NiW/pseudoboehmite+SBA-15 for the Hydrotreating of Waste Sunflower Oil and/or Light Cycle Oil.

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Abstract: Currently, fossil and waste feedstocks are being used to obtain more environmentally friendly fuels. We studied the catalytic activity and co-processing effects on catalysts, using light cycle oil (LCO) and/or waste sunflower oil (WSO). Naphthalene (as model molecule) hydrogenation activity was also studied. Commercial NiW/SiO_2-Al_2O_3 and research NiW/(pseudoboehmite-SBA-15) materials were tested in an autoclave and characterized by ATR, RAMAN, XRD, XRF, TGA. Liquids were analyzed by SimDis, density, C, H, N, S elemental analysis and ATR. NiW/(pseudoboehmite-SBA-15) was the most active for the WSO decarboxylation and for the net naphthalene hydrogenation to tetralin. Commercial catalyst presented the highest hydrocracking activity.
Keywords: Co-processing, Waste oil, LCO.

1. Introduction (11-point boldface)

Nowadays, the increasing crude oil demands can be covered by several methods: increase the use of renewable resources, deeper treating of heavy fractions[1] of crude oils or increase in crude oil production. To protect the environment, the combination of renewable and fossil resources seems to be highly promising. These processes are the characteristic technology of oil refineries for by-products utilization[2] and the addition of triglycerides based materials is commonly used for the green diesel production. By other side, million cubic meters per day of LCO are produced worldwide. LCO is one of the products resulting from the fluid catalytic cracking (FCC)[3] of vacuum distillates, atmospheric residues and other high boiling fractions. However, the physical and chemical properties of the LCO make difficult its using as fuel. Nevertheless, LCO could be upgraded by different ways for having more similar properties to the allowed ones by the European Union.[4] Different commercial processes (hydrotreating and/or hydrocracking) are being used now with the aim of upgrading the LCO. The hydrotreating process is selected for obtaining diesel or fuel oil range products and the hydrocracking process could be selected for naphtha range products. The co-processing of aromatic LCO and paraffinic vegetable oil has the potential to generate synergy for further improvement of the product quality.[5] Our aim was to study the catalytic activity and co-processing effects on the catalysts, using light cycle oil (LCO) and/or waste sunflower oil (WSO) using a high content (1:1) of LCO.

2. Experimental

Pseudoboehmite and mesoporous silica SBA-15 were mixed and homogenized in 5.5:1 weight ratio. Then, they were shaped into tablets, using a manual tablet press. Then, they were dried 120 °C overnight and finally calcined. This solid was impregnated by aqueous solution containing ammonium metatungstate, nickel nitrate and ammonium fluoride to obtain a final catalyst (NiWlab) with 12, 22 and 3 wt.% of Ni, W and F respectively. A commercial (sulphided catalyst, previously activated in plant) NiW/SiO_2-Al_2O_3 (NiWcomm) catalyst, with approximately 22 and 8 wt.% of W and Ni contents respectively, was used.

Attenuated total reflectance technique (ATR) using an instrument Nicolet iS 10-Thermo Scientific (crystal diamond; number of scans = 64; resolution 4 cm^{-1}) was used for the FT-IR measurements. XRF,

XRD, RAMAN and specific surface area BET were carried out using the same methodology described in the literature.[6] The simulated distillation (SimDis), density of the liquids, C, H, N, S elemental, gas and TGA analyses were performed using the methodology described also in literature.[7]

Experiments were carried out in a batch high pressure and high temperature Parr Instrument Company autoclave 4575/76 (300 mL volume of reaction vessel). Before each experiment, the NiWlab catalyst was activated with dimethyl disulphide. The reaction was performed at 365 °C; 5 g of catalyst; 95 bar (H_2); 1 h.

3. Results and discussion

NiWlab catalyst was the most active for the WSO hydro-deoxygenation and for the net naphthalene hydrogenation to tetralin with a conversion of 82 wt.%. NiWcomm Commercial catalyst presented the highest WSO hydrocracking activity and a conversion of naphthalene to tetralin of 64 wt.%.

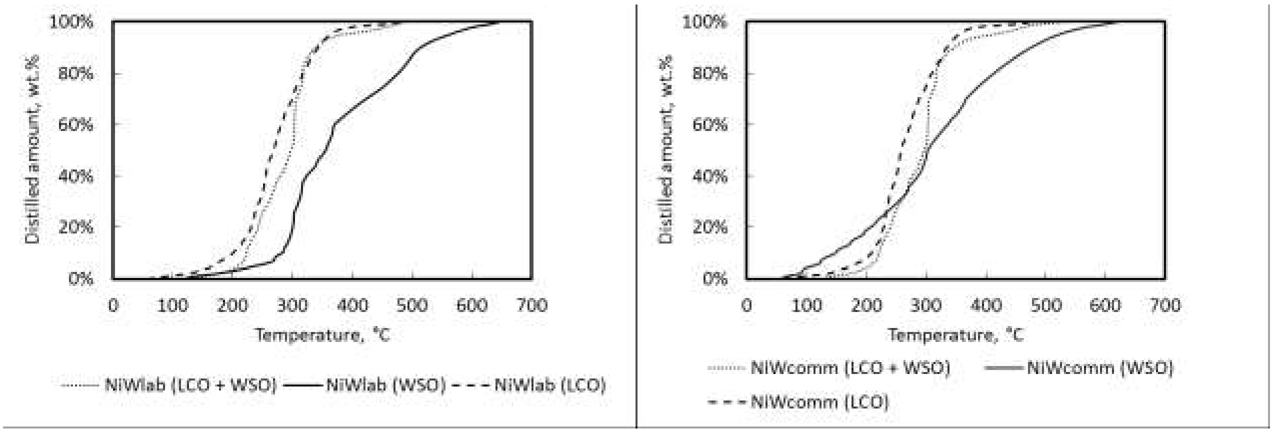

Figure 1. SimDis of the liquid products.

Elemental analysis showed a higher amount of hydrogen in the products from the WSO and WSO + LCO tests using the NiWlab catalyst. These results were also confirmed by ATR in which the signals attributable to C=O (ester carbonyl groups) and free fatty acids shoulder were only detected for products from WSO + LCO tests using NiWcomm catalyst. The gases production (<C5 compounds) was lower than 5 wt.% in all cases presenting higher amounts of CO_2 when WSO was used informing us about the production of C17 hydrocarbons by the decarboxylation of linoleic acid.

4. Conclusions

NiWlab was the most active catalyst for the hydrotreatment of WSO + LCO mixtures and selective for the production of C17 paraffins. NiWcomm presented the highest hydrocracking activity using WSO. ATR resulted to be a really useful tool for the evaluation of WSO and LCO co-processing evaluation. In the case of the hydrotreating of LCO, similar activity was found for both catalysts.

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