

HYDROREFINING OF TYRE PYROLYSIS DERIVED LIQUID FRACTIONS

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The main goal of the studies was hydrorefining of waste rubber and tire derived pyrolytic liquid fractions. It was found that hydrorefining process carried out in the presence of new commercial catalyst and severe process parameters improves its properties. The obtained hydrorefining products presents quite satisfactory properties, sulphur content less than 0.1 wt % and bromine number less than 20 g Br₂/100 g, light yellow colour and because of high content of aromatic compounds low cetane index (less than 35). The obtained hydrorefining products are suitable components to fuel oil blending.

Keywords: pyrolysis, used tyres, waste rubber, pyrolytic oil, hydrorefining,

1. Introduction

The product of car tires pyrolysis is usually 35-50% of liquid product, pyrolysis oil, up to 10% gas and 45-55% of solid carbon residue containing in dependence on tire type a few percent of steel cord [1,2]. The capacity of the liquid product changes and depends on the final temperature of the pyrolysis process. It is usually a dark liquid with a large content of olefinic and aromatic hydrocarbons and sulfur, above 0.7% wt and final boiling point up to about 350 °C. The potential use of such a fuel is possible only after prior refining. As shown earlier [2] hydrotreating process can be used for this purpose, although the results are not entirely satisfactory. The presented in this presentation research uses commercial hydrotreating catalysts used in recent years in the domestic refining industry.

2. Experimental

Pyrolytic fraction was obtained from industrial batch pyrolysis process. Process was realized in horizontal rotary reactor. One batch of the pyrolysed feed was composed from mixture of waste rubber and the whole spend tires, total weight of the one batch to the pyrolysis reactor about 10 tons. Temperature of pyrolysis process attained 450 °C and vapour pyrolysis product was cooled and condensed in cooler system. Non-condensed hydrocarbon gas was applied as fuel gas in the plant.

Two commercial refinery nickel molybdena catalysts were applied (Table 1). They differed in composition of catalyst support, alumina and silica alumina). The determination of physicochemical properties was not allowed. The whole pyrolysis derived fraction (i.b.p. 20-to f.b.p., ca 350 °C) was submitted to hydrorefining process.

Table 1

Composition of the used commercial catalysts (other properties are unknown)

| Properties\ Commercial Catalysts | NiOMoO ₃ /Al ₂ O ₃ | NiOMoO ₃ /SiO ₂ -Al ₂ O ₃ |
|--|---|---|
| Molybdenum content [% m/m MoO ₃] | 16 | 16 |
| Nickel content [% m/m NiO] | 5 | 5 |

Two hydroprocessing experiments were realized in the laboratory scale continuous flow apparatus previously described by Walendziewski et.al. [1], Fig. 1. The applied series of

experiments are presented in Table 1. In each hydroprocessing series one of two commercial hydrodesulphurisation NiMo/Al₂O₃ or NiMo-SiO₂/Al₂O₃-SiO₂ catalysts was used in this research. 50 cm³ of the catalyst was packed to the reactor tube (total reactor volume 300 cm³). Before hydrorefining tests the applied catalyst was sulfided with H₂S obtained by hydrogenolysis of diethyl sulfide in hydrogen stream (solution of sulfiding agent in gas oil fraction as a feed). After hydrorefining the the received samples of the liquid product, were leached with sodium hydroxide solution in order to remove residual hydrogen sulphide, rinsed with water to remove soda lye and dried before analysis with anhydrous sulphate. Table 2 presents parameters of the realized hydroprocessing experiments.

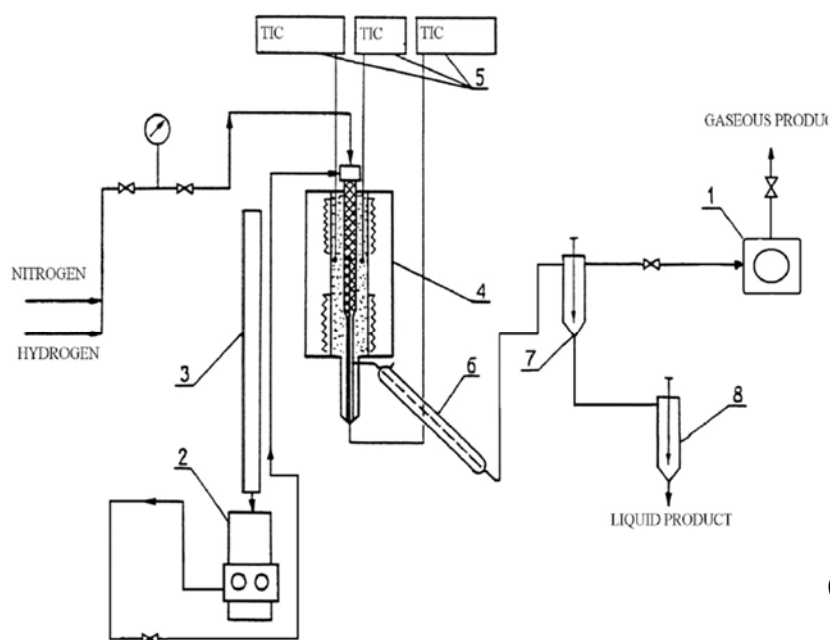


Fig. 1. Schematic view of hydrorefining apparatus [24]. (1) gasometer, (2) pump, (3) feed tank, (4) reactor, (5) temperature controllers, (6) water cooler, (7) pressure gas-liquid separator, (8) atmospheric separator

Table 2

The hydroprocessing parameters, sample numbers

| Sample N ^o | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|------------------------------------|---|-----|-----|-----|---|-----|-----|-----|
| Catalyst/ | NiOMoO ₃ /Al ₂ O ₃ | | | | NiOMoO ₃ /Al ₂ O ₃ /SiO ₂ | | | |
| H ₂ pressure, MPa, | 3 | | | | 5 | | | |
| LHSV, h ⁻¹ | 1,5 | | | | 1,5 | | | |
| H ₂ /oil ratio(mol/mol) | 6 | | | | 6 | | | |
| Temperature, °C | 320 | 340 | 360 | 380 | 320 | 340 | 360 | 380 |

The following physiochemical properties and standard test methods were used:

- Sulphur content - X-ray fluorescence, equipment ED 2000 OXFORD.
- Olefin content by Bromine number - ASTM D 1491-60(1971 standard).
- Product density - EN ISO 3675 standard.
- Kinematic viscosity - PN-EN ISO 3104:2006 standard.
- Fractional composition (atmospheric pressure) PN-EN ISO 3405:2006 standard.
- Flash point - Pensky - Martens – closed cup - EN ISO 2719
- Pour point - ASTM method D97.
- Cetane index (CI) - PN-EN ISO 4264 standard.

3. Results and discussion

The obtained results clearly indicate that, similarly to our previous studies [2], the influence of the catalyst used and its work parameters on the obtained hydrotreating results of the liquid hydrocarbon fraction from tire pyrolysis is clearly visible. The color of the hydrotreated samples shown in Fig. 2 unambiguously indicates that increasing the pressure and temperature of the process allows a significant change in the color of the products from very dark pyrolysis oil, sample 0 to light or straw-bright for samples 4 and 7 and 8. This requires the use of a relatively high process temperature, at least 360 ° C and 3 MPa hydrogen pressure. Significant improvement of the color of hydrotreated oil fraction in the process has been confirmed in the physicochemical tests of product properties (Tables 2 and 3).

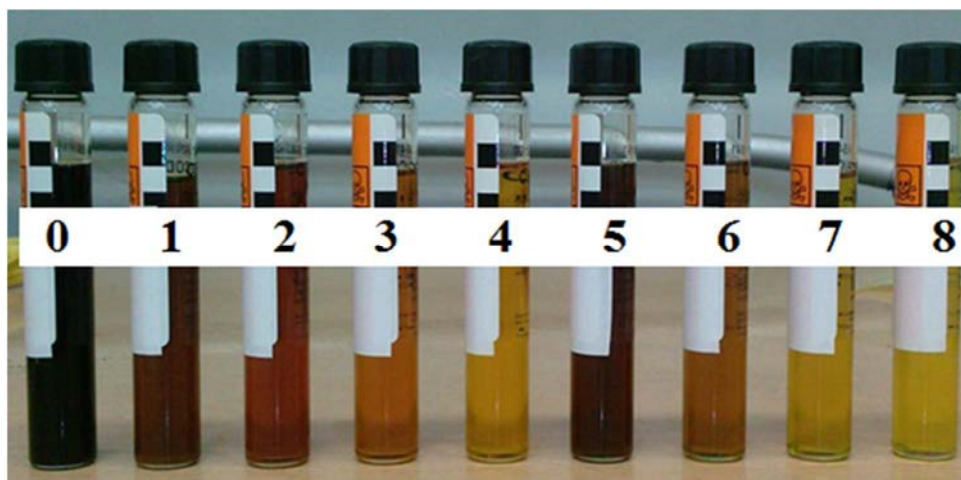


Fig. 2. View of color of the obtained hydrorefining products (sample 0 =the feed, sample obtained using catalyst 1)

Table 2

. Physicochemical properties of the feed, pyrolysis oil and the hydrorefined products obtained in the hydroprocessing process

| Sample Properties/Catalyst No | | Feed (0) | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|----------|------|------|------|------|-------|------|------|------|
| Pour Point, °C | 1 | -57 | -23 | -21 | -26 | -26 | -27 | -21 | -18- | -17 |
| | 2 | -57 | -47 | -44 | -37 | -32 | -46 | -43 | 35 | -30 |
| Sulfur content, wt % ^{a)} | 1 | 0.87 | 0.55 | 0.31 | 0.28 | 0.09 | 0.450 | 0.19 | 0.09 | 0.07 |
| | 2 | 0.87 | 0.69 | 0.56 | 0.45 | 0.27 | .57 | 0.47 | 0.29 | 0.15 |
| Bromine number gBr ₂ /100g ^{a)} | 1 | 64.7 | 35.9 | 23.7 | 19 | 15.6 | 31 | 22.8 | 10.2 | 9.3 |
| | 2 | 647 | 63.1 | 60.4 | 43.1 | 26.9 | 60.3 | 40.1 | 29.2 | 19.1 |
| Cetane index ^{b)} | 1 | 20 | 21 | 27 | 32 | 34 | 27 | 33 | 34 | 35 |
| Density, kg/m ^{3b)} | 1 | 916 | 911 | 910 | 907 | 903 | 909 | 907 | 904 | 900 |
| Viscosity, mm ² /s ^{b)} | 1 | 4.55 | 4.36 | 3.86 | 4.34 | 4.03 | 4.30 | 4.01 | 3.85 | 4.21 |
| Flash point, °C ^{b)} | 1 | - | 73 | 71 | 75 | 74 | 75 | 75 | 77 | 76 |

a) Properties of the wide pyrolysis oil fraction, with gasoline fraction

b) Properties of the oil fraction, after separation of gasoline fraction (ibp. above 180 °C)

Definitely better results, better product properties were obtained using catalyst 1 (supported on alumina) than using catalyst 2 (aluminosilicate). Along with the change of the process parameters (catalyst 1) an increase in the degree of hydrogenation of olefins and desulfurisation is

observed, presented by the reduction of the bromine number to about 10 gBr₂ / 100 g and the sulfur content to 0.07 wt%. The results obtained with the catalyst 2 process were clearly less satisfactory. Along with the change of color, reduction of sulfur content and hydrogenation of olefins, an increase in the pour point of the oil fraction as well as an increase in the cetane number and a slight decrease in its viscosity are observed. It seems that this is the result of partial hydrogenation of aromatic hydrocarbons under quite stringent process conditions and olefins to the corresponding paraffin hydrocarbons. This is also confirmed by a slight reduction in the density of the obtained hydrorefining products compared to crude pyrolysis oil. There is also a slight influence of process parameters on distillation of hydrorefinates obtained. As a result of partial hydrogenolysis and hydrocracking of hydrocarbons, a slight decrease in the initial boiling temperature is observed during the process. Due to their properties, mainly sulfur content, high density and low cetane number, the oil refinery products from tire pyrolysis can be used at best as a component of fuel oils.

Table 3

Distillation data of the applied feed, pyrolysis oil and the obtained hydrorefined samples

| N° Vol.% | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | Feed |
|-------------|-----|-----|-----|-----|-----|-----|-----|-----|------|
| IBP% | 64 | 64 | 62 | 62 | 60 | 60 | 57 | 55 | 64 |
| 20% | 174 | 181 | 179 | 179 | 184 | 180 | 178 | 179 | 183 |
| 50% | 255 | 263 | 255 | 260 | 280 | 265 | 252 | 262 | 259 |
| 90% | 358 | 320 | 360 | 356 | 327 | 335 | 345 | 354 | 359 |
| FBP | 358 | 336 | 361 | 361 | 324 | 335 | 345 | 354 | 352 |

4. CONCLUSIONS

- Application of last generation Al₂O₃ based NiMo catalyst shows higher activity in the hydrorefining process of tire derived pyrolytic oil than the SiO₂-Al₂O₃ based one.
- Increasing the process temperature increases hydrodesulfurization level of oil, i.e. lowering of sulfur content and the degree of hydrogenation of olefins which is determined by measuring the bromine number in refined oil.
- Quite satisfactory quality refined oils can be obtained using alumina based NiMo catalyst and temperature process at least 360 °C.
- Hydrogenation of olefins in the hydrotreating process increases the pour point of refined hydrocarbon fraction and cetane index while its lowers density.
- The products of hydroprocessing of oil fraction from tire pyrolysis is rather not suitable for use as diesel fuel component but it can be used as a component of heating oils or as a special fuel (alternative).

References:

- [1] Martinez JD, Puy N, Murillo R, Garcia T, Navarro MV, Mastral AM. *Renew. Sustain. Energy Rev.* 2013; 23:179–213.
- [2] Debek C, Walendziewski J., *Fuel*, 2015, 159, 659-665.

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