



## Tire pyrolysis oil processing in refineries

### Introduction

End-of-life tires can be processed in pyrolysis plants to produce a partly renewable and partly circular pumpable oil called tire pyrolysis oil (TPO) for further upgrading to fuels and products. In EU the potential is about 590 kton/year TPO. Since natural rubber is part of the tires the produced TPO can be used for sustainable production of liquid transport fuels. The TPO can have a renewable fraction of up to about 50% and is miscible with ordinary hydrocarbon streams in a refinery although depending on specific hydrocarbon compositions minor phase separations could be anticipated upon blending.

### Catalytic cracking of TPO

In 1976 researcher from ERAP (France) patented the application of co-processing TPO (1-30%) in a catalytic cracking process and they observed improved yields of gasoline and liquefied gas. In recent years the research group of Professor Bilbao at University of Basque Country have studied coke formation and yields from co-processing scrap tire pyrolysis oil in laboratory fluid catalytic cracking (FCC) test equipment in several publications and their results point to a viable and economically attractive valorization route for discarded tires. For example, they observed that co-processing TPO with vacuum gas oil (VGO) increased the naphtha and light cycle oil yield thus promoting the high-interest hydrocarbons for refineries.

Preem carried out full scale demonstration trials of about 200-ton TPO in a fluid catalytic cracker in early 2023. No severe influence on the FCC unit operation could be observed during the trial which was executed during a few days, but of course smaller changes compared to only processing conventional feed could be noted, such as more H<sub>2</sub>S in the dry gas. Since TPO contain about 1% of sulfur it will also end up in the FCC liquid products such as gasoline. Larger volumes of TPO targeted for the FCC application thus needs to be desulfurized, either upfront or downstream the FCC unit. This could be achieved by extraction, adsorption or hydroprocessing.

### Sulfur and nitrogen species in TPO

Sulfur compounds identified in the TPO were sulfurous acid cyclohexyl esters of varying carbon chain length and benzothiazole, but a full list of sulfur species demands a dedicated analytical approach. The TPO also contain significant levels of N (about 0.5 %) which were identified in e.g., quinoline, 2,4-dimethyl and hexadecanitrile. These compounds in turn originate from sulfur in cross-linking bridges in polymer chains from the vulcanization process and from accelerants such as mercaptobenzothiazole (MBT)

and inhibitors such as cyclohexylthiophthalimide. Sulfenamide derivatives are produced by reacting MBT and mercaptobenzothiazole disulfide (MBTS) with primary amines (cyclohexylthiophthalimide) or secondary amines (dicyclohexyl-2-benzothiazolesulfenamide).

### **Hydroprocessing of TPO**

Several research papers are available from e.g., Debek et al. ([Fuel 159 \(2015\) 659-665](#)) and Straka et al. ([Chem. Eng. Journal 460 \(2023\) 141764](#)) describing standalone hydrodesulfurization (HDS) of TPO. Straka et al. also investigated the hydrodenitrification (HDN). On the other hand, a more realistic approach would be to hydroprocess the TPO together with other petroleum and renewable feeds within a refinery to use existing large-scale infrastructures as opposed to building new and small-scale dedicated TPO hydroprocessing reactors.

We therefore investigated 20% co-hydroprocessing of TPO with a light gas oil (LLGO) at conventional fixed bed hydrotreating conditions (70 bar, 360-380 °C, LHSV 1 h<sup>-1</sup>, GTO 500) using a NiMo/Al<sub>2</sub>O<sub>3</sub> hydrotreating catalyst in a continuous fixed bed reactor. The N and S contents of the TPO were 5000 and 8700 mg/kg, respectively, whereas the fossil co-feed reference had 100 and 480 mg/kg, respectively. The tests showed successful desulfurization and denitrification as expected. The N content in hydrotreated products were between 6 and 11 mg/kg, whereas sulfur was about 100-200 mg/kg. It is likely that ammonium sulfides formed in the hydroprocessing reactor and a water wash of the hydrotreated products reduced N < 3 mg/kg and S < 100 mg/kg. Total acid number (TAN) was reduced after hydrotreatment (< 1) and the density was about 0.83 kg/dm<sup>3</sup>.

TPO is highly olefinic and aromatic, but its exact hydrocarbon structure depends on type of tires and pyrolysis process used. In the continuous hydroprocessing test here the olefins were completely saturated and aromatics to some extent according to <sup>1</sup>H-NMR analysis. The hydrogen consumption was surprisingly low during co-processing and could be a synergistic effect from the co-feed or from the catalyst and conditions used. Whether this was an experimental artefact or actual result needs to be repeated and verified.

It was also found by filtration experiments that TPO contain a small fraction of waxy material forming a filter cake, which by GC-MS could be identified to include long-range hydrocarbons such as octosane (C<sub>28</sub>H<sub>58</sub>), tricontane (C<sub>30</sub>H<sub>62</sub>) and hentricontane (C<sub>31</sub>H<sub>64</sub>). The obtained filter cake also contains an even smaller fraction of organic black particles with atomic H/C of 1.88 and which by IR spectra showed presence of different type of hydrocarbons and it was therefore concluded they were not residual carbon black originating from the pyrolysis process. Thermogravimetric analysis (TGA) of the isolated particulate matter in nitrogen atmosphere showed a 28% weight loss from 40 to 90 °C, a 67 % weight loss from 135 to 430 °C and a large combustion exotherm after switching atmosphere to air at 600 °C, but with very little weight loss. No remaining ash content was observed. Pyro GC-MS of the organic black particulate matter identified toluene (probably residuals from solvent used to isolate the particulate matter from the filter cake), aromatic nitrogen compounds such as aniline, pyridine, 4-methyl-N-phenyl benzeneamine, N-phenyl-1,4-Benzenediamine and pyridine-phenylmethyle as well as

thiol and thiazole. The particle matter found in the TPO thus resembles conventional asphaltene material found in petroleum feedstocks.

Despite the waxy material and particulate matter within the TPO no pressure drop build-up during the hydroprocessing run could be observed but in a commercial operation such material could, if necessary, likely be removed upstream the fixed bed hydrotreater with different filtration technologies or for example using state of the art solvent extraction.

More detailed testing and results will be summarized in a manuscript and published in a scientific paper by researchers from Chalmers in the future as part of the activities within the Competence Center for Catalysis.

### **Distillation of TPO**

Alternatively, distillation of crude TPO can be carried out to use TPO in different applications. Laboratory scale and batch distillation experiments were published as early as 2006 by Stanciulescu and Ikuria ([Journal of Analytical and Applied Pyrolysis 75 \(2006\) 217-225](#)) aiming to isolate limonene from the naphtha fraction. Wądrzyk et al. ([Energy Fuels 34 \(2020\) 5917-5928](#)) studied vacuum distillation of TPO to obtain cuts with similar properties as automotive and heating fuels. In a recent publication by Martínez et al. ([Fuel 358, Part B \(2024\) 130266](#)) it is summarized that the light fraction (70 - 176 °C), are rich in single-ring aromatics (such as BTX and limonene) and the heavy fraction (285 - 550.9 °C) concentrates both the sulfur and the heaviest polyaromatic compounds. The authors also reported results from Aspen Hysys modeling complemented with experimental trials in a continuous 20 kg/h pilot distillation apparatus and concluded that it is technically feasible to fractionate TPO using industrially relevant conditions in a packed distillation column. However, to date no industrial scale distillation trials have been reported.

### **Conclusions**

We have studied co-processing of TPO in conventional catalytic cracking reactors (both laboratory and industrial scale) and in pilot fixed bed hydrotreatment reactors which point to a viable production patch of transportation fuels from tire pyrolysis oils. Alternatively, it has also been shown in the scientific literature that distillation of TPO is possible which thereby open a possibility to also co-process the TPO with crude oil. This route seems to be easily implemented. Overall, injection of TPO to the crude distillation tower, catalytic cracker or fixed bed hydrotreaters seem doable as long as the asphaltene like material, S and N is properly managed with for example technologies previously used for conventional petroleum processing.