

Kinetic modeling of the hydrotreatment of light cycle oil and heavy gas oil using the structural contributions approach

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Abstract

The kinetics of the hydrodesulfurization of light cycle oil (LCO) and heavy gas oil (HGO) over a CoMo/Al₂O₃ catalyst were investigated in a perfectly mixed flow reactor with stationary basket of the Robinson-Mahoney type at temperatures of 330, 310 and 290 °C, H₂/HC molar ratios of 2.8, 3.6 and 7.2 and a pressure of 65 bar. Hougen-Watson type rate equations were derived for the conversion of dibenzothiophene, substituted (di)benzothiophene and their products. To avoid having to deal with a huge number of model parameters, a methodology based upon structural contributions was applied. In the absence of own kinetic data on key components a number of kinetic and adsorption parameters were taken from published work on a very similar catalyst. For a given value of H₂/HC only a small number of experiments was required to determine the value of the very complex denominators DEN_σ and DEN_τ appearing in the rate equations for the hydrodesulfurization of LCO and of HGO and of their evolution with the conversion of the feedstock. With the rate equations constructed in this way the calculated total conversion of DBT, its conversion into biphenyl and into cyclohexylbenzene were in excellent agreement with the experimental values.

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1. Introduction

Oil fractions such as heavy (atmospheric) gas oil (HGO) or light cycle oil (LCO) have a high sulfur and nitrogen content that has to be reduced for environmental and technical reasons prior to their use in our society.

Until now the hydrotreatment, more particularly the hydrodesulfurization (HDS), of oil fractions has been expressed in terms of lumps of sulfur components which are converted according to first- or second-order kinetics. Modeling deep HDS requires more accurate kinetic modeling that considers individual components and rate equations of the Hougen-Watson type, i.e. accounting for the adsorption of the various species. If the kinetic modeling is based upon individual components – an approach called here molecular – the number of rate parameters becomes awesome. A different approach is required to reduce this number. A methodology based upon structural contributions has been proposed by

Froment et al. [1]. In this concept the rates of transformation of substituted S components are related to that of the unsubstituted head of family or parent molecule. The methodology has been applied to the HDS of oil fractions such as LCO [2,3].

The purpose of the work reported here was to check if the structural contribution parameters determined for one LCO can be applied to a different LCO and even to other oil fractions as well, provided that the catalyst is the same. To do so the methodology was applied to the kinetic modeling of HDS of the family of (di)benzothiophenes, considering DBT as the parent molecule. LCO and HGO contain (di)benzothiophene, various methyl-substituted (di)benzothiophenes, dihydro(di)benzothiophenes and naphthothiophenes that are relatively refractory to hydrodesulfurization.

2. HDS of LCO and HGO

2.1. Experimental unit

Fig. 1 shows the experimental unit. The HDS of LCO, containing 2.94 wt% S and of HGO, containing 0.453 wt%, was

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Nomenclature

BET	Brunauer–Emmett–Teller method
C_i	liquid concentration of component i (kmol/mL ³)
F_{DBT}^0	molar feed flow rate of dibenzothiophene (kmol/h)
$k_{i,\sigma}$	rate coefficient for the reaction of component i on σ -sites (kmol/(kg _{cat} h))
$k_{i,\tau}$	rate coefficient for the reaction of component i on τ -sites (kmol/(kg _{cat} h))
$K_{i,\sigma}$	adsorption coefficient of component i on σ -sites (mL ³ /kmol)
$K_{i,\tau}$	adsorption coefficient of component i on τ -sites (mL ³ /kmol)
n_{exp}	number of experiments
r_i	total rate of disappearance of component i (kmol/(kg _{cat} h))
R_{gas}	gas constant (kJ/kmol K)
R_i	net production rate of component i (kmol/(kg _{cat} h))
S	objective function
T	temperature (K)
W	total mass of catalyst (kg _{cat})
x_i	conversion of component i
\hat{x}_i	calculated conversion of component i
y_i	mole fraction of component i in HGO and LCO feed

Greek symbols

σ	with respect to the hydrogenolysis function
τ	with respect to the hydrogenation function

Subscripts

BPH	biphenyl
CHB	cyclohexylbenzene
DBT	dibenzothiophene
4,6-DiMeDBT	4,6-dimethyldibenzothiophene
H	atomic hydrogen
H ₂	molecular hydrogen
HHDBT	hexahydro(di)benzothiophene
4-MeDBT	4-methyldibenzothiophene
THDBT	tetrahydro(di)benzothiophene

performed on a commercial CoMo/Al₂O₃ catalyst at a total pressure of 65 bar, temperatures of 330, 310 and 290 °C and molar hydrogen to hydrocarbon ratios of 2.8, 3.6 and 7.2 for LCO and 2.8 for HGO. The feed rates were such that the DBT space time (W/F_{DBT}^0) was varied from 3000 to 5000 kg_{cat} h/kmol. The reaction products of the HDS of DBT were biphenyl (BPH), cyclohexylbenzene (CHB), and H₂S. The hydrogenation products of (substituted)DBT, the various tetra-(THDBT) and hexa-hydro(di)benzothiophenes (HHDBT), were not detected.

The catalyst was supplied by the Mexican Petroleum Institute. It contains 13.1–16.1 wt% MoO₃, 3.2–3.8 wt% CoO. The total pore volume is 0.5 cm³/g and the BET surface

area 215 m²/g. In Table 1 it is compared with a catalyst used by Vanrysselberghe and Froment in a study of LCO hydrodesulfurization [2]. The catalyst was crushed to 850–1000 μm to avoid diffusional limitations. The physical properties of the heavy gas oil and the LCO are listed in Table 2.

The experiments were performed in a 1.0 L Robinson-Mahoney stationary catalyst basket reactor with complete mixing of the gas and liquid phase. Baffles inside and outside the annular catalyst basket serve to control vortices. The rotating shaft is equipped with two impellers that force the fluid into the center of the annulus at the top and bottom and through the catalyst bed. The reactor is made of stainless steel and can operate at pressures up to 140 bars and temperatures up to 450 °C. The temperature was measured and controlled. The pressure was controlled by a back pressure regulator. The effluent of the reactor, consisting of gas and liquid phases at high pressure and high temperature, was separated under reactor conditions by means of a cyclone coupled with a demister. The gas phase was analyzed on-line by means of a gas chromatograph (GC) with a TCD detector. The liquid product was cooled in a liquid level controller. The effluent of this controller was flashed to ambient conditions. The light gases from this flash were collected in a glass burette in which their amount was measured. The GC-TCD was used to analyze and quantify H₂, H₂S, and methane. The liquid product from the flash was measured and analyzed off-line by means of GC–MS.

In the GC–MS analyses of LCO and HGO, more than 550 peaks could be integrated in each case. More than 150 were identified using the retention times given by Depauw and Froment [4]. In LCO the amount of (s)BT amounts to 1.135 wt%, that of (s)DBT to 2.274. In HGO the corresponding amounts were 0.095 and 1.021 wt%.

By way of example Fig. 4 illustrates that for the same operating conditions the total conversion of DBT in the LCO is higher than that in the HGO. Further experimental results will be presented in later sections, together with the calculated results based on the kinetic model.

2.2. DBT reaction network

Fig. 3 shows the reaction scheme for the decomposition of dibenzothiophene. DBT is converted along two parallel routes. The first directly eliminates the S-atom by hydrogenolysis, which is a scission of the C–S bond and is commonly called Direct Desulfurization (DDS). The second begins with hydrogenation. Its products undergo C–S scission. Along this route the hydrogenation is the rate determining step. Hydrogenolysis and hydrogenation steps occur on different sites: σ -sites for the first and τ -sites for the latter [3,6–10].

2.3. Reaction rates

The net production rates, R_i for biphenyl, cyclohexylbenzene and bicyclohexyl, derived from DBT as shown in Fig. 2,

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