

## ULSD production at moderate operating pressure with a NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst and a middle distillates mixture defined by sulfur distribution.

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### Highlights

- ULSD production at moderate pressure and mild operating conditions.
- Middle distillates mixture defined by sulfur distribution.
- Type II active phase ULSD catalyst. Existing hydrotreater with a new distribution tray.

### 1. Introduction

Many countries around the world have introduced stringent environmental regulations to reduce the sulfur content of diesel fuel trying to reduce diesel engine's harmful exhaust emissions and improve air quality. The oil refining industry have overcome this considerable operational and economic challenge by producing ultra-low sulfur diesel (i.e. ULSD), and attempting to meet the increasing market demand [1]. Flexibility to process heavy fractions and low-grade streams into ULSD is needed to produce and supply additional volume of ULSD. Numerous research studies have been developed to enhance hydrotreating catalysts [2-4], feed quality and reactor internals and minimize inhibition, kinetic and thermodynamic effects influencing the ultra-deep desulfurization of the least reactive sulfur compounds [1]. In this work, a cost-effective solution is proposed to produce ULSD using a new generation ULSD catalyst, processing a mixture of middle distillates at moderate hydrogen partial pressure, low reaction temperature and medium liquid hourly space velocity (i.e. LHSV). Sulfur distribution is a key factor of the methodology followed in this work, which may be applied in an existing moderate operating pressure hydrotreater, without a major revamp, just improving the feed distribution in the reactor by using a high efficiency vapor/liquid distribution tray.

### 2. Methods

A NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (i.e. Ni: 2.0-10.0 wt%; Mo: 15-30 wt%) commercial catalyst with: Bulk density: 0.70-1.20 g/cm<sup>3</sup>; pore volume: 0.40-0.80 cm<sup>3</sup>/g; and BET area: 200-300 m<sup>2</sup>/g, was crushed, sieved (i.e. 60/100 mesh), dried in an oven at 120-150 °C for 2-5 h and mixed 1:1 vol/vol with CSi (i.e. 60/100 mesh) prior to be loaded into the fixed-bed trickle reactor (i.e. Vol: 75-150 mL; internal diameter: 2.0-2.6 cm; down-flow mode). This type II active phase ULSD catalyst was presulfided in-situ using kerosene spiked with dimethyl disulfide (i.e. Sulfur: 2.0-2.5 wt%) at Temperature: 200-330 °C; Pressure: 5.0-5.5 MPa; LHSV: 2.0-2.7 h<sup>-1</sup>; Hydrogen/Hydrocarbon (i.e. H<sub>2</sub>/Hc) ratio: 0.35-0.40 L/mL; and Time: 20-30 h. After the activation step and before the test feed introduction, a soak period was considered at Temperature: 300-330 °C; Pressure: 5.0-5.5 MPa; LHSV: 2.0-2.7 h<sup>-1</sup>; H<sub>2</sub>/Hc ratio: 0.35-0.40 L/mL; Time: 40-50 h, and Feed: Kerosene. Then, the operating conditions were adjusted to the test values: Temperature: 340-370 °C; Pressure: 5.0-5.5 MPa; LHSV: 1.5-2.0 h<sup>-1</sup>; H<sub>2</sub>/Hc ratio: 0.35-0.40 L/mL and Time: 32 h for each experimental point.

Experiments were conducted processing a feedstock integrated by straight run gas oil (i.e. 35-45 vol%), kerosene (i.e. 25-35 vol%) and jet fuel (i.e. 25-35 vol%) with: Sulfur: 0.80-1.0 wt%; Nitrogen: 100-150 wtppm; Aromatics: 25-30 wt%; 4,6-dimethyl dibenzothiophene: 100-150 wt ppm; Br nr.: 3.0-5.0 g Br/100 g; IBP/FBP: 160-180/345-360°C; °API: 35-40; K: 10-12; MW: 180-220; and Cetane index: 45-55.

The reactor effluent was fractionated in a vapor-liquid separator into a rich-hydrogen stream and a liquid stream, which was put under a continuous N<sub>2</sub> flow of 10-20 L/h at 80-100 °C for 2-5 h, washed with a NaOH (i.e. 10-20 wt%) aqueous solution, weighted for mass balance, and characterized by ASTM methods.

Péclet number, wall and wetting effects and hydrogen partial pressure were calculated prior to the tests to validate the experimental design [5]. After the tests, hydrogen consumption was estimated by means of an in-house correlation and a kinetic model was developed to evaluate the catalyst performance in terms of the required temperature to achieve 10 wtppm of sulfur. This kinetic model, based on power law (i.e. Order of reaction: 1.0-1.5) and Arrhenius equations, considered test temperature and LHSV and product sulfur.

### 3. Results and discussion

Comparison of values (i.e. actual vs min) of the Péclet number (i.e. 83 vs 72), and wall (i.e. 48 vs 20), and wetting (i.e. 3.465E-02 vs 5.0E-06), effects validated the experimental design properly. The hydrogen partial pressure remained at 4.22 MPa during the experiments but the hydrogen consumption varied from 0.05 to 0.09 L/mL depending on the operating temperature and LHSV.

The sulfur concentration in the product changed from 3.5 to 6.5 wtppm (i.e. 15 wtppm max, spec), aromatics from 15.9 to 20.5 wt% (i.e. 35 wt% max, spec), and cetane index from 55.8 to 56.8 (i.e. 45 min, spec); the nitrogen content was always below 0.30 wtppm. That is, all products satisfied the corresponding specification (i.e. spec), value. The kinetic model provided required temperatures to achieve 10 wtppm of sulfur (i.e. 348 °C max), lower than the test temperatures because of the high catalyst activity; sulfur varied in a tight interval (i.e. 3 wt ppm), limiting the effects of temperature and LHSV. If 370°C as end-of-run temperature and 0.90 °C/month as deactivation rate are considered, the cycle length will be 24 months.

Figures 1 and 2 show the removal of sulfur compounds from the processed feedstock. Benzothiophene (i.e. BT), and its derivatives and lighter sulfur compounds were totally removed. Only some dibenzothiophene derivatives (i.e. C<sub>2</sub>DBT and C<sub>3+</sub>DBT), appeared in the product slightly.

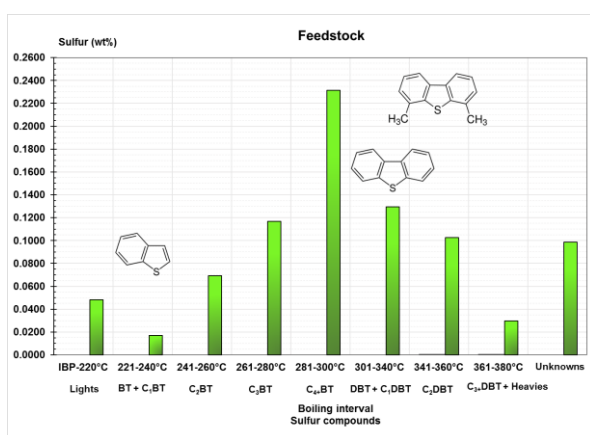


Figure 1. Sulfur distribution in the feedstock.

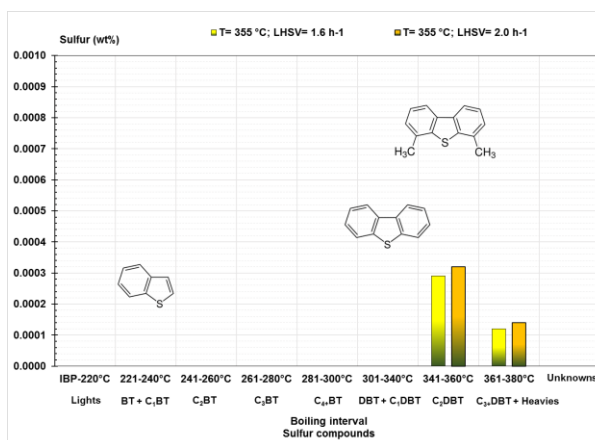


Figure 2. Sulfur distribution in the products.

### 4. Conclusions

The technological solution presented in this work is a cost-effective option for producing ULSD at moderate pressure and mild operating conditions. It considers existing units with new reactor internals, an ULSD catalyst with high hydrogenation activity and a middle distillates mixture defined by sulfur distribution.

### References

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### Keywords

Hydrotreating; ULSD; Sulfur-distribution.