Gas Chromatographic Investigations of Composition of Spent Tyre Pyrolysis Gasoline

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Abstract

This paper describes a case study in which multiple analytical techniques were used to identify and characterize the composition of spent tyre pyrolysis gasoline obtained from the tyre pyrolysis process. The objective of the study was to describe the spent tyre pyrolysis gasoline and determine its suitable commercial application.The analytical techniques used for analyses of spent tyre pyrolysis gasoline included gas chromatography-mass spectrometry, gas chromatography with sulfur-chemiluminescence detector and capillary gas chromatography with flame-ionization detector. Examination of the chemical composition of the spent tyre pyrolysis gasoline showed that nearly 90

Index terms— GC - MS, GC - FID, GC - SCD, spent tyre pyrolysis gasoline, pyrolysis gasoline from naphtha stream cracking, straight run naphtha, fluid catalytic cra

1 Introduction

crap tyres are a growing environmental problem because they are not biodegradable and their components cannot readily be recovered. It is estimated that the annual production of scrap tyres throughout the world is 1000 million. (1) Since tyres are designed to be extremely resistant to physical, chemical, and biological degradation, the possibilities for their reuse and recycling by mechanical or chemical means are limited currently.

However used tyres represent a source of energy and raw chemical products for the petrochemical industry. A different alternative is the recovery of the tyre components by hydrogenation, liquefaction, or pyrolysis. (2,3) Pyrolysis is an alternative disposal method with the possibility for recovery of valuable products from waste tyres and also attractive environmentally and it has been widely studied for years. (4)(5)(6)(7)(8) After tyre pyrolysis, three phases are obtained: solid, liquid and gas. The liquid product from the tyre pyrolysis was reported that may be used as fuel oil and diesel fuel. (9)(10)(11)(12) Benallal (6) and Roy (13) reported that the light fraction of pyrolytic oil may be used as gasoline additives in amount of about 2% vol. A suitable application of the light pyrolytic product can't be found without measuring of its chemical properties and comparing of its values with the ones specified in products like of gasoline and naphtha.

The aim of this work is to characterize the spent tyre pyrolysis gasoline and determine its suitable commercial application. The spent tyre pyrolysis gasoline, straight run naphtha, fluid catalytic cracking (FCC) gasoline and pyrolysis gasoline from naphtha stream cracking were examined for organic composition by gas chromatography coupled with a mass spectrometry detector, gas chromatography -flame ionization detector and gas chromatography -sulfur chemiluminescence detector.

2 II.

3 Resources and Techniques a) Samples

The liquid pyrolytic products were obtained by using proprietary catalytic pyrolysis process of tyre particles at reaction temperature of 400 0 C and pressure of 50 Pa. The yield of products obtained from the pyrolysis process was following: liquid product 46 %, carbon black 38 %, steel 11 % and gas 5 %. The liquid pyrolytic product was distilled by AUTODEST 860 Fisher column that has 15 theoretical trays according to ASTM D 2892 in order to obtain a spent tyre pyrolysis gasoline. (14) The reflux ratio was 10. The liquid pyrolytic product was fractionated in two fractions: gasoline fraction (

4 b) Apparatus

The spent tyre pyrolysis gasoline and the rest gasoline and straight run naphtha samples were analyzed directly by gas chromatography techniques. To quantify the different compounds, gas chromategraphy equipped with a flame ionization detector was used. To identify the compounds in the samples analyzed, gas chromatography/mass spectrometry was utilized. The sulfur compounds distributions were determined by gas chromatography equipped with a sulfur chemiluminescence detector.

Gas chromatography-mass spectrometry analysis was performed with a 7890A GC System equipped with a HP PONA 50 length m × 0.2 mm id × 0.5 ?m film thickness, capillary column and 5975C Inert XL EI/CI mass selective detector (Agilent Technologies, Inc., USA). The oven column temperature conditions identical to those used with the gas chromatograph with flame ionization detector. High purity helium was used as carrier gas at a flow rate of 0.8 mL min -1 . The injection port was held at 250 °C and the injection volume of sample 0.1 µL of sample.

The mass-selective detector was operated in the electron impact ionization mode (70 eV) with continuous scan acquisition from 15 to 250 m/z at a cycling rate of approximately 1.5 scan/s. The parameters were set up with the electron multiplier at 1224 V, source temperature of 230 ºC, and transfer line temperature at 150 ºC.

System control and data acquisition was achieved by HP G1033A D.05.01 MSD ChemStation revision E.02.00.493. The compounds were identified by means of the NIST MS Search version 2.0 mass spectral library using similarity indices of > 85 %, or by comparison with published GC-MS data for similar products.

The gas chromatograph with flame ionization detector was a model 5890 series II Hewlett Packard (Agilent Technologies, Inc., USA). A capillary column, HP PONA (50 m length × 0.20 mm id x 0.5 ?m film thickness), was used and was provided with split injector. The instrument parameters were as follow: initial oven column temperature of 40 °C, then increased at increments of 2 °C.min -1 to 130 °C and second temperature gradient of 5 °C.min -1 to 180 °C and held for 20 min at 180 °C. Helium was used as a carrier gas at a flow rate of 0.5 mL min -1 . The injector and the detector temperatures were 250 °C and 260 °C respectively. The volume that was injected and analyzed was 0.1 µL.

Data acquisition parameters, instrument operation and chromatographic data were collected and recorded by means of Clarity 2.6.

The gas chromatograph was a model 7890A coupled to a sulfur chemiluminescence detector series model 355 (Agilent Technologies, Inc., USA). A 30 m HP-1 capillary column 320 ?m id with 4 ?m film thickness was used. The GC separation was performed under the following conditions: helium as carrier gas, column temperature programmed from 50 ºC 4 min to 120 °C at a rate of 20 °C.min -1 , hold 4 min and to 220 °C at a rate of 10 °C.min -1 , hold 4 min. Injector in split mode at a temperature of 240 °C (split vent 131.7 ml.min -1 , column 2.6 ml.min -1 , purge vent 3 ml.min -1 , split ratio 50 : 1) was used. The SCD detector was set to the following conditions: burner temperature 800 °C, vacuum of burner 370 torr, vacuum of reaction cell 7 torr, hydrogen 40 ml.min -1 , air 60 ml.min -1 . The injection volume was 1.0 ?l.

5 III.

6 Discussion

The main objective was to investigate the composition of spent tyre pyrolysis gasoline and to examine its application as additions to feedstock for hydrotreatment or petrochemical production units for further processing or to petrochemical products suitable for direct use as a fuel or raw chemical feedstock.

There are more than 300 individual compounds which are defined in the spent tyre pyrolysis gasoline. It can be seen that, the investigated spent tyre pyrolysis gasoline is a very complex mixture of organic compounds. However, it is sufficient to identify and characterize several dozens of major hydrocarbons in the C 4 -C 12 range. The most abundant compounds, with peak areas around or great 0.3 % are listed in Table 1. The isomeric structures of compounds 1-methyl-4-(1-methylethenyl)-cyclohexene (limonene) (?? 39 -41) has not been determined, due to the limitation of the GC -MS to differentiate isomers. There are such a great number of compounds in the spent tyre pyrolysis gasoline that the peak areas are very low and in the same table the concentrations of these compounds is not given.

Data Table 1 show that there are several oxygenated compounds, such as alkylfurans, alcohols and ketones, which amount up to 0.50 -0.70 %. The oxygenate compounds in the spent tyre pyrolysis gasoline were also detected by previous studies. (16,17) The presence of sulfur and oxygenate compounds may be explained by thermal decomposition of the tyre additives used as agents of vulcanization. (18) GC analysis revealed that the spent tyre pyrolysis gasoline is formed from mixture of low and high molecular weight organic compounds. They are identified by GC -MS full scan analysis of sample and are classified into different classes of compounds-components (sulfur and oxygen) and unknowns to facilitate interpretation of the spent tyre pyrolysis gasoline composition. A comprehensive list of identified compound groups is presented in Table 2. Data results compare the PONA analyses of spent tyre pyrolysis gasoline and the rest gasolines and straight run naphtha samples. The majority hydrocarbon compounds in spent tyre pyrolysis gasoline and fluid catalytic cracking (FCC) gasoline are in the C 4 -C 12 carbon range, but C 4 -C 9 and C 4 -C 11 carbon ranges are detected respectively in pyrolysis gasoline from naphtha stream cracking and straight run naphtha samples. The study showed that the spent tyre pyrolysis gasoline, containing C 4 -C 12 hydrocarbons, are comprised mainly of C 6 -C 10 hydrocarbons, and which are dominated by aromatic hydrocarbons (35.6 %) and significant amounts of naphthenes (29.6 %). The saturated hydrocarbons are mostly paraffins and there is a difference between their levels in the samples investigated. The content of paraffins in the spent tyre pyrolysis gasoline is 9.36 %, while the one represent a potentially high level in the pyrolysis gasoline from naphtha stream cracking, straight run naphtha and fluid catalytic cracking (FCC) gasoline samples (18.68 %, 51.03 % and 23.75 %, respectively).

Olefins present C 4 -C 10 carbon range in spent tyre pyrolysis gasoline and theirs content is 15.93 %. The olefins content in the rest investigated gasoline and straight run naphtha samples is 22.11 %, 35.29 % and 0.93 %, respectively. The result 15.93 % for olefins in spent tyre pyrolysis gasoline falls well within the range of the olefins in tested samples. The spent tyre pyrolysis gasoline and pyrolysis gasoline from naphtha stream cracking contain some undesirable compounds like the di-alkenes which are highly reactive to polymerization and plug the downstream refining processes. These compounds also affect the gasoline samples stability. Table 2 presents the comparison between measured content of di-alkenes in tested samples. The content of majority di-alkenes in spent tyre pyrolysis gasoline is 7.76 % and they are in the C 6 -C 10 carbon range, while in the pyrolysis gasoline from naphtha stream cracking same are 17.16 % and they are in the C 5 -C 8 carbon range.

Light aromatics such as benzene and toluene are found in significant quantities (10.46 %) in the spent tyre pyrolysis gasoline as compared to straight run naphtha and fluid catalytic cracking (FCC) gasoline (1.69 % and 5.76 %, respectively). The aromatic hydrocarbons are composed mainly of single ring alkyl aromatics, including benzene derivatives such as alkyl and alkenyl groups. The radical chains attached to the benzene ring ranged from C 1 to C 5 . Alkyl-naphthalenes are observed in the spent tyre pyrolysis gasoline but only in minor quantities ? 0.7 %.

Identification of compounds are studied in detail and based on GC peak comparisons in the analyzed samples the distribution of hydrocarbon groups is shown in Figure **??**. It is interesting to note that the composition of the spent tyre pyrolysis gasoline distinguishes from that of the samples investigated.

Identification of sulfur compounds is carried out by using standard sulfur compounds and the result of GC -MS combined with the retention time of the compounds by GC -SCD. Sulfur compounds such as thiols, alkylsulfides, alkyldisulfides, and alkylthiophenes are detected in the spent tyre pyrolysis gasoline. The most distinguished sulfur compounds identified are shown in Table 3 and they are ethanethiol, 2 -propanethiol, 1 -propanethiol, 2 -methyl -2 -propanethiol, 2 -methyl -1 -propanethiol, 1 -pentanethiol, thiophene, 2 -methylthiophene, 3 -methylthiophene, 2 -ethylthiophene, 3 -ethylthiophene, 2, 5 -dimethylthiophene, 2, 4 -dimethylthiophene, 2, 3 -dimethylthiophene, 2 -[1 -methylethyl] -thiophene, 2 -butylthiophene. Table 3 data shows that spent tyre pyrolysis gasoline contain considerable quantity alkylthiophenes. The presences of alkylthiophenes are in agreement with the published data of similar products. (6) With respect to sulfur containing compounds, alkylthiols are only identified components in this research. The total sulfur content in sample analyzed varies between 0.056 % and 0.48 % and alkylthiophes and alkylthiols percentages are between 15 % and 77 %, and 5 % and 63 %, respectively.

The spent tyre pyrolysis gasoline is examined for their properties as a regular gasoline and these values are compared to those of the fluid catalytic cracking (FCC) gasoline, pyrolysis gasoline from naphtha stream cracking and straight run naphtha samples (Table 4). Compared with the rest gasolines and naphtha samples (content of aromatics varies from 13.8 % to 51.56 %) the aromatics of the spent tyre pyrolysis gasoline, respectively 35.60 %, are close to that for pyrolysis gasoline from naphtha stream cracking and fluid catalytic cracking (FCC) gasoline, and it is also within the prescribed value 35.0 % given in EN 228:2012. (15) The olefins content of spent tyre pyrolysis gasoline is found to be lower than that in fluid catalytic cracking (FCC) gasoline and pyrolysis gasoline from naphtha stream cracking samples and it is also within the prescribed value 18.0 % given in EN 228 : 2012. The content of benzene of the spent tyre pyrolysis gasoline is found to be lower than that in fluid catalytic cracking (FCC) gasoline and pyrolysis gasoline from naphtha stream cracking samples and it also within the prescribed value 1.0 % v/v.

The spent tyre pyrolysis gasoline has high contents of sulfur what is a reason to make it directly used inapplicable. The straight run naphtha has lowest content of sulfur and the spent tyre pyrolysis gasoline could be blended with the feedstock (fluid catalytic cracking (FCC) gasoline) for hydrotreatment or with the pyrolysis gasoline from naphtha stream cracking for further processing as a feedstock for the production of aromatic hydrocarbons which are required for organic synthesis.

IV.

7 Conclusion

This research study sought to understand the composition of spent tyre pyrolysis gasoline obtained from catalytic pyrolysis process of tyre and the connection between spent tyre pyrolysis gasoline properties and the fluid catalytic cracking (FCC) gasoline, pyrolysis gasoline from naphtha stream cracking and straight run naphtha samples investigated. A desired to understand how to use best advantage this spent tyre pyrolysis gasoline provide motivation for this work.

7 CONCLUSION

In view of the fact that the gasoline properties strongly depend on chemical composition, the GC quantitative profiles of spent tyre pyrolysis gasoline, pyrolysis gasoline from naphtha stream cracking, straight run naphtha and fluid catalytic cracking (FCC) gasoline are investigated. For comparison, data of samples compositions are given, using GC -FID and GC -SCD analyses and GC -MS identification. Data interpretation clearly indicates that a detailed identification and quantitative compound analysis was successfully carried out. Distribution of hydrocarbons, sulfur-and oxygen-containing compounds is researched and the evaluation of the possible ways of reusing such obtained liquid product is completed. The spent tyre pyrolysis gasoline from spent tyres may be processed in a hydrotreatment unit or co-processed with stream cracking pyro-gasoline. [1] [2] [3]

Figure 1:

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?	Compound

1 2 3 4 5 6 7 8 9 10 2,2,4,4-Tetramethyl-pentane n-Pentane n-Hexane n-Heptane n-Nonane n-Dodecane 2,4-I

12 1-Butene

13 Isobutylene

14 2-Methyl-1-butene 15 4-Methyl-1-pentene 16 2-Methyl-1-pentene 17 2-Methyl-2-pentene 18 3-Methyl-2-pe

42 3,7,7-Trimethyl-bicyclo[4.1.0]heptane
(tr-Caren)
43 1,4,6,6-Tetramethyl-cyclohexene
44 Cyclopentene
45 1-Methylcyclopentene
45 Cyclohexene
47 4,4-Dimethylcyclopentene

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Hydrocarbons range	Composition, wt%					
	Paraffines (n-alkanes and isoalkanes)	Olefins		Naphthenes	Aromatics	Total
		Mono -alkenes	Di-alkenes			
Spent tyre pyrolysis gasoline						
C 4	0.05	0.90	-	-	-	0.95
C 5	0.53	0.70	0.14	2.41	-	3.78
C 6	0.66	2.67	0.99	3.05	0.48	7.85
C 7	1.67	2.02	1.97	4.99	4.38	15.03
C 8	1.54	0.93	0.32	5.33	10.04	18.16
C 9	1.95	0.95	2.27	1.60	11.11	17.88
C 10	1.30	-	2.07	12.20	8.90	24.47
C 11	0.98	-	-	-	0.69	1.67
C 12	0.68	-	-	-	-	0.68
Pyrolysis gasoline from naphtha stream cracking						
C 4	-	1.44	0.59	-	-	2.03
C 5	5.96	3.38	8.67	2.77	-	20.78
C 6	12.09	0.13	3.25	3.83	14.78	34.08
C 7	0.63	-	1.62	0.71	13.49	16.45
C 8	-	-	3.03	0.30	13.22	16.55
C 9	-	-	-	0.04	10.07	10.11
Straight run naphtha						
C 4	0.10	-	-	-	-	0.10
C 5	0.12	-	-	0.05	-	0.17
C 6	0.12	0.32	-	0.40	0.01	0.85
C 7	6.65	-	-	6.20	1.68	14.53
C 8	14.89	0.61	-	11.40	5.54	32.44
C 9	15.04	-	-	8.36	4.24	27.64
C 10	11.77	-	-	2.69	2.33	16.79
C 11	2.34	-	-	-	-	2.34
Fluid catalytic cracking (FCC) gasoline						
C 4	0.38	2.18	-	-	-	2.56
C 5	5.51	11.48	-	0.68	-	17.67
C 6	5.83	9.17	-	1.94	1.08	18.02
C 7	4.47	6.02	-	2.90	4.68	18.07
C 8	2.53	2.78	-	2.05	8.57	15.93
C 9	2.06	1.82	-	1.15	7.85	12.88
C 10	1.79	1.09	-	0.99	5.10	8.97
C 11	0.54	0.75	-	0.40	0.96	2.65
C 12	0.64	-	-	0.21	0.15	1.00

Figure 3: Table 2 :

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Sulfur compounds	Sulfur content, mg.kg -1			
	Spent tyre pyrolysis gasoline	Pyrolysis gasoline from naphtha stream cracking	Straight run naph- tha	Fluid catalytic cracking (FCC) gasoline
C 1 -thiol	-	-	-	1.0
C 2 -thiols	270	45	95	39
C 3 -thiols	151	36	225	23
C 4 -thiols	439	39	30	2.0
C 5 -thiols	125		-	2.0
Total alkylthiols	985	120	350	67
Hydrogen sulfide	-	-	20	1.4
Carbonyl sulfide	-	15	-	0.4
Carbon disulfide	-	-	-	1.1
C 2 -sulfide	13	15	63	1.4
C 3 -sulfide	27	40	45	2.1
C 4 -sulfide	10	-	-	4.1
C 5 -sulfide	15	-	-	2.4
Total alkylsulfides	65	70	128	13
C 1 -disulfides	38	-	-	74
C 2 -disulfides	32	140	-	128
Total alkyldisulfides	70	140	-	202
Tiophene	180	175	25	115
C 1 -tiophenes	3000	306	57	280
C 2 -tiophenes	150	50	-	364
C 3 -tiophenes	125	20	-	-
C 4 -tiophenes	96	-	-	-
Tetrahydrogen tiophene	145	-	-	27
Total alkyltiophenes	3696	551	82	786
Benzotiophene	-	100	-	167
C 1 -benzotiophene	-	-	-	96
Total alkylbenzotiophene	-	100	-	263

Figure 4: Table 3 :

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Parameter	Spent tyre pyrolysis gasoline, %	Pyrolysis gasoline from naphtha stream cracking, %	Straight run naphtha, %	Fluid catalytic cracking (FCC) gasoline, %	Regular gasoline, % v/v
Aromatics	35.60	51.56	13.80	28.39	35.0
Olefins	15.93	22.11	0.93	35.29	18.0
Benzene	0.48	14.78	0.01	0.97	1.0
Sulfur	0.48	0.098	0.056	0.13	0.0010

Figure 5: Table 4 :

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