Inhibition of the catalytic hydrogenation of phenanthrene by organic nitrogen

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Abstract: To comply with the stricter regulations regarding carcinogenic content in mineral oil products, it is important to study the hydrogenation reaction of polyaromatic hydrocarbons. The effects of process conditions as well as the addition of the organic nitrogen compounds carbazole and acridine on the hydrogenation of phenanthrene, a model compound of a polyaromatic hydrocarbon, have been studied. A design of experiments methodology was applied to get a statistically optimized experimental matrix. The results indicate that the hydrogenation of phenanthrene is affected by the addition of nitrogen compounds as well as the change in process conditions.

Keywords: Hydrogenation, Nitrogen Inhibition, Design of Experiments

1. Introduction

With a growing energy demand, the usage of unconventional crude oils is expected to increase. This type of crude oils typically contains a considerably higher amount of polyaromatic hydrocarbons (PAHs) compared to conventional crude oils. Since the PAHs are known to be carcinogenic, the crude oil fractions from the distillation are treated with hydrogen in a so called hydrotreating process. The catalysts used in these kinds of processes are typically Ni or Co promoted Mo sulfides on an alumina support. For transportation fuel producers, hydrodesulfurization is traditionally the most important hydrotreating reaction since it is critical to meet the legislated 10 ppm or lower sulfur content. However, due to stricter legislative requirements concerning PAHs, it has become increasingly important also to substantially reduce the PAH content in the mineral oil based products. The PAHs are lowered via the hydrogenation reactions called hydrodearomatization. These types of reactions are typically inhibited by competitive adsorption of other compounds such as organic nitrogen compounds on the active sites of the catalyst. Thus, it is of interest to study if the process conditions can be optimized to reduce the inhibition effects and thereby maximize the reduction of carcinogenic compounds.

Using a model compound system, is an easy way to gain insight on more complex systems by a simple experimental procedure and analysis. Phenanthrene is a typical model substance utilized for studying the catalytic hydrogenation of PAHs. In Figure 1 the reaction network of phenanthrene is shown.

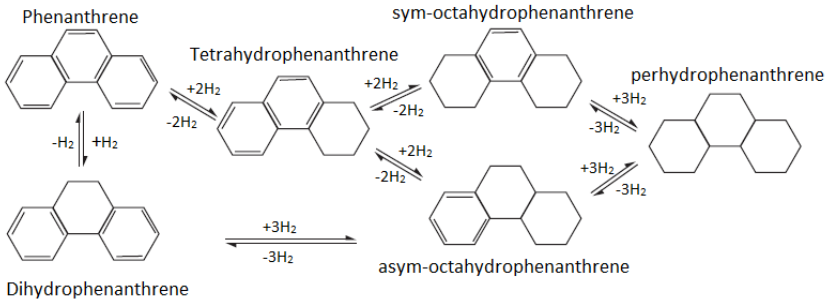

Figure 1. Reaction network for the hydrogenation of phenanthrene.

2. Experimental

The inhibition effect of organic nitrogen compounds on hydrogenation of phenanthrene was studied at industrial relevant process conditions. A commercial hydrotreating catalyst of the NiMo type was used. The inhibition of hydrogenation reactions of phenanthrene by nitrogen compounds has been demonstrated in other studies[1,2]. However the effect of interaction between process conditions and nitrogen content on the hydrogenation reactions has typically not been studied. In the present study, the nitrogen compounds carbazole and acridine were blended into the feed in a controlled manner to study their effect on the product yield. Design of experiments methodology was applied to get a statistically optimized experimental matrix.

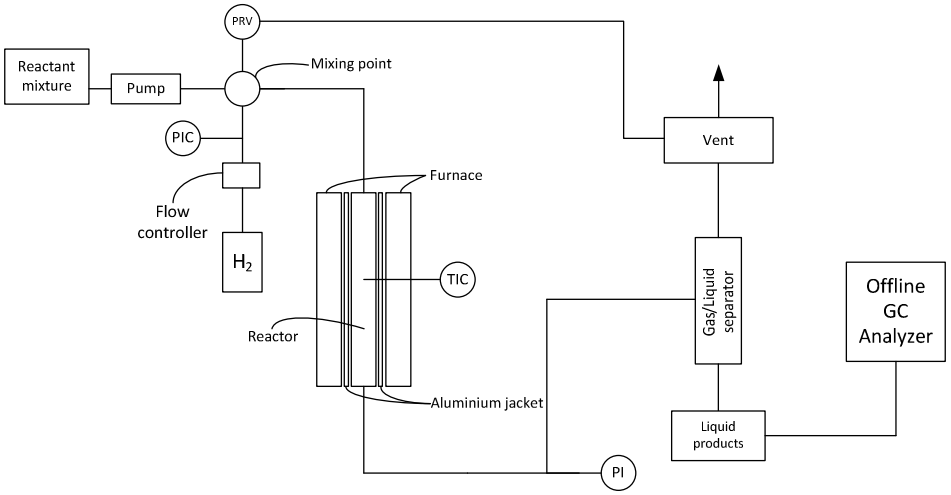

Figure 2. Schematic diagram of the experimental setup. TIC (Temperature indicator controller), PIC (Pressure indicator controller), PI (Pressure indicator), PRV (Pressure relief valve).

The microflow system used in the study can operate at temperatures up to 380 °C and pressures up to 170 bars, and is schematically shown in Figure 2. The reactor is made of a stainless-steel pipe (10 mm internal diameter) and operates isothermally at downflow mode. The isothermicity of the system was found satisfactory, i.e. within 1°C, using a sliding thermocouple. To minimize channeling effects and bypassing within the reactor catalytic bed, it was packed with a size gradient of SiC particles. The size gradient of SiC also eliminates the risk of SiC slip and establish ensures that the vapor-liquid equilibrium is reached established before reaching the catalyst zone. Additionally, the particle size of the SiC in the catalytic bed was chosen to ensure complete irrigation of the catalyst and to minimize the wall effects and the influence of axial dispersion based on the criteria found in literature. The system was tested for and considered free of internal and external diffusion limitations.

The yield of different products from phenanthrene hydrogenation, as shown in Figure 1, was analyzed offline using a GC-MS system for qualitative analysis and a GC-FID for the quantitative analysis.

3. Results and discussion

The experimental results indicate that the process conditions as well as the addition of organic nitrogen compounds have an impact on the conversion of phenanthrene and its hydrogenated products.

4. Conclusions

The experiments showed that the process conditions and addition of organic nitrogen compounds have an effect on the conversion of phenanthrene.

References

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