Catalyst memory effects during mode switches in hydrotreaters

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Highlights

- A mode switch in a pilot hydrotreater was investigated with real feedstocks.
- The memory effect was observed comparing the time constants of output parameters.
- The response of two parameters followed a linear first order model.

1. Introduction

The production of lubrication base oils is carried out via hydrotreatment of suitable distillates. During hydrotreatment, undesired compounds such as organic sulfur and nitrogen can be removed with hydrogen using a sulfided NiMo catalyst. A multitude of different base oils, ranging from low viscosity base oils to very viscous base oils, can be produced in a single hydrotreater. Given their inherently different properties, these products cannot be produced at the same time and thus, a sequential process is used. Going from one product to another (a mode switch), the catalyst activity can vary due to compositional differences of the feedstock (Figure 1). There is a stabilization time required to reach the new steady state [1,2] and this could be due to a memory effect of the catalyst. Understanding and managing these catalyst memory effects are crucial in optimizing hydrotreating units for efficiency, selectivity, and overall performance. In model feedstock experiments, it is suggested that organonitrogen compounds are adsorbed strongly on the catalyst surface [3,4] and thus, the hydrodenitrogenation (HDN) kinetics are a critical component in describing the stabilization time required. In this study, open-loop step response experiments are performed using real feedstocks to investigate the hydrotreater dynamics and model the mode switch using a phenomenological model.

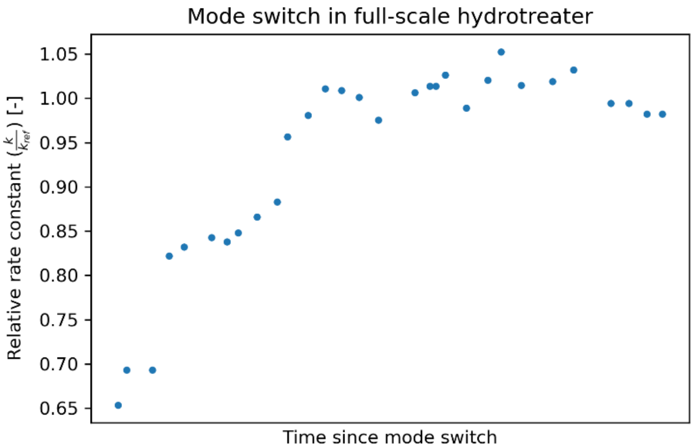

Figure 1. Relative transient activity of a full-scale hydrotreater during a mode switch.

2. Methods

The experiments were performed in a pilot hydrotreatment reactor setup at Nynas AB in Nynäshamn, Sweden; the total catalyst volume in the reactor system is 100 cm^3 and it is operated isothermally and in isobaric manner. The temperature is controlled along the reactor to ensure isothermal operation. To discriminate between reactor influence and mixing effects in the pilot unit; experiments by-passing the reactor were performed.

Two vacuum gas-oils (VGO) with different boiling point distributions (BPD)(ASTM D2887) were used in this study. To evaluate the extent of hydrotreatment, the oils were characterized using typical methods for hydroprocessing. The mid boiling point (T50) and refractive index (ASTM D1218) were used as tracer data for investigating the dynamic response of the system in the by-passing experiment.

3. Results and discussion

The step response experiments fitted very well to a linear first order response model. Thus, it was possible to estimate the time constant for the mode switch. The findings are shown in Table 1 and Figure 2. For the T50, it can be seen that the time constant is the same as for the by-pass experiment, while the dead time has increased by 1.5 h; this indicates that the reactor operates in a plug flow mode. However, comparing the time constants for the refractive index (RI), it can be noted that it is significantly larger than for the by-pass experiment. RI is used indirectly to measure the extent of hydrotreatment. This suggests that the hydrotreating kinetics impact the reactor response over a timespan that exceeds the residence time.

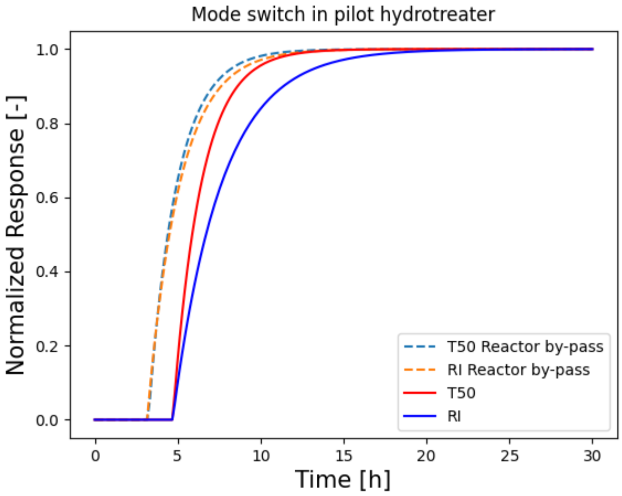

Figure 2. Normalized step responses for refractive index (RI), mid boiling point(T50) as well as the T50/RI for reactor by-pass experiment. Only the model fit is shown for clarity.

Table 1. First order step response characteristics for one of the experiments performed.

	Dead time [h]	Time constant [h]
By-pass reactor system, T50 (RI)	3.2 (3.2)	1.7 (1.9)
Full system, T50	4.7	1.7
Full system, RI	4.7	2.9

4. Conclusions

T50 and RI worked well as tracers for the case when reactor was by-passed; however, in the full system, RI was observed to deviate from the T50 response. This is most likely related to the kinetics and results in RI being a means of differentiating transient behaviors of a hydrotreating reactor.

References

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Keywords
Hydrotreating, transient, step response, reactor dynamics