar and solid particles may cause the formation of deposits in the injection system.

In a previous study thermal cracking of the model seven components mixed plastics (HDPE, LDPE, LLDPE, PP, PVC, PET, PS) into oils/waxes [7], woody material (beech wood) alone [8] and copyrolysis of plastics and biomass [9] were decomposed to find out the effect of the experimental conditions on products yields and composition.

In the present work, was thermally converted of scrap tyres with the aim of studying the experimental conditions that maximized liquid yields. The aim of next research of scrap tyres, mixing plastic and forestry biomass will to improve the liquid fraction of the oils/waxes, and evaluate the H-donor effect of the plastic type, as plastic wastes pyrolysis will produce a liquid medium, which may facilitate mass and heat transfer and consequently biomass and scrap tyre pyrolysis reactions.

2. Experimental

2.1. Scrap tyres

Even with the move to radial tyres and the increasing use of steel in the constructions of both car and truck tyres, the greatest weight in the rubber compound. This is between 80% and 85% for the most tyres of tyre, except car cross-ply tyres in which it is typically around 75%.

The automotive scrap tyres used in the bench-scale fixed-bed pyrolyser represented a mixture of light-duty and were shredded to 1-3 cm² pieces. The table 1 shows the properties of a typical scrap tyre feedstock [1, 10, 11]. The tyres represented a mixture of Slovakia types and grades. An indicative list of ingredients found in a typical rubber compounds is given in Table 1.

Its main components are : natural rubber (SMR 5CV), 29.59 wt.% ; styrene-butadiene rubber (SBR 1507), 29.59 wt.%; carbon black (ISAF N220), 29.59 wt.%. Other components are : stearic acid, 0.59 wt.%; IPPD (n-isopropyl-n'-phenyl-p-phenyldiamine), 0.89 wt.%;

zinc oxide, 2.96 wt.%; phenolic resin, 2.37 wt.%; sulphur, 0.89 wt.%; CBS (n-cyclohexyl-2-benzothiazol-sulfenamide), 0.89 wt.%; H-7 (hexamethylenetetramine), 0.18 wt.%; PVI (n-cyclohexylthio)-phthalimide), 0.12 wt.%; aromatic oil, 2.37 wt.%. The density is 1140 kg m^{-3} and the high calorific value (determined in a Parr 1356 isoperibolic bomb calorimeter) is $38.847 \text{ kJ kg}^{-1}$ [15].

Table 1 Typical tyre compound

Composition of tyre rubber compound [1]			Ultimative analysis, wt. %	
Component	% by weight	Sources	[10]	[11]
Rubber hydrocarbon	51	C	84.3	86.1
Carbon black	26	H	6.7	7.2
Oil	13	O ^a	2.6	0.1
Sulphur	1	N	0.4	0.2
Zinc oxide	2	S	1.6	1.5
Others	7	H/C	0.96	0.83

^a Calculated from difference

It should be noted pyrolysis is limited by heat and mass transfer within the particle and, consequently, as particle size is decreased the apparent kinetic constant increases. A size of 1 mm is a suitable value, given that much more energy is required for grinding to a smaller size and the kinetics is not affected when smaller sizes are used.

2.2. Thermal decomposition

We used a similar apparatus as in our previous work [12] without cooler operating at 90°C. We fed the batch reactor with 15g of scrap tyres and closed it. The experiment were run in inert atmosphere. The flow of nitrogen (inert) gas was 50 ml.min^{-1} . The time of tyres thermal degradation took around 100 min. The final temperature at thermal decomposition of tyres was 450°C. The following program for thermal cracking of tyres was used: heating rate $16.5^\circ\text{C min}^{-1}$ to 350°C, 8 min. temperature stabilization, heating rate 9°C min^{-1} up to 440°C, heating rate of $7.5^\circ\text{C min}^{-1}$ up to 480°C. However, final real temperature in the reactor was 450°C and 570°C respectively. The temperature was controlled by thermocouples. Detailed description of thermal cracking is given in literature [12].

2.3. Analysis of gaseous and liquid products

Analysis of the gases obtained from pyrolysis of tyres was performed with gas chromatograph Hewlett Packard HP 6890⁺. The three-PLOT chromatographic column system consist of two parallelly installed detectors FID and TCD and of three switching valves. Helium was used as a carrier gas. The temperature in the injection chamber was 150°C. The time of analysis was about 40 min.

The liquid obtained from pyrolysis of tyres was performed with gas chromatograph CHROM 5. The gas chromatograph system consist of the DB-PETRO column and of the FID detector. Helium was used as a carrier gas. The temperature in the injection chamber was 240°C. The time analysis was about 80 min. The analytical procedure was described in detail in [12, 13].

3. Results and discussion

Pyrolysis of scrap tyres was performed in a batch reactor, working with 15 g of sample. The sample consisted of shredded scrap tyres. The tyres were first freed from metal cords and textiles. The tyre shred was pyrolysed at two end temperatures, namely 450°C and 570°C. As the reaction system was heated to the end temperatures, changes in composition of gaseous and liquid products were observed. The material balances for the scrap tyre pyrolysis that was running at 450°C and at 570°C (Table 2) were calculated in the same way as in the case of thermal cracking of the seven model components mixed plastics into oil/waxes [7], pyrolysis of woody material [8] and thermal cracking of mixtures of plastics and woody material [9]. The gas samples were taken in a similar way as in the previous works [7-9], at temperatures 400°C, 450°C and one hour after reaching the temperature 450°C in the first experiment, and on reaching the temperature 570°C in the second experiment. The composition of pyrogas at temperature 450°C is in Table 3 and the composition at temperature 570°C can be found in Table 4.

Table 2. Material balance of thermal cracking of the scrap tyres at 450° and at 570° C

Temperature, °C	450			570		
Yields	Y (mass)			Y (mass)		
	Liquid	Gas	Solid residue	Liquid	Gas	Solid residue
g	6.4	1.6	7.0	7.5	1.4	6.1
% wt.	42.6	11.1	46.3	50.0	9.3	40.7

Table 3. Product distribution (%wt.) of components in gases obtained by thermal cracking of scrap tyre at 450°C

Temperature, °C	400	450	450	
Time of experiment, min.	20	42	102	
Components, % wt.	Composition, % wt			Average gas composition
Carbon dioxide	8.8	9.7	0.8	6.5
Carbon monoxide	65.8	63.1	13.3	47.4
Methane	1.1	1.0	25.7	9.3
Ethane	2.8	2.3	15.1	6.7
Ethylene	2.7	2.1	8.8	4.5
Propane	2.8	2.7	11.8	5.7
Propene	7.6	6.9	8.9	7.8
Methylpropane	0.1	0.1	1.7	0.6
n-Butane	1.3	1.5	1.5	1.4
trans-2-Butene	0.3	0.4	0.3	0.3
1-Butene	2.2	2.3	1.0	1.8
Methylpropene	1.4	1.6	9.7	4.2
1,3-Butadiene	0.3	0.4	0.5	0.4
trans-2-Pentene	-	-	0.2	0.1
cis-2-Butene	0.3	0.3	0.2	0.3
C ₄ -hydrocarbons	0.7	1.1	0.1	0.7
n-Pentane	1.2	2.3	0.1	1.2
2-Methyl-2-butene	0.3	0.3	0.03	0.2
1-Pentene	-	-	0.04	0.01
2-Methyl-1-butene	-	-	0.1	0.03
C ₅ -hydrocarbons	0.3	0.5	0.03	0.3
Isoprene	-	-	0.1	0.04
Benzene	-	1.3	0.1	0.5

The products obtained in the pyrolysis of tyres have been grouped into two fractions : the char or solid residue and the volatile fraction. The char consists mainly of the original carbon black, with its properties depending on pyrolysis conditions. The volatile fraction is a complex mixture of hydrocarbons, from methane to compounds of high molecular weight. From non-hydrocarbons components there are present carbon monoxide and carbon dioxide. Hydrogen was not present. The analysis of the results in fractions allows for a simple representation of the product distribution.

The components have been grouped into five fractions : gas (C₁-C₄ hydrocarbons and carbon oxides), non-aromatic liquid fraction (non-aromatic C₅-C₁₀ hydrocarbons), aromatic liquid fraction (single-ring C₁₀ aromatic hydrocarbons), tar (which includes C₁₁ hydrocarbons, independently of their aromatic or non-aromatic nature) and char (solide residue). In the liquid pyrolytic products, besides hydrocarbons there can be found sulphuric substances in amounts from 0.659 wt.% at 340°C to 0.546 wt.% at 570°C. In this temperature interval the level of the total amount of sulphur in the liquid products decreases with increasing temperature [16]. The GC analysis of the derived oils has identified the following sulphur-containing compounds : hydrogen sulphide, carbonyl sulphide, carbon disulphide, thiophene, 2- and 3-methyl thiophene; 2,3-, 2,4- and 2,5-dimethylthiophene and 2-ethylthiopene, tritienyl and benzothiazol, based on the available chemical standards. The sulphur components identified in the pyrolysis oil seems to be less complex than that of diesel fuels at similar sulphur content level. Sulphur in the pyrolysis oils has also been reported by other researches [1, 17, 18]. The results of sulphur determination verify that the overall

desulphurization from the pyrolysis reaction is affected by the ultimate pyrolysis temperature [16]. In the Table 5 is showed only content of methylthiophene (0.3-0.2 wt. %).

Table 4. Product distribution (%wt.) of components in gases obtained by thermal cracking f scrap tyres at 570°C

Temperature, °C	500	570	570	570
Time of experiment, min.	22	39	99	
Components	Composition, % wt.		Average gas composition	
Carbon dioxide	3.8	1.3	17.1	7.4
Carbon monoxide	14.1	8.4	5.7	9.4
Methane	16.5	17.0	17.7	17.0
Ethane	8.6	11.3	11.4	10.4
Ethylene	10.5	10.7	9.2	10.1
Propane	7.9	9.2	8.1	8.4
Propene	9.8	11.6	9.7	10.4
Methylpropane	1.6	1.7	1.3	1.5
n-Butane	1.4	1.8	1.6	1.6
trans-2-Butene	0.7	0.1	0.7	0.8
1-Butene	1.3	2.0	1.7	1.7
Methylpropene	14.8	14.0	9.7	12.8
1,3-Butadiene	2.2	1.8	1.1	1.7
trans-2-Pentene	0.5	0.6	0.5	0.5
1,3-Pentadiene	0.1	0.1	-	0.1
cis-2-Butene	0.4	0.6	0.5	0.5
C ₄ -hydrocarbons	0.2	0.3	0.2	0.2
n-Pentane	0.2	0.2	0.2	0.2
2-Methyl-2-butene	0.7	1.1	0.7	0.8
1-Pentene	0.7	1.0	0.1	0.6
2-Methyl-1-butene	-	-	0.6	0.3
C ₅ -hydrocarbons	0.2	0.2	-	0.2
Isoprene	3.6	4.1	2.2	3.3
Benzene	-	0.1	-	0.

Table 5 shows the evolution of the yields of the different fractions with temperature in the range studied. As observed, there are some clear trends, such as the increase in C₁-C₄ gas fraction with temperature, which has also been observed by other authors [15, 18]. The yield of the gas fraction increases with temperature as a result of more severe thermal cracking at higher temperatures.

The gases comprise mainly methane, C₂-C₄ – olefins and carbon oxides and, given that their yield is low in the temperature range studied, always around 10 wt. %, their recovery is not viable. Consequently, it is best burnt to produce energy for pyrolysis process. In the first measured gas products at 400°C the dominant component was carbon monoxide (65.8 wt.%) (see Table 3). At 450°C it was represented only by 13.3 wt.%. Out of hydrocarbons contained in the gas the highest percentage was represented by methane, ethane, ethylene, propane, propene and methylpropene, the production of which considerably increased when the temperature of the pyrolysis was kept at 450°C, especially methylpropene increased 7-fold. The amount of butane was approximately the same in all taken samples (Table 3). Regarding to the carbon monoxide and carbon dioxide percentage, it is observed that the fast decarboxylation of fatty acids (stearic acid), decomposition of phenolic resins and ZnO decreases at long reaction times due to the higher amount of light hydrocarbons in the produces gases.

In pyrolysis with the end temperature 570°C (Table 4) the amount of carbon oxide decreased. On the other hand, the amount of carbon dioxide in the gas increased immediately between the temperatures 500°C and 570°C. At 570°C the dominant component in the pyrogas was methane. The other components that were liberated on pyrolysis of scrap tyres are: ethane, ethylene, propane, propene and methylpropene. The amounts of these hydrocarbons during pyrolysis at 570°C nearly did not change (Table 4). The liquid products of pyrolysis are of aromatic character with profiling representation of benzene (3.2–4.7 wt.%). With increasing temperature the production of aromates C₇ – C₁₀ decreased.

This behaviour of aromatic fraction is due to Diels-Alder reactions that promote the formation of aromatic compounds from olefins. Isoprene and benzene with temperature and the yield of aromatic C₇-C₁₀ fraction decreases, which is due to thermal cracking and secondary reactions at high temperatures.

Table 5. Yields of gaseous and liquid components from thermal cracking of scrap tyres at 450 and 570°C

Temperature, °C	450	570
Time of experiment, min	102	99
Conversion to gases and liquids, %	0.537	0.593
Components	Yields, %wt.	
Carbon dioxide	0.7	0.7
Carbon monoxide	5.2	0.9
Methane	1.0	1.6
Ethane	0.7	1.0
Ethylene	0.5	0.9
Propane	0.6	0.8
Propene	0.9	1.0
Methylpropane	0.1	0.1
n-Butane	0.2	0.1
trans-2-Butene	tr.	0.1
1-Butene	0.2	0.1
Methylpropene	0.5	1.2
1,3-Butadiene	0.1	0.2
trans-2-Pentene	tr.	0.2
cis-2-Butene	tr.	0.1
C ₄ -hydrocarbons	0.1	0.1
n-Pentane	0.1	tr.
1-Pentene	tr.	0.1
C ₅ -hydrocarbons	tr.	tr.
2-Methyl-2-butene	tr.	0.1
2-Methyl-1-butene	-	tr.
Isoprene	5.0	7.2
Benzene	3.2	4.7
Toluene	2.1	1.2
Methylthiophene	0.3	0.2
Ethylbenzene	1.0	0.6
p-+ m-Xylene	1.2	1.0
Styrene	0.7	0.6
o-Xylene	-	0.5
Σ Ethyltoluenes	0.8	0.1
Methylstyrenes	1.2	1.2.
d, l-Limonene	9.0	4.6
Naphthalene	1.7	0.9
Σ Methylnaphthalenes	0.1	-
Nonidentified	16.5	27.2

tr. - traces

The heavy fraction, or tar, made up of C₁₁ components (nonidentified fraction in the Table 5), has no clear trend in the temperature range studied. The maximum yield of the tar fraction is obtained at 570°C, which accounts for 27.2 wt %. This complex behaviour of the tar fraction with temperature is a result of two opposite processes. On the one hand, the thermal cracking of tar to yields gases at high temperatures and, on the other, the condensation of aromatic ring to yield heavy aromatic hydrocarbons.

The yield of char or solid residue decreases in the temperature range studied from 46.3 wt. % at 450°C to 40.7 wt. % at 570°C. The char is mainly the original carbon black and the effect of temperature is to decrease deposited hydrocarbons on its surface, which cases a slight decrease in the mass of solid residue obtained.

Table 5 show the evolution with temperature of the more abundant compounds in the volatile fraction. The gaseous fraction is mainly made up of olefins whose yield significantly increases with temperature. Isoprene is the more important compound in C₅ fraction and

its yield remains between 5.0 and 7.2 wt % in the temperature range studied. This component is produced by the by the pyrolysis of natural rubber and its yields are higher than those obtained operating in batch conditions by Arabiourrutia et al. [19, 20]. In the batch conditions a maximum yield of 3.3 wt. % was obtained at 500°C. In the continuous processes [15], a maximum yield of 5.7 wt. % was obtained at 500°C.

Other interesting compound obtained in the tyre pyrolysis process are those BTX fraction, ethylbenzene and styrene. The content of aromatics, olefins and sulfur compounds in the liquid is rather high, which may limit its direct application as motor fuel (may be as heating fuel), particularly in the case of the liquids obtained at 570°C, in which the amount of aromatic and polyaromatic compounds is considerable high. The liquid fraction may be processed in a refinery by feeding the pyrolysis liquid to hydrocracking (or hydrotreating) units for reducing aromatic, olefin and sulfur compounds content.

The largest individual component in the liquid fraction is limonene, which reaches its maximum yield of 9.0 wt. % at 450°C (21.1 wt. % in pyroliquid). Limonene is very unstable at high temperatures and operating under these conditions its yield undergoes a reduction to 4.6 wt. % at 570°C. Other authors have observed a similar behaviour of limonene with temperature. Thus, Cunliffe and Williams obtained a maximum yield of 3.1 wt. % (by mass unit of the liquid) by operating in a fixed bed reactor at 450°C and a decreasing trend in yield as temperature is increased [18]. Li et al. carried out tyre pyrolysis in a rotary kiln and observed a decrease in limonene concentration in the pyrolysis liquid from 5.4 wt. % at 450°C to 0.07 % at 650°C [21]. Laresgoiti et al. operated in a fixed bed reactor and obtained a limonene concentration of 8.2 % in liquid at 400°C and lower concentration of 3.2 % at 600°C [22]. Dai et al. obtained 23.9 % of limonene in liquid by operating in a fluidized-bed reactor at 500°C [23]. Limonene is the main component of the citric oil and is commonly obtained from orange and lemon peel. Limonene has increased in recent years, being used to produce industrial solvents, resins and adhesives and in the cosmetic industry.

4. Conclusion

The batch reactor is a suitable technology for tyre scrap slow thermal conversion. Temperature has an important effect on product distribution by increasing the gas and the aromatization of the volatile fraction yield. Moreover, the quality of the solid residue (adulterated carbon black) is improved by operating at high temperatures.

The liquid fraction is of suitable quality for its use as heating fuel (high sulphur content) or it can be interesting feedstock for a refinery, especially for the hydrotreating and hydrocracking processes. Pyrolysis oil contains interesting products for petrochemistry, in high concentrations depending on the operating conditions, such as isoprene, d,l-limonene, BTX fraction, ethylbenzene and styrene.

The adulterated carbon black has enough BET surface area for its recycling, but a desulphurization is needed for this purpose. Furthermore, commercial quality active carbons can be obtained from residual black by means of an activation process.

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