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Pyrolysis Oil from Waste Tyres as Component of Heavy Fuel

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Abstract- Recycling of rubber waste is a very important issue, as such waste is not biodegradable and has a negative impact on the environment. In addition, recycled rubber should be considered as a source of new material with economic impact. The present paper studied the thermal cracking process of waste tyres in laboratory condition. Experiments were conducted at a different temperature range 500 - 650 ºC and contact time from 180 to 210 minutes. The results indicate that the obtained product (pyrolysis oil) has an application as additional quantities of dark fuels.

Keywords:- Recycling, Rubber waste, Dark fuel, Thermal cracking, Pyrolysis oil.

I. INTRODUCTION

The accumulation of waste from rubber processing plants and worn-out rubber products is becoming a particularly pressing economic and environmental problem. Their high resistance to atmospheric and bacterial processes requires the development of many methods for the absorption of worn tread vulcanizates. The most used method for their recycling is the chemical decomposition of polymer waste in two ways: thermal and catalytic.

In recent years, in Europe and North America, the recycling of polymers has been carried out by thermal cracking- pyrolysis [2, 7, 8]. They undergo pyrolysis from whole tires to grinds from them. It can be carried out in an environment of oxygen deficiency, in vacuum, in an aqueous atmosphere, in the presence and absence of a catalyst, in reactors with periodic and continuous action, in a fluidized bed, at different temperatures [1, 2, 3].

It has been established that during the thermal decomposition of a wide range of products, the temperature varies from 500 to 900 ºC. A method of Flash pyrolysis of a polystyrene in a free-fall reactor at 700-875 °C, gave benzene, styrene, toluene, naphthalene, and C_1-C_4 has been described [5].

In catalytic pyrolysis, the temperature drops significantly, the appropriate catalyst and reactor make it possible to control both the product yield and the temperature drop depending on the composition of the product obtained, which leads to a more cost-effective process [4].

In this study were considered experiments of thermal cracking with raw material - protected vulcanizates acquired from the Transport and Engineering Company, Alexandria, Egypt in laboratory conditions at different temperatures and contact times. The possibility of using of obtained pyrolysis oil as a component to dark fuels was also investigated.

II. MATERIALS AND METHODS

All reagents used for the experiments were commercially available and were not purified further. The raw material used was produced by Transport and Engineering Company, Alexandria, Egypt.
The process of thermal cracking of these raw materials was performed by the methods described in [6].

The scheme of the laboratory installation is shown on Figure 1. The quantity of chunks put into the stainless reactor (1). The stainless reactor is provided with thermal couple (2) and manometer (3) with acicular valve (4). The obtained products pass into copper cooler (5) for condense of vapors as higher distillates catch into receptacle (6) and the lighter absorbed by solar oil in Drexel (7). The obtained gasses are summarized in gasses collector (8). After finishing the experiment, the reaction products were cooled and subjected to follow investigations.

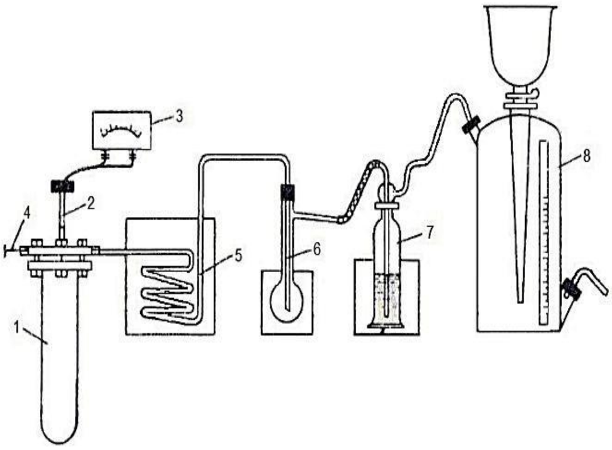

Fig 1. The scheme of the laboratory installation.

The obtained pyrolysis oil was thermo gravimetrically analyzed by instrument NETZCHSTA 449 F3, Germany to establish its caloricity.

Infrared spectra of the pyrolysis oil were recorded with a Tensor 27 Brucker instrument (Germany) within the 4000-400 cm^{-1} region. The samples were prepared as KBr pellets and were put at the same conditions without water vapor and CO_2.

For the analyzed mixtures we used heavy oil, produced from Polysan AD, Russse, Bulgaria.

III. RESULTS AND DISCUSSION

We performed a laboratory process of thermal cracking of protected vulcanizate under the conditions specified in Table1. The process of thermal cracking was conducted within the temperature interval from 500 to 650 ºC for 180-210 minutes, at pressure from 2, 5 - 3, 0 MPa.

Table 1. Conditions and material balance of the experiments.

S. No.	Tempera-ture in reactor, °C	Contact time, minute	Pyrolysis products, g		
			Oil	Gas	Coke
1	500	180	23.40	9.60	14.90
2	500	210	22.90	9.80	15.20
3	550	180	26.05	9.25	14.55
4	550	210	25.10	9.30	14.70
5	600	180	25.30	9.70	14.90
6	600	210	24.20	9.60	15.55
7	650	180	24.90	10.05	15.00
8	650	210	23.50	10.40	15.85

From the above material balances in Table 1 of the individual laboratory processes of thermal cracking of the raw material, it can be concluded that with increasing contact time and temperature increases the yield of coke soot, and also increases the amount of gas. The yield of pyrolysis oil under the selected conditions varies in the range 45.8 ÷ 52.1%. The best yield of pyrolysis oil - 52.1% we obtained at 550 °C and a contact time of 180 minutes.

The obtained liquid product was measured by instrument NETZCHSTA 449 F3, Germany to establish its caloricity. The best data is presented on the diagram shown on figure 2. As you can see the obtained liquid product has high caloricity.

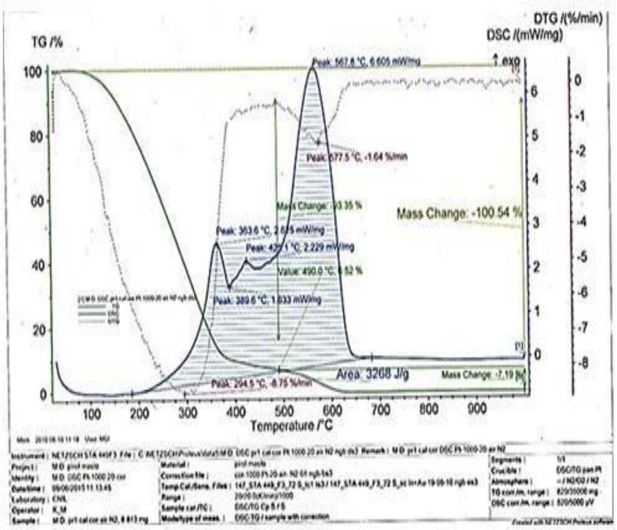

Fig 2. Thermogravimetry diagram of obtained pyrolysis product.

The obtained liquid product was investigated by physico-chemical analysis and its properties are given in Table 2.

The present data (Table 2) has shown that pyrolysis oil, which was obtained in laboratory conditions, on one hand presented excellent combustion parameters, but on the other hand does not fully adhere to the ecological norms of the international standards (ISO, ASTM, BSS, etc.) for blend fuel oils, because it has too many coke residue and ash content. It has also been noted that the obtained product has the correct sulphur content for dark fuels, but its kinematics viscosity is too low for it to be used in turbines.

The data from Table 2 shows that it's possible through application of industrial thermal processes to utilize protected vulcanizates to obtain additional components of fuels and additives on one hand and to solve a serious ecological problem through treatment of the raw materials instead of burning them and polluting the air on the other.

Table 2. Physico-chemical characteristics of pyrolysis oil obtained from thermal cracking.

Parameters	Methods	Value
1. Density at 15 °C, kg/m^3	ISO 3675	886.6
2. Kinematic viscosity at 50 °C, mm^2/s	ISO 3104	2.11
3. Flash point, °C	ISO 2719	57.3
4. Coke residue, % (m/m)	ISO 10370	5.1
5. Sulphur content, % (m/m)	ISO 8754	0.59
6. Ash content, % (m/m)	ISO 6245	0.41
7. Water content, % (v/v)	ISO15512	Neal
8. Color	ISO17.180.20	3.05
9. Specific heat, kJ/kg	ISO 11357	39.37
10. Initial point, °C	ISO 3405	47,5
11. Final boiling point, °C	ISO 3405	>385
12. Distillation characteristic, % (v/v)	ISO 3405	
200 °C		33.7
250 °C		51.0
300 °C		63.2
350 °C		75.9

The infrared spectrum of the obtained pyrolysis oil is shown in figure 3.

In the range 3000-2800 cm^{-1} we observe the asymmetric C-H stretch of the methyl and methylene groups (2955 and 2926 cm^{-1}, respectively). Methyl C-H asym. / sym. bend is observed in 1464 and 1377 cm^{-1}.

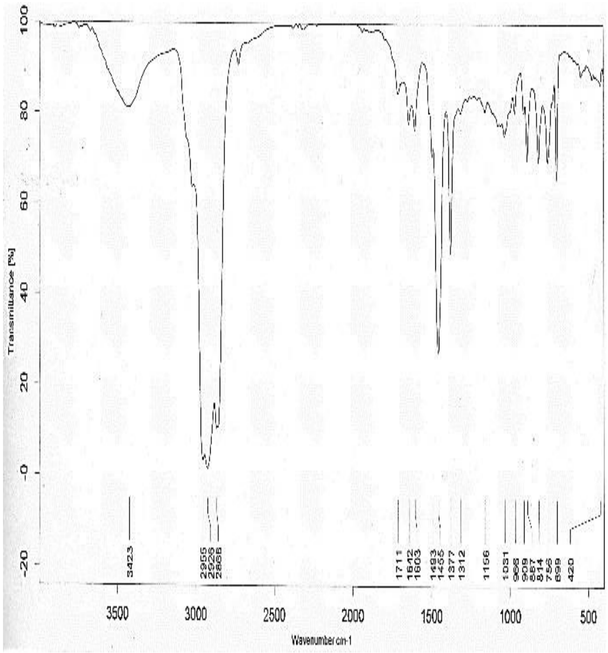

Fig 3. Infrared spectra of the obtained liquid product.

The alkenyl stretch ν (C = C) occur in the range 1680-1640 cm^{-1}, while the bands of the out-of-plane deformation δ (C-H) of the double C = C, γ (C-H) are observed in the range 1000- 675 cm^{-1}.

The aromatic ring stretch is observed as stripes in the range 1640-1420 cm^{-1}. The band at 1490 cm^{-1} is the most intense and is most important in the analysis, as it does not overlap with the bands of the olefin ν (C = C) or δ (CH_2) and δ as (CH_3) of the alkanes.

The obtained pyrolysis oil was investigated for its possibility to be used as a component for heavy fuel. In accordance of ASTM D 4057 4 mixtures were prepared. The composition contents are given in Table 3.

Table 3. Composition consists of prepared mixtures.

№	Heavy fuel, wt %	Pyrolysis Oil, wt %
1	95	5
2	85	15
3	75	25
4	65	35

The obtained mixtures were investigated by the physico-chemical methods and the obtained results are given in Table 4.

Table 4. Physico-chemical properties of obtained mixtures.

Parameters	Composition Values			
	1	2	3	4
Density at 20 °C	0.9298	0.9090	0.8885	0.8815
Kinematic viscosity at 50 °C, mm^2/s	14.25	14.20	14.35	14.35
Specific heat (lower), KJ/kg	39.90	36.00	40.85	41.10
Water soluble acids and base	Neal	Neal	Neal	Neal
Sulphur, %	1.17	1.15	1.13	1.16
Ash content, % (m/m)	0.34	0.31	0.32	0.25
Flash point, °C	214	188	171	163
Freezing point, °C	-9	-11	-12	-12
Water content, %	Neal	Neal	Neal	Neal

From the performed analyzes and the obtained results it is proved that the mixtures do not contain water and mechanical impurities, but have an increased sulfur content, which does not respond to European standards. The value of sulphur content for all mixtures is higher than the maximum for Europe -1.0 for boiler fuels. But the mixtures respond the international standard, which accepts the sulfur content of marine fuels up to 2.7%.

All mixtures show an increased value of ash content, according to the international standard - the norm is max. 0.2, which when using the mixtures would lead to deteriorating environmental performance during combustion. It is known that the ash in the mixtures is obtained from the sulfur content in the pyrolysis oil, ash is making from its impurities - aluminum, mercury, zinc and other heavy metals accompanying sulfur powder, which is used in the manufacture of tires. The values of flash point and freezing point for the all of obtained mixtures are excellent and fully respond to all standards. The obtained results can be used as a basis to develop and obtain components which can be used as component of heavy fuel.

IV. CONCLUSIONS

For the first time the thermal processes for utilization of protected vulcanizates was applied in Yemen in a laboratory condition. The obtained liquid product – pyrolysis oil cannot be differentiated from dark oil fractions. The results from the laboratory experimentation are promising. With some more future research, this process can be integrated into the industry. On the basis of the obtained results, we may conclude that the obtained liquid product may be used as a component in dark fuel.

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