Performance comparison of tire pyrolysis oils in hydrotreating toward high-quality fuel

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Highlights

- Tire pyrolysis oils containing lower heteroatomic compounds exhibit a higher hydrodenitrogenation conversion
- Similar performance in hydrodesulfurization of tire pyrolysis oil and fossil fuels
- Tire pyrolysis oils have a lower aromatic ring hydrogenation than that of fossil fuels

1. Introduction

In order to achieve a more reliable energy supply and reduce greenhouse gases emissions in the transportation sector, recent research efforts have focused on investigating alternative fuels. Using waste-derived fuels to supplement or replace conventional transportation fuels is very promising as it offers environmental benefits, diversifies fuel resources and reduces reliance on fossil fuels.

The substantial quantity of waste tires disposed each year, together with their high C and H contents, makes them a promising resource for fuel production [1]. One of the valorization methods of waste tires is pyrolysis to produce carbon black and pyrolysis oil, also referred to as tire pyrolysis oil (TPO). However, TPOs cannot directly be used as a fuel such as gasoline or diesel due to their high viscosity and the large content of impurities, i.e., nitrogen, sulfur, oxygen-containing compounds. Hydrotreatment is a promising process that utilizes existing facilities in refineries to upgrade the TPO by reducing the N, S, O content.

In this context, the present work aims to investigate the hydrotreatment of different TPOs by comparing their reactivity to that of petroleum straight run vacuum gas oil (VGO) in hydrodenitrogenation (HDN), hydrodesulfurization (HDS), hydrodeoxygenation (HDO) and aromatic ring hydrogenation (HDCa).

2. Methods

Experimental tests were carried out in a 500-mL batch autoclave reactor. The experimental data included three TPO feedstocks (denoted as A, B, C) and one VGO at the same operating conditions. The reactor was loaded with 200 g of feedstock and 50 g of commercial NiMo catalyst that had been sulfided ex-situ in H_2S. After sealing the reactor, it was first flushed with nitrogen to remove the entrapped air, after which it was pressurized with hydrogen. The Rushton type agitator was stirred at 1000 rpm. The reactor was heated with a temperature ramp of 20 °C/min until reaching the set temperature. The reactor was operated at 362 °C, 140 barg for 4 hours. The temperature and pressure were maintained constant during reaction. Once reaching the desired reaction time, the reaction was quenched by decreasing the temperature using peripheral vortex air circulation. Finally, the gaseous and liquid products were collected for characterization.

The total nitrogen content was determined using chemiluminescence, while the total sulfur content was analyzed using X-Ray Fluorescence. The oxygen content was determined by combustion-infrared detection. For the aromatic carbon content, ^{13}C NMR analysis was used to analyze the unsaturated hydrocarbon. Since olefins are also present in TPOs, it is reasonable to assume they were all hydrogenated due to their high reactivity and the deep hydrogenating conditions.

The conversion rate of each reaction is then calculated using m_{feed} and $m_{product}$ which are the weight of the feedstock and of the liquid products respectively (g) and C_{feed} and $C_{product}$ which are the concentration of an element (N, S, O, aromatic carbon) in the feedstock and in the liquid products respectively (wt%):

$$X = \frac{m_{feed}C_{feed} - m_{product}C_{product}}{m_{feed}C_{feed}}$$

3. Results and discussion

Figure 1 shows the hydrotreating performances for different feedstocks (histogram, left y-axis) and feed element content (symbol, right y-xis). TPOs have a larger amount of nitrogen, oxygen and a lower amount of sulfur than VGO. HDN performance of feed A is lower than that of VGO, although it must be noted that feed A is very rich in nitrogen. The HDS conversion is similar for all feeds. Feed C containing a lower heteroatomic content than feed A and B, yet more than the VGO, results in a higher HDN, HDO conversion than that of other TPOs. It is observed that feed B has the lowest activity in terms of HDS, HDO and HDCa. Regarding the aromatics carbon, VGO has a higher conversion than that of TPOs which are around 10 – 25 %.

From overall performances, it is observed that the HDS of TPO mainly results from the hydrogenolysis reaction without the aromatic ring saturation as the HDCa of TPOs is quite low in comparison with the one of VGO. This is coherent with the observations by Palos et al [2]. At this reaction temperature, the HDO performances of TPOs cannot reach 100 %. Additional experiments will be performed at higher temperatures or longer reaction times to assess the possibility of full hydrotreating.

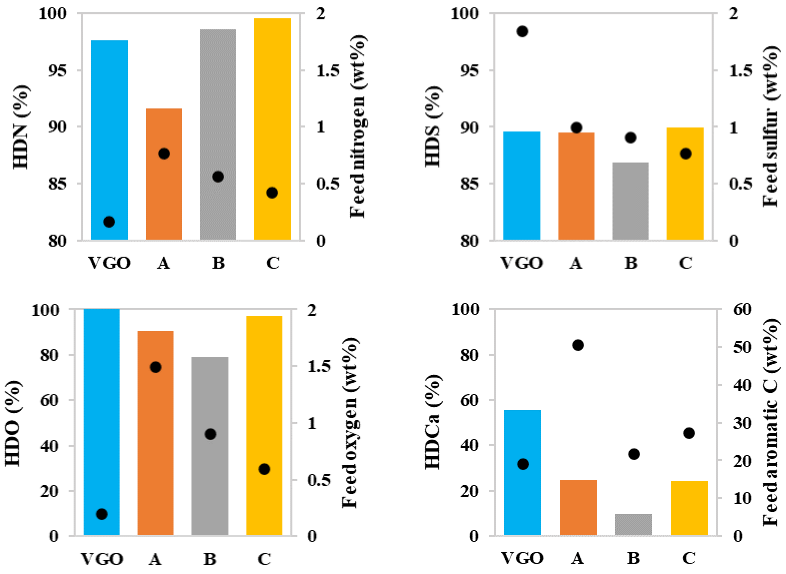

Figure 1. Hydrotreating conversion for different feedstocks (conversion: histogram, feed element content: point)

4. Conclusions

Hydrotreating performances of different TPO feedstocks are compared to VGO in this work. TPO containing lower heteroatomic compounds gives a higher HDN conversion. However, the conversion of HDCa is significantly reduced compared to VGO, which motivates the need of the advanced analyses such as mass spectrometry, sulfur, nitrogen and oxygen speciation to study the refractory compounds controlling the reaction.

References

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Keywords

Waste tire valorization; Hydrotreating; Pyrolysis.