Petroleum & Coal
ISSN 1337-7027

Available online at www.vurup.sk/petroleum-coal
Petroleum & Coal 57(6) 676-686, 2015

IS IT POSSIBLE TO UPGRADE THE WASTE TYRE PYROLYSIS OIL TO FINISHED MARKETABLE FUELS?

Tanya Tsaneva[1], Dicho Stratiev[2], Magdalena Mitkova[1]

[1] University Assen Zlatarov, Burgas, Bulgaria; [2]LUKOIL Neftohim Burgas
e-mail: Stratiev.Dicho@neftochim.bg

Received November 13, 2015; Accepted December 29, 2015

Abstract

In this work an investigation of four different routes for refinement of liquid product from pyrolysis of waste tyres was carried out. These routes were: 1) Fractionation to light (gasoline fraction) and heavy pyrolytic oils and two stage hydrotreatment of the gasoline fraction; 2) Hydrotreatment of a blend of the whole pyrolytic oil with straight run diesel fraction from Russian Export Blend Crude Oil (REBCO); 3) Processing of the whole pyrolytic oil along with REBCO in a crude distillation unit; 4) Direct blending of the whole pyrolytic oil with a commodity fuel oil. It was found that during fractionation of the liquid pyrolytic oil in two fractions: light and heavy, the heavy fraction meets the specification of fuel oil and marine fuel. The light fraction was hydrotreated in a laboratory hydrotreating unit in two stages and the hydrotreated product contained less than 10 ppm sulphur and had octane numbers of RON = 88.9 and MON = 77.0 with a loss of 4.7 points of RON and 3.0 points of MON. The hydrotreatment of a blend of the whole pyrolytic oil with straight run diesel fraction (SRDF) from REBCO showed that pyrolytic oil inhibited the hydrogenation of the mononuclear aromatics and plugged the laboratory hydrotreating reactor when its content in the blend with the straight run diesel was raised to 20%. The addition of the pyrolytic oil to the crude oil REBCO improved the yields of distillates in the laboratory atmospheric-vacuum distillation unit, but the quality of the distillates deteriorated due to the chemical instability of the waste tyre pyrolytic oil components. The four route allows production of marketable fuel oil by blending of not more than 3% of pyrolytic oil to a commodity fuel oil whose closed cup flash point is not lower than 86°C.

Key words: waste tyre pyrolysis; liquid pyrolytic oil hydrotreatment; blending; fuel oil flash point.

---

1. Introduction

It is well known that waste tyre disposal presents an environmental concern, because tyres are extremely resistant to physical, chemical, and biological degradation, and the possibilities for their reuse and recycling by mechanical or chemical means are very limited [1]. It is estimated that 2.5 million tones per year are generated in the European Union, 2.5 million tones in North America and around 1 million in Japan [2]. One of the most investigated technologies to utilize waste tyre is their processing by pyrolysis.

Many studies have been devoted to this technology [1-30]. After tyre pyrolysis, three phases are obtained: solid, liquid and gas and their composition is related to the temperature of the thermal treatment. The gas product can be used as a make-up heat source for the pyrolysis process [20]. The solid product after demineralization may be used as a suitable adsorbent [10, 22]. It also may be used as a solid fuel in coal fired power station because its caloric value (28.9 MJ/kg) is close to that of the coal (33.2 MJ/kg). However, nearly all of the chlorine present in the original tyre ends up in the solid fraction. This should be taken into account when the solid fraction is to be considered as a fuel, since a gas cleaning process should be necessary of the combustion gases [19]. The liquid product from the tyre pyrolysis was reported that may be used as fuel oil and diesel fuel [6, 11-12, 15]. However, the value of the liquid product flash point (~ 30°C) is much below the specification for fuel oil and diesel fuel – 60 and 55°C respectively [16]. Moreover, it is known that the liquid pyrolytic product is rich of olefins and di-olefins [1, 9, 31] which make this product chemically unstable. For that reason it is prone to form gums which can easily settle down on process equipment and causes fouling. Equipment fouling by sediments formed in refining units can lead to enormous financial burdens in terms of increased costs of operation, maintenance and shutdown. There is still no sufficient data in open literature about upgradation of the waste tyre pyrolytic oil to finished marketable fuels which meet the stringent requirements of European directives and norms for quality of the fuels. We decided to fill this gap by investigating the upgrading of the waste tyre pyrolytic oil in refining processes: fractionation; hydrotreatment, and blending. The aim of this study is to discuss the obtained results in this investigation.

2. Experimental

The liquid pyrolytic product was obtained by using proprietary catalytic pyrolysis process [32] at following conditions: reaction temperature of 400°C; residence time of 50 minutes; reaction pressure of 50 Pa. The process used a proprietary catalyst [33] consisting of 35-50% alumosilicate; 15-30% active aluminum, 10-20% zinc oxide, 5-15% activated clay; 5-15% kaolin. The catalyst-to-tyre ratio was 5:1000 wt./wt. The yield of products obtained from the pyrolysis process was following: liquid product = 46%, Carbon black = 38%: Steel = 11%; Gas = 5%. The distillation characteristics of the liquid pyrolytic product are given in [1]. A fractionation of the liquid pyrolytic product was carried out in the AUTODEST 860 Fisher column that has 15 theoretical trays. The reflux ratio was 10. The liquid pyrolytic product was fractionated in two fractions: light fraction (IBP-200°C); and heavy pyrolytic oil fraction (200°C – FBP).

The light fraction (IBP-200°C) was hydrotreated in a trickle bed pilot plant. A detailed scheme of the pilot plant is presented in Figure 1.

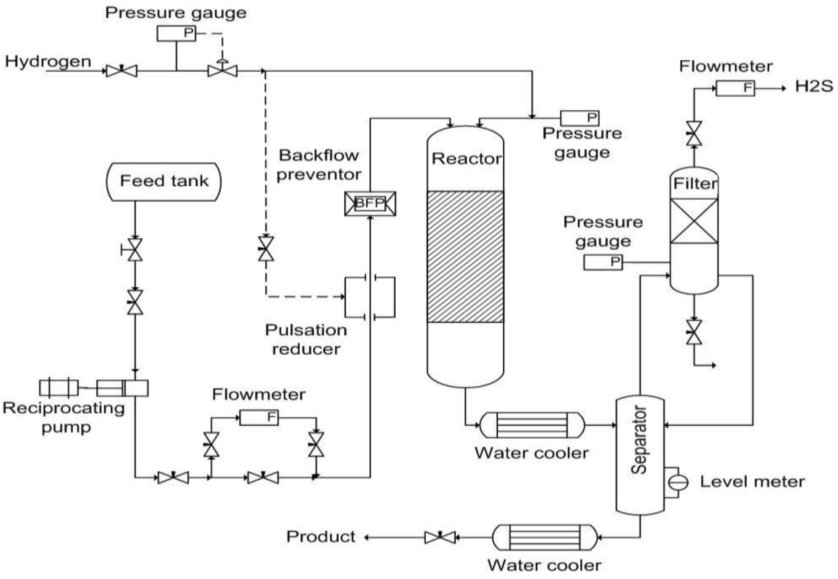

Figure 1 Schematic diagram of the HDS pilot plant unit

The hydrotreatment was performed in two stages, selective hydrogenation-the first stage, and full hydrogenation-the second stage. In the selective hydrogenation catalyst PGC-3S was employed, while in the full hydrogenation catalyst TK-576 was used. The selective hydrogenation is designed for selective hydrogenation of diolefins to olefins, converting the light mercaptans and light sulphur compounds in heavier ones and izomerization of external olefins to internal olefins. The process takes place on Pd-containing PGC-3S catalyst. The full hydrogenation saturates olefins to paraffins along with decomposition of organic sulphurous-, nitric-, and oxygen-compounds, during which hydrogen sulphide, ammonia and water are formed respectively. The process takes place on Co-Mo TK-576 catalyst.

The operating conditions of the hydrotreatment experiments were following for the first stage: reaction temperature - 100°C; reactor pressure -35 kg/cm^2; liquid hourly space velocity (LHSV)–2.0 h^{-1}; treating gas/oil ratio of -380Nm^3/m^3. The treating gas contained 99% hydrogen, for the second stage: reaction temperature - 280°C; reactor pressure -35 kg/cm^2; liquid hourly space velocity (LHSV)–2.0 h^{-1}; treating gas/oil ratio of - 200Nm^3/m^3. The treating gas contained 99% hydrogen.

Then the whole waste tyre pyrolytic oil was also hydrotreated in the trickle bed pilot plant in blends with a diesel fraction obtained during atmospheric distillation of REBCO. The blends consisted of 10% waste tyre pyrolytic oil and 90% REBCO diesel fraction, and 20% waste tyre pyrolytic oil and 80% REBCO.

Two blends of crude oil – REBCO and the whole waste tyre pyrolytic oil (5% pyrolytic oil / 95% REBCO, and 20% pyrolytic oil / 80% REBCO) were also investigated in the process of atmospheric and vacuum distillation. The distillation of the studied crude oil-pyrolytic oil blends was carried out in TBP Euro Dist System from ROFA Deutschland GmbH, designed to perform according to ASTM D2892 requirements. Its fractionation column is equipped inside with packing, equivalent to 15 theoretical plates and the condenser provides the standard's mandatory reflux ratio of 5:1.

The pressure profile of the analysis for separation the samples into definite narrow cuts (IBP-EBP) has been tuned according to cuts boiling point intervals as follows: IBP up to 180°C at pressure 760 mm Hg; 180°C - 260°C at pressure 100 mm Hg; 260°C - 320°C at pressure 10 mm Hg and 320°C - 375°C at pressure 2 mm Hg. The obtained gas fraction in the debutanization step of the analysis is included in the first narrow cut (IBP - 65°C) since its quantity is not permanent for a sample and varies with time. The crude oil residue from the TBP laboratory distillation plant is transferred to the Potstill Euro Dist System where vacuum distillation, according to ASTM D5236 requirements, takes place. Pressure profile in Potstill apparatus is as follows: the fraction which boils up to 430°C is separated from the atmospheric residue at pressure 1 mm Hg, and the other narrow cuts (up to 540°C) – at pressure of 0.2 mm Hg. Finally, the results in terms of weight % evaporated up to definite temperature from both TBP and Potstill plants are combined and a continuous TBP distillation curve of the evaluated samples is generated.

Blending of commodity heavy fuel oil, produced in LUKOIL Neftohim Burgas refinery, with the whole waste tyre pyrolytic oil was studied by measuring closed cup flash point of the heavy fuel and its blends with the whole waste tyre pyrolytic oil in accordance with ASTM D-93.

3. Results and discussion

The distillation characteristics according to ASTM D 86 methods of both gasoline and heavy pyrolitic oil fractions are presented in Table 1. The data in Table 1 show that the light and heavy fractions obtained from the whole pyrolytic oil have distillation characteristics typical for gasoline (the light fraction) and diesel (the heavy fraction) fuels.

Table 1 Distillation characteristic of the waste tyre pyrolytic liquid fractions: the light and the heavy fractions

Waste tyre liquid pyrolitic fraction	Light fraction	Heavy fraction
Density at 15°C, g/cm^3	0.8127	0.937
Distillation ASTM D-86 vol.%		
IBP	52	192
5	82	216
10	96	230
20	113	253
30	126	268
50	146	297
60	157	315
70	166	328
80	175	345
90	194	357
95	217	363
FBP	238	390
Recovery, vol.%	98	98

The data in Table 2 summarizes the physical and chemical properties of both waste tyre pyrolytic fractions (gasoline and diesel fractions). These data indicate that octane numbers (research and motor octane numbers = RON and MON) of the pyrolytic gasoline fraction are relatively high: RON = 93.0; MON = 80.0. However the gasoline fraction high sulphur content (2000 ppm) does not allow direct blending of this material in the finished automotive near zero sulphur gasoline (< 10 ppm sulphur). Moreover the relatively high content of highly reactive diolefinic hydrocarbons (8.4%) makes the waste tyre pyrolytic gasoline fraction chemically unstable and prone to form undesirable gums. Therefore this gasoline fraction must be hydrotreated before its use as a component for production of automotive gasoline grades.

The data in Table 2 also indicate that the waste tyre pyrolytic heavy fraction meets the specification of the heavy oil products: fuel oil and marine oil. The distillation characteristics of the heavy waste tyre pyrolysis fraction as was mentioned earlier correspond to those of diesel fuel. However the low cetane index (25), and high viscosity, as well as high sulphur content do not allow the use of this material as a component for direct blending in the process of production of automotive near zero sulphur diesel (<10 ppm sulphur). Never-theless a hydrotreatment of the heavy waste tyre pyrolytic fraction with refinery diesel streams may allow the use of this fraction for the production of automotive near zero sulphur diesel. Without any additional treatment the heavy waste tyre pyrolytic fraction may be used as finished fuel oil or marine fuel.

Table 2 Properties of both light (gasoline) and heavy pyrolytic oil fraction

Light fraction		Heavy fraction		
Group hydrocarbon composition	**wt.%**		Measured value	Specified value for heavy fuel oil and marine fuel oil
Normal alkanes	4.09	Bromine number, gBr$_2$/100g	102,9	
Iso-alkanes	2.97	Kinematic visosity at 50°C, mm^2/s	6.61	max 380
Cycloalkanes	11.74	Kinematic visosity at 80°C, mm^2/s	3.165	max 115
Normal alkenes	1.14	Relative viscosity at 80°C, °E	1.24	max 15
Iso-alkenes	7.72	Sulphur content, wt.%	0.81	max 3.0
Cycloalkenes	18.62	Pour point, °C	-18	max 30
Normal dialkenes	1.49	Freezing point, °C	-20	max 25
Iso-dialkenes	5.5	Ash	0.015	max 0.15
Cyclodialkenes	1.37	Flash point in closed cup, °C	77	min 60
Arenes	35.6	Flash point in opened cup, °C	92	min 110
Oxygen containing compounds	**%**	Water, vol.%	0.1	max 0.5
		Lower heat content, MJ/kg	41.363	min 39.8
Methylisobytyl ketone	0.7	Water soluble acids and basis	absent	absent
Sulphur containing compounds	**%**	Water and sediments, vol.%	0.4	max 1.0
		Al, ppm	8	Al+Si = max 80
Mercaptane sulphur	0.2	Si, ppm	11	
2- Methylthiophene	0.3	V, ppm	13	max 600
Unidentified compounds	10	Cetane index	25.35	max 60
Octane numbers of waste tyre pyrolysis gasoline				
RON	93.6			
MON	80.0			

The main problem with hydrogenation of oil fractions having high olefins content is the high reactor ΔT, because the hydrogenation reaction is exothermic. As a result of the exothermic hydrogenation reaction in the reactor of the pilot plant it was recorded ΔT of the inlet and outlet of the reactor = 38°C for the first stage and 28°C for the second stage. In order to estimate the ΔT in a commercial hydrotreating unit, which consists of two consecutive reactors for selective hydrogenation and full hydrogenation of gasoline fraction (IBP-200°C), we used the relationship developed in [34] between the content of olefins in the feedstock and the heat of the commercial reactor. The calculations were based on the data for the bromine number, the molecular weight of the gasoline fraction (molecular weight was calculated based on the data for density and T_{50}) and the correlation of Goosens [35]. Calculations showed that during the two-stage hydrotreating of the waste tyre pyrolytic gasoline fraction in an industrial reactor, it could be expected a total temperature difference of the reactor block in an order of 226°C. The reason for the much higher temperature difference of the industrial hydrotreating reactor is the significantly lower heat losses, compared to the pilot plantreactor. Temperature of 66°C in a pilot plant reactor would correspond to 226°C in an industrial reactor. In order to prevent excessive temperature increase in a commercial hydrotreating unit the waste tyre pyrolytic gasoline fraction should be processed in a mixture with another petroleum fraction, or using a reactor with a sectionated catalyst with intermediate cooling or using a recycle of hydrotreated pyrolytic gasoline to regulate the temperature difference of the process within reasonable limits.

After the two stage hydrotreatment of the waste tyre pyrolytic gasoline fraction a loss of 4.7 point RON, and 3.0 MON was registered. The hydrotreated gasoline fraction had sulphur level below 10 ppm and octane numbers RON = 88.9 and MON = 77.0. These octane numbers are very low and do not allow the use of the hydrotreated waste tyre pyrolytic gasoline fraction as finished automotive gasoline. Therefore blending with higher octane number gasoline compounds is obligatory to obtain finished automotive gasoline that meets EN-228 requirements.

The second option for refining of the pyrolytic oil investigated in this work was its hydrotreatment with SRDF obtained from crude oil – REBCO. Properties of the REBCO SRDF and its blends with the whole pyrolytic oil are presented in Table 3. It is evident from these data that the addition of 10 and 20% of the whole pyrolytic oil to the REBCO SRDF leads to a reduction of the SRDF cetane index from 55.9 to 49.8 due to the higher aromaticity of the pyrolytic oil. The data in Table 3 indicate that the hydrotreatment of 100% REBCO SRDF and the blend 90% SRDF/10% whole pyrolytic oil increases the cetane index by 5 points of both feeds. The pyrolytic oil seems to inhibit the hydrogenation of most difficult to hydrogenate mono nuclear aromatics. While the total aromatics content of the hydrotreated 100% REBCO SRDF was reduced from 28.6 to 19%, that of the hydrotreated 90% REBCO SRDF / 10% Pyrolytic oil dropped marginally from 27.8 to 27.3%. The hydrotreatment of the easier to hydrogenate polynuclear aromatics was not affected by the waste tyre pyrolytic oil. During the hydrotreatment of the blend 80% REBCO SRDF / 20% Pyrolytic oil the pilot plant reactor was plugged due to excessive coke formation. It deserves mentioning here that the waste tyre pyrolytic oil did not blend well with the SRDF and layered during prolonged stay. It could be concluded based on these data that the whole waste tyre pyrolytic oil is not suitable as a feedstock for hydrotreatment because of its chemical instability which can cause reactor plugging.

The third option for refining of the pyrolytic oil investigated in this work was to blend the whole pyrolytic oil with crude oil - REBCO and fractionate the blend in the laboratory TBP atmospheric and vacuum distillation, simulating commercial crude distillation unit operation. The REBCO was blended with 5 and 20% waste tyre pyrolytic oil and then fractionated in the ROFA TBP Euro Dist System Figures 2-4 present photographs of bottles that contain wide fractions (light naphta, heavy naphtha, kerosene, diesel, vacuum gas oil, and vacuum residue) obtained from TBP distillation of 100% REBCO, 95% REBCO / 5% waste tyre pyrolytic oil, and 80% REBCO / 20% waste tyre pyrolytic oil.

Table 3 Properties of the feeds, consisting of petroleum diesel and its blends with whole waste tyre pyrolytic oil (A) and products (B) from hydrotreatment

Properties A	**REBCO diesel fraction**	**10% Pyrolytic Oil / 90% diesel fraction**	**20% Pyrolytic Oil / 80% diesel fraction**	**Properties B**	**Hydrotreated diesel fraction**	**Hydrotreated blend of 10% Pyrolytic Oil / 90% diesel fraction**
Density at 20°C, g/cm^3	0.8504	0.8545	0.8600	Density at 20°C, g/cm^3	0.8362	0.8366
Distillation D 86				**Distillation D 86**		
wt.%	Temperature, °C			wt.%	Temperature, °C	
	REBCO diesel fraction	10% Pyrolytics Oil / 90% diesel fraction	20% Pyrolytic Oil / 80% diesel fraction		Hydrotreated diesel fraction	Blend of hydrotreated 10% Pyrolytic Oil / 90% diesel fraction
IBP	225	203	190	IBP	213	198
5	259	251	237	5	247	236
10	268	260	250	10	259	248
20	277	272	266	20	273	263
30	284	281	278	30	282	273
50	299	297	297	50	298	289
70	317	318	320	70	320	308
80	328	327	330	80	332	320
90	345	348	357	90	351	340
FBP	370	386	409	FBP	381	372
Composition, wt. %				Composition, wt. %		
mono-aromatics	20.7	21.1	21.9	mono-aromatics	18.5	27.1
di-aromatics	7.6	6.4	7.0	di-aromatics	0.5	0.2
tri-aromatics	0.3	0.4	0.4	tri-aromatics	0.0	0.0
total aromatics	28.6	27.8	29.3	total aromatics	19.0	27.3
sulphur compounds	0.82			sulphur compounds		
Cetane index	55.9	52.9	49.8	Cetane index	61.0	57.9

Table 5 Properties of the fractions obtained from the two blends of REBCO and the whole waste tyre pyrolytic oil

100% REBCO					5% pyrolytic oil / 95% REBCO					20% pyrolytic oil / 80% REBCO				
Density at 20 °C, g/cm^3														
IBP-110	**110-180**	**180-240**	**240-360**	**360-550**	**IBP-110**	**110-180**	**180-240**	**240-360**	**360-550**	**IBP-110**	**110-180**	**180-240**	**240-360**	**360-550**
0.6874	0.7622	0.8057	0.8534	0.904	0.7275	0.7644	0.7955	0.8485	0.9088	0.7329	0.7777	0.8100	0.8540	0.9144
Kw	11.9	11.8	11.7	11.9	**Kw**	11.9	11.8	11.7	11.9	**Kw**	11.8	11.6	11.5	11.8
wt. %	Distillation ASTM D 2887				wt. %	Distillation ASTM D 2887				wt. %	Distillation ASTM D 2887			
	110-181	**180-241**	**240-361**	**360-551**		**110-181**	**180-241**	**240-361**	**360-551**		**110-181**	**180-241**	**240-361**	**360-551**
IBP	84	76	200	293	IBP	82	69	175	330	IBP	82	89	180	270
5	101	168	220	342	5	101	158	207	356	5	103	164	206	323
10	112	174	229	360	10	113	168	216	369	10	113	172	214	342
20	122	184	239	384	20	124	176	231	389	20	125	177	226	365
30	129	191	253	403	30	132	182	245	406	30	134	181	236	385
40	136	196	266	420	40	139	187	256	421	40	140	186	248	403
50	143	199	279	436	50	146	192	270	437	50	150	191	257	421
60	150	204	294	453	60	152	196	285	453	60	157	195	270	440
70	158	210	308	471	70	161	197	302	471	70	164	197	288	460
80	166	216	324	492	80	168	202	318	491	80	173	201	306	483
90	174	220	346	514	90	177	209	342	513	90	177	207	329	510
95	181	226	363	527	95	183	215	358	527	95	182	213	346	525
FBP	203	240	407	543	FBP	201	230	396	543	FBP	203	225	387	542

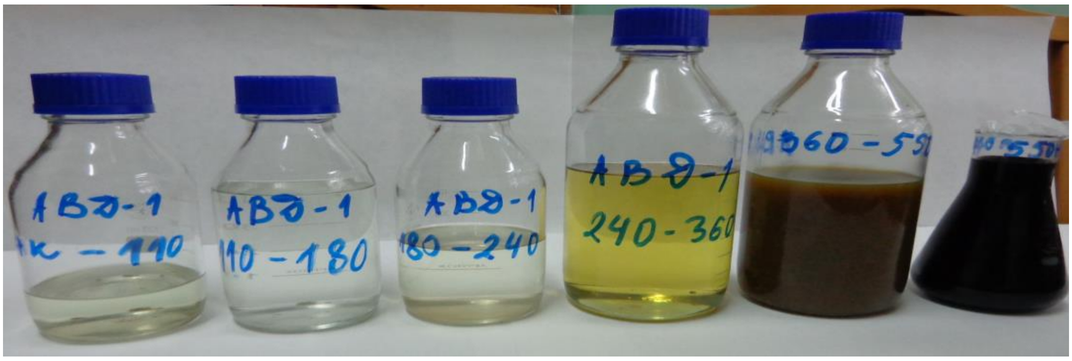

Fig. 2 Photograph of appearance of the wide fractions obtained during TBP distillation of 100% REBCO

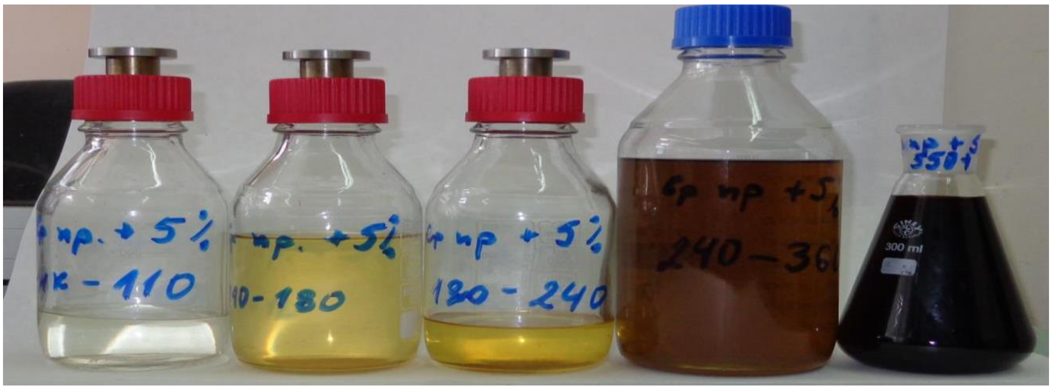

Fig. 3. Photograph of appearance of the wide fractions obtained during TBP distillation of the blend 5% waste tyre pyrolytic oil / 95% REBCO

Fig. 4. Photograph of appearance of the wide fractions obtained during TBP distillation of the blend 20% waste tyre pyolytic oil / 80% REBCO

These pictures clearly show that the wide fractions obtained from the crude blends that contain pyrolytic oil change their colours. For example the REBCO fractions light naphtha (IBP-110°C), heavy naphtha (110-180°C), and kerosene (180-240°C) are colourless, while the heavy naphtha and the kerosene obtained from the crude blend containing 5% pyrolytic oil have yellow colour, and the heavy naphtha and the kerosene obtained from the crude blend containing 20% pyrolytic oil have brown colour. The change in the colour of the fractions obtained from the crude blends that contain pyrolytic oil suggest these fractions are chemically unstable and are prone to oxidation. After performing the experiments the laboratory column should be cleaned due to formation of gums inside the packing. Table 4 presents data of yields of wide fractions obtained during TBP distillation of REBCO and its blends with the pyrolytic oil.

Table 4 Wide cut yields from TBP distillation of REBCO and its blends whit whole waste tyre pyrolytic oil

Fractions	100% REBCO	95%REBCO/5% Pyrolytic Oil	80%REBCO/20% Pyrolytic Oil
Gas	1.0	1.0	1.0
IBP-70	3.0	3.0	3.0
70-110	3.0	3.0	3.3
110-180	9.0	10.2	11.2
180-240	10.0	9.0	9.0
240-360	22.4	21.0	22.0
360-540	28.6	30.4	30.0
>540	23.0	22.3	20.5
Total	100.0	100.0	100.0

These data indicate that the addition of the pyrolytic oil to REBCO increases the yields of heavy naphtha and vacuum gas oil and decreases the yields of kerosene, diesel, and vacuum residue. The simulated distillation characteristics and densities of the heavy naphtha, kerosene, diesel and vacuum gas oil obtained from the three crudes are given in Table 5. These data indicate that T_{50} of the heavy naphtha increases from 143°C for the 100% REBCO to 150°C for the blend 80%REBCO / 20% Pyrolytic oil. T_{50} of the kerosene drops from 199°C for the pure REBCO to 191°C for its blend with 20% pyrolytic oil. T_{50} of the diesel decreases from 279°C for the pure REBCO to 257°C for its blend with 20% pyrolytic oil.T_{50} of the vacuum gas oil diminishes from 436°C for the pure REBCO to 421°C for its blend with 20% pyrolytic oil. These data suggest that the pyrolytic oil contains lower molecular weight components boiling in the range of the kerosene, diesel, and vacuum gas oil than the crude oil REBCO. In contrast the heavy naphtha from the pyrolytic oil may contain higher molecular weight components than the crude oil REBCO. The densities of the wide fractions from the crude blends containing pyrolytic oils are lower due to their higher content of lower molecular components. Kw characteristic factors of the wide fractions from the crude blends containing pyrolytic oils are lower than those of the pure REBCO fractions, which supports the statement that the lower densities of the wide fractions from the crude blends containing pyrolytic oils are due to higher content of lower molecular components.

As a whole the addition of the pyrolytic oil to the crude oil REBCO improves the yields of distillates, but the quality of the distillates deteriorates due to the chemical instability of the waste tyre pyrolytic oil components. Processing of the waste tyre pyrolytic oil in a crude oil distillation unit may create problems with plugging of trays or packing due to the chemical instability of the pyrolytic oil.

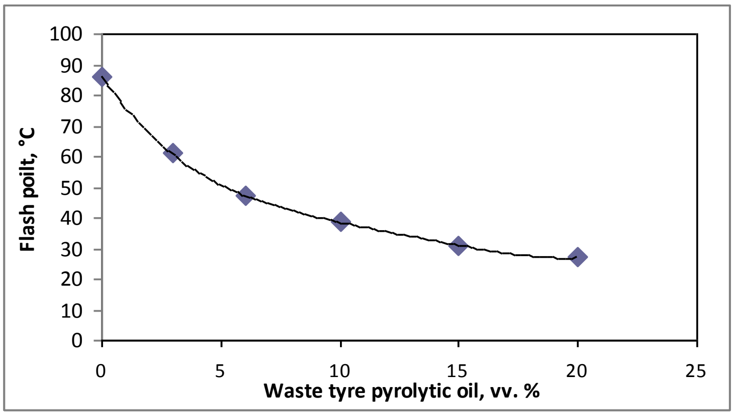

Fig. 5 Dependence of flash point of blends with petroleum fraction

The fourth option for refining of the pyrolytic oil investigated in this work was to blend the whole pyrolytic oil with a commodity fuel oil. Commodity fuel oil taken from LUKOIL Neftohim Burgas refinery with a closed cup flash point of 86°C was blended with 3, 6, 10, 15, and 20% of waste tyre pyrolytic oil. The closed cup flash point of the blends was measured in accordance with ASTM D-93 and the dependence of the fuel oil flash point on the content of the waste tyre pyrolytic oil is presented in Figure 5. It is evident from these data that the addition of the pyrolytic oil decreases the fuel oil flash point. It falls from 86°C at 0% pyrolytic oil to 27°C at 20% pyrolytic oil in the fuel oil. The specification of minimum 60°C flash point for the fuel oil can be met if the content of the pyrolytic oil is not more than 3%.

4. Conclusions

The liquid product from pyrolysis of waste tyres was investigated to refine by four different routes. 1) Fractionation to light (gasoline fraction) and heavy pyrolytic oils and two stage hydrotreatment of the gasoline fraction; 2) Hydrotreatment of a blend of the whole pyrolytic oil with straight run diesel fraction from REBCO; 3) Processing along with REBCO in a crude distillation unit; 4) Direct blending with a commodity fuel oil.

The first route can provide production of commodity fuel oil from the heavy pyrolytic oil fraction and hydrotreated gasoline with octane numbers of RON = 88.9 and MON = 77.0, which requires blending with higher octane number gasoline compounds to obtain finished automotive gasoline with octane numbers RON = 95 and MON = 85.

The second route is questionable due to the chemical instability of the pyrolytic oil that can cause plugging of the hydrotreating reactor, a fact that was registered during processing of a blend of 80% REBCO straight run diesel and 20% pyrolytic oil after only of one day of operation of the laboratory hydrotreating unit.

The third route is also questionable due to the same reason as that described above. The addition of the pyrolytic oil to the crude oil REBCO improves the yields of distillates, but the quality of the distillates deteriorates due to the chemical instability of the waste tyre pyrolytic oil components. Processing of the waste tyre pyrolytic oil in a crude oil distillation unit may create problems with plugging of trays or packing due to the chemical instability of the pyrolytic oil.

The four route allows production of marketable fuel oil by blending of not more than 3% of pyrolytic oil to a commodity fuel oil whose closed cup flash point is not lower than 86°C.

References

[1] Stratiev D, Shishkova I, Pavlova A, Stanulov K, Mitkova M, Skumov M, Tsaneva T. Characterization of the Waste Tyre Catalytic Pyrolysis Liquid Products. Petroleum & Coal 2013; 55 (4):283-290, 2013.

[2] Rodriguez IM, Laresgoiti MF, Cabrero MA, *et al*. Pyrolysis of Scrap Tyres. Fuel Process. Technol. 2001;72 (1):9−22.

[3] Roy C, Chaala A. Vacuum Pyrolysis of Automobile Shredder Residues. Resour. Conserv. Recycl. 2001; 32 (1):1−27.

[4] Dai X W, Yin X L, Wu C Z, et al. Pyrolysis of Waste Tyres in a Circulating Fluidized-bed Reactor. Energy 2001;26 (4):385−399.

[5] Benallal B, Roy C, Pakdel H, Chabot S, Poirier A M. Characterization of Pyrolytic Light Naphtha from Vacuum Pyrolysis of Used Tyres Comparison with Petroleum Naphtha. Fuel 1995; 74 (11):1589-1594.

[6] Shah J, Rasul Jan M, Mabood F. Catalytic Conversion of Waste Tyres into Valuable Hydrocarbons. J Polym Environ 2007;(15):207–211.

[7] Shah J, Rasul Jan M, Mabood F. Catalytic Pyrolysis of Waste Tyre Rubber into Hydrocarbons Via Base Catalysts. Iran J Chem. Chem. Eng 2008;27 (2):103-109.

[8] Williams T Paul, Brindle J Alexander. Catalytic Pyrolysis of Tyres: Influence of Catalyst Temperature. Fuel 2002; 81:2425–2434.

[9] Arabiourrutia M, Lopez G, Elordi G, Olazar M, Aguado R, Bilbao J. Characterization of the Liquid Obtained in Tyre Pyrolysis in a Conical Spouted Bed Reactor. International Journal of Chemical Reactor Engineering 2007;5 (A96).

[10] Shah J, Rasul Jan M, Mabood F, Shahid M. Conversion of Waste Tyres into Carbon Black and Their Utilization as Adsorbent. Journal of the Chinese Chemical Society 2006; 53:1085-1089.

[11] Rombaldo SFC, Lisbôa LCA, Méndez AOM, Coutinho dos Reis A. Effect of Operating Conditions on Scrap Tire Pyrolysis. Materials Research 2008; 11 (3):359-363.
[12] Kennedy RZ, Rathinaraj D. Exhaust Emissions and Performance of Diesel Engine Fuelled with Tyre Based Oil Blends. IE(I) Journal-MC 2007;88:13-18.
[13] Sugano M, Tamaru T, Hirano K, Mashimo K. Additive Effect of Tyre Constituents on the Hydrogenolyses of Coal Liquefaction Residue. Fuel 2005;84:2248–2255.
[14] Jie Z, Yong-Rong Y, Xiao-hong R, Siegfried S. Investigation of Reinforcement of the Modified Carbon Black from Wasted Tires by Nuclear Magnetic Esonance. J Zhejiang Univ SCIENCE A 2006; 7 (8):1440-1446.
[15] Murugan S, Ramaswamyand C M, Nagarajan G. A Comparative Study on the Performance, Emission and Combustion Studies of a DI Diesel Engine Using Distilled Tyre Pyrolysis Oil–Diesel Blends. Fuel 2008;87 (10-11):2111-2121.
[16] Rofiqul MI, Hanin H, Rafiqul BA. Limonene-Rich Liquids from Pyrolysis of Heavy Automotive Tire Wastes. Journal of Environment and Engineering 2007;2 (4).
[17] Murillo R, Aranda A, Aylón E, Callén SM, Mastral MA. Process for the Separation of Gas Products from Waste Tire Pyrolysis. Ind. Eng. Chem. Res. 2006;45 (5):1734–8.
[18] Murillo R, Aylón E, Navarro V M, Callén S M, Aranda A, Mastral M A. The Application of Thermal Processes to Valorise Waste Tyre. Fuel Processing Technology 2006; 87 (2):143-147.
[19] Dıez C, Sanchez EM, Haxaire P, Martınez O, Moran A. Pyrolysis of Tyres: A Comparison of the Results from a Fixed-Bed Laboratory Reactor and a Rilot Plant (Rotatory Reactor). J. Anal. Appl. Pyrolysis 2005;74:254–258.
[20] Roy C, Chaala A, Darmstadt H. The Vacuum Pyrolysis of Used Tires end Uses for Oil and Carbon Black Products. J. Anal. Appl.Pyrolysis 1999;51: 201.
[21] Mastral AM, Murillo R, Callen, MS, Garcia T, Snape CE. Influence of Process Variables on Oils from Tyre Pyrolysis and Hydropyrolysis in a Swept Fixed Bed Reactor. Energy & Fuels 2000;14 (4):739–744.
[22] Mui ELK, Ko DCK, McKay G. Production of Active Carbons from Waste Tires-a Review. Carbon 2004;42 (14):2789-2805.
[23] Williams TP, Brindle JA. Aromatic Chemicals from the Catalytic Pyrolysis of Scrap Tyres. Journal of Analytical and Applied Pyrolysis 2003;67:143–164.
[24] Kar Y. Catalytic Pyrolysis of Car Tire Waste Using Expanded Perlite. Waste Management 2011; 31:1772–1782.
[25] Kyari M, Cunliffe A, Williams TP. Characterization of Oils, Gases, and Char in Relation to the Pyrolysis of Different Brands of Scrap Automotive Tires. Energy & Fuels 2005;19:1165-1173.
[26] Rushdi I A, BaZeyad Y A, Al-Awadi S A, Al-Mutlaq F K, Simoneit T R B. Chemical Characteristics of Oil-Like Products from Hydrous Pyrolysis of Scrap Tires at Temperatures from 150 to 400°C. Fuel 2013;107:578–584.
[27] Na J.G., Lee SH, Chang HK Soo HCh. Coke Deposition on The Reactor Surface in Waste Tyre Pyrolysis. The 5th ISFR (October 11-14, 2009, Chengdu, China).
[28] Jones CJ. Comment on "The Application of Thermal Processes to Valorise Waste Tyre" by R. Murillo, E. Aylón, M.V. Navarro, M.S. Callén, A. Aranda, and A.M. Mastral. Fuel Processing Technology 2006; 87:753.
[29] Quek A, Balasubramanian R. Liquefaction of Waste Tires by Pyrolysis for Oil and Chemicals—A review. Journal of Analytical and Applied Pyrolysis 2013;101:1–16.
[30] Williams T P, Bottrill P R, Cunliffe M A. Combustion of Tyre Pyrolysisi Oil. Trans. IChemE 1998;76 (B), 1998.
[31] Pavlova A, Stratiev D, Shishkova I, Mitkova M, Skumov M, Tsaneva T. Gas Chromatographic Investigations of Composition of Waste Tyre Pyrolysis Gasoline. Global Journal of Medical Research Interdsciplinary 2013;13 (4).
[32] Patent PCT/CN2006/001282.
[33] Patent PCT/CN2006/003500.
[34] Stratiev D, Argirov G, Tzingov T, Minkov D. Upgrading of Visbreaker Naphtha. 0179-3187/06/10 2006.
[35] Goossens A. Prediction of Molecular Weight of Petroleum Fractions. Ind. Eng. Chem. 1996;35:985-988.