

Selectivity and conversion of the naphthalene hydrogenation towards BTX production

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Highlights

- Selectivity and conversion of the naphthalene hydrogenation towards BTX production.
- Effects of the operating conditions and some organic inhibitors were considered.
- Selectivity to tetralin higher than 78% and conversion higher than 96% were achieved.

1. Introduction

Light cycle oil (i.e. LCO) is a low quality middle distillate produced in the Fluid Catalytic Cracking unit. It contains high concentrations of sulfur (i.e. up to 4 wt%), nitrogen (i.e. up to 1,000 wtppm) and aromatics (i.e. up to 75 wt%) [1]. Aromatic compounds which have been identified in the LCO are mainly diaromatics (i.e. Naphthalene derivatives). An attractive economic option for LCO upgrading is the production of high commercial value monoaromatics such as benzene, toluene, and xylenes (i.e. BTX), by combined hydrogenation and hydrocracking steps, as represented in Figure 1 [2].

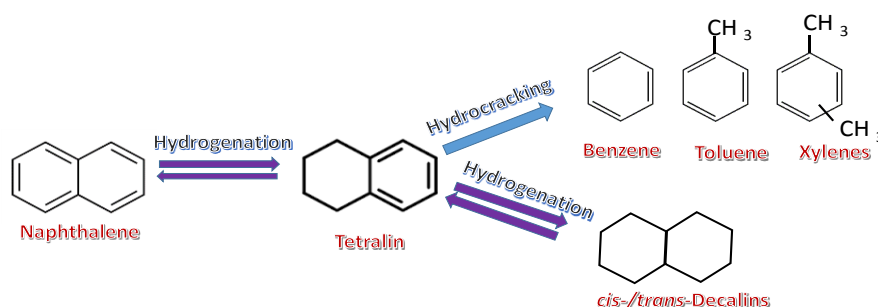


Figure 1. Reaction pathways involved in the BTX production.

Even though naphthalene hydrogenation has been studied previously [2], a model mixture of naphthalene with di-alkyl naphthalene, sulfur and nitrogen compounds as inhibitors, has not been tested. In this work, selectivity and conversion were studied using a commercial catalyst at given experimental conditions.

2. Methods

Naphthalene (i.e. 99.99 %), n-hexadecane (i.e. 99.99 %), 2,6-dimethylnaphthalene (i.e. 2,6-DMN, 90.32%), dibenzothiophene (i.e. DBT, 98%), carbazol (i.e. CZ, 98%), were purchased in Sigma-Aldrich and used in the experiments without further purification. Also, a NiMo/ γ -Al₂O₃ catalyst (i.e. Ni: 2.0-5.0 wt%; Mo: 10.0–20.0 wt%) was used in the tests with the following properties: Bulk density: 0.60 - 0.70 g/cm³; pore volume: 0.55 - 0.65 cm³/g; BET area: 180 - 250 m²/g. Four model mixtures were prepared (Table 1).

Table 1. Composition of model mixtures

Model mixture, wt%	Naphthalene	2,6-DMN	DBT	CZ
1	10	--	--	--
2	10	1.40	--	--
3	10	--	1.50	0.05
4	10	1.40	1.50	0.05

The experiments were performed in a bench-scale setup equipped with a fixed-bed trickle reactor (i.e. Vol.: 10 mL; Internal diameter: 1 cm), which was operated in the down-flow mode. The NiMo catalyst was activated in-situ for 18 h using a desulfurized naphtha spiked with DMDS (i.e. Sulfur: 1.5 - 2.5 wt%) at Temperature: 200 - 315 °C; Pressure: 4.0 MPa; Liquid Hourly Space Velocity (i.e. LHSV): 1.0 h⁻¹; and Hydrogen/Hydrocarbon (i.e. H₂/Hc) ratio: 300-380 m³/m³. After the activation step, operating conditions were adjusted to the corresponding experiment: Case 1: Mixtures 1 and 2; Temperature: 250 °C; Pressure: 1.96 MPa; LHSV: 1.3 h⁻¹; H₂/Hc ratio: 794 m³/m³; Case 2: Mixtures 3 and 4; Temperature: 300 °C; Pressure: 2.94 MPa; LHSV: 1.3 h⁻¹; H₂/Hc ratio: 794 m³/m³. The reactor effluent was sent to a vapor-liquid separator, where the rich-hydrogen stream was analyzed by gas chromatography and the liquid stream from the bottom was collected in a metal container, weighted for mass balance purposes and characterized in a FID-GC Bruker, by comparing the retention times with standard mixtures of the hydrocarbons involved. Selectivity was calculated by dividing the amounts of each of the compounds in the hydrogenated mixtures by the corresponding initial amounts of them and naphthalene in the mixtures. Percentages of hydrodesulfurization (i.e. HDS) and hydrodenitrogenation (i.e. HDN) were calculated considering the difference between the inlet and outlet mass flow rates divided by the inlet mass flow rates of each species.

3. Results and discussion

The results are shown in Table 2. The hydrogenation of the model mixtures 1 and 3 produced tetralin and decalin; note that the presence of DBT and CZ in model mixture 3 decreased the selectivity to tetralin and increased the selectivity to decalin. The hydrogenation of the model mixtures 2 and 4 showed similar selectivity results; a difference was the appearance of 2,6-DMT in the hydrogenated products, which was favored by the presence of DBT and CZ in the model mixture 4. Neither DBT nor CZ were found in the hydrogenated products of the mixtures 3 and 4; therefore, HDS and HDN were considered 100%. Naphthalene conversion was always lower than 100% and slightly enhanced by the presence of DBT and CZ.

Table 2. Selectivity and conversion of the naphthalene hydrogenation.

Model mixture	Selectivity, wt%			Conversion, %	
	Tetralin	Decalin	2,6-DMT	Naphthalene	2,6-DMN
1	96.8	3.2	--	96.2	--
2	89.8	2.7	69.1	97.3	96.4
3	88.0	12.0	--	96.8	--
4	78.7	12.4	76.3	97.5	98.1

4. Conclusions

The selectivity of the naphthalene hydrogenation to tetralin is decreased by the presence of 2,6-DMN, DBT and CZ in the model mixtures. Although the naphthalene conversion remained quite high in the experiments, the formation of decalin derivatives is undesirable towards BTX production. Even if HDS and HDN were completed, additional changes in the operating conditions may be considered to achieve the prime goal.

References

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Keywords

Naphthalene-hydrogenation; BTX; LCO.