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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 $CoMo/Al_2O_3$ 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, H_2/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 H_2/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.

Keywords: Hydrotreatment; Light cycle oil; Heavy gas oil; Structural contributions; Kinetics

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^0_{DBT}	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 $CoMo/Al_2O_3$ 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^0_{DBT}) was varied from 3000 to 5000 kg$_{cat}$ h/kmol. The reaction products of the HDS of DBT were biphenyl (BPH), cyclohexylbenzene (CHB), and H_2S. 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% MoO_3, 3.2–3.8 wt% CoO. The total pore volume is 0.5 cm^3/g and the BET surface area 215 m^2/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 vortexes. 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 H_2, H_2S, 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,

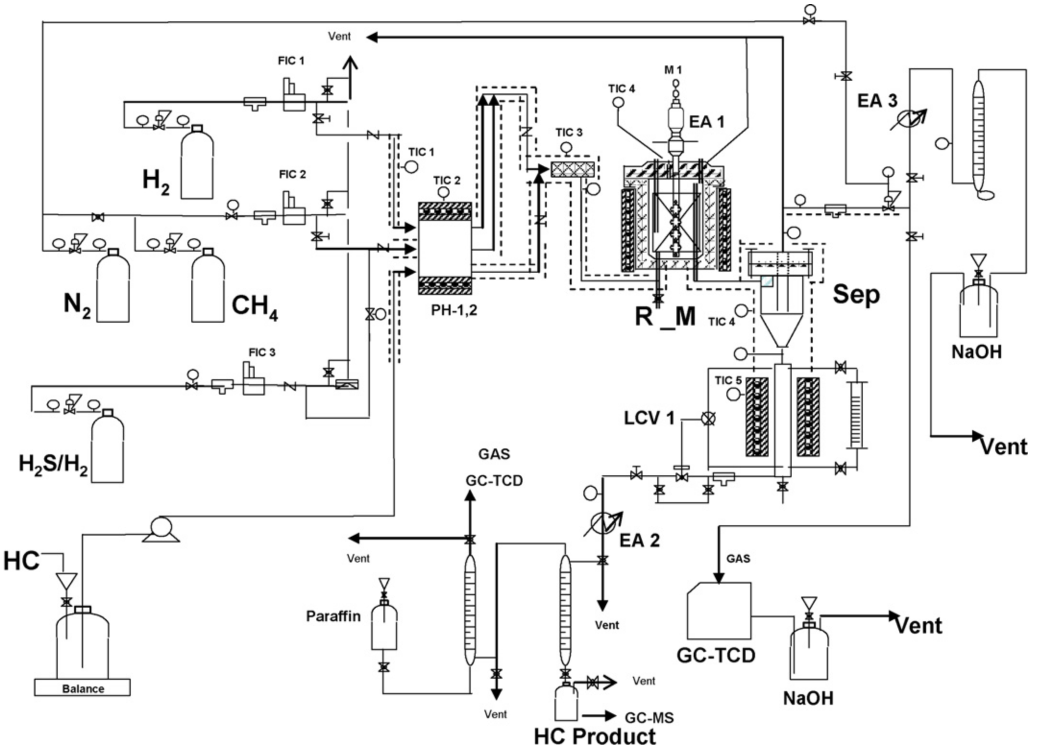

Fig. 1. Schematic of high pressure experimental setup for the hydrotreatment of HGO and LCO. (R_M): Robinson-Mahoney reactor.

are defined by

$$R_{\mathrm{BPH}} = r_{\mathrm{DBT},\sigma} - r_{\mathrm{BPH},\tau} \tag{1}$$

$$R_{\mathrm{CHB}} = r_{\mathrm{DBT},\tau} + r_{\mathrm{BPH},\tau} - r_{\mathrm{CHB},\tau} \tag{2}$$

$$R_{\mathrm{BCH}} = r_{\mathrm{BCH},\tau} \tag{3}$$

Table 1
Properties of the catalysts used in the HDS of LCO and HGO

Component	AKZO Ketjenfine 742[a]	HDS-1[b]
MoO_3 (wt%)	5–30	13.1–16.1
CoO (wt%)	1–10	3.2–3.8
SiO_2 (wt%)	0–6	NA
P_2O_5 (wt%)	0–10	NA
Surface area (m^2_{cat}/g_{cat})	264	215
Pore volume (cm^3/g_{cat})	0.52	0.50
Support	Al_2O_3	Al_2O_3

[a] Catalyst used by Vanrysselberghe and Froment [11].
[b] Catalyst used in this work. NA: Not available.

Table 2
Characteristics of the oil fractions used in the present work

Physical and chemical properties	Heavy gas oil	Light cycle oil
Specific gravity @ 15 °C	0.9318	0.9096
Initial boiling point (°C)	151	182
Final boiling point (°C)	406	399
Total sulfur (wt%)	0.453	2.94
Hydrogen	10.84	Na
Carbon	88.29	Na

The total rate of disappearance of DBT is the sum of the rate of consumption of DBT by hydrogenolysis and hydrogenation

$$R_{\mathrm{DBT}} = r_{\mathrm{DBT},\sigma} + r_{\mathrm{DBT},\tau} \tag{4}$$

Accounting for adsorption and reaction for the various steps of the network of Fig. 2 Froment et al. [1] counted at the molecular level for the complete set of DBT, 44 substituted DBT, 29 (s)BPH, 84 (s)THDBT, 84 (s)HHDBT, 55 (s)CHB, H_2S and H_2 a total of 1193 parameters. To avoid such an untractable number of rate parameters they introduced the structural contribution approach for the kinetic modeling.

2.4. Structural contributions approach

In this approach the rate and adsorption parameters of the (s)DBT and the reaction products are related to those of the

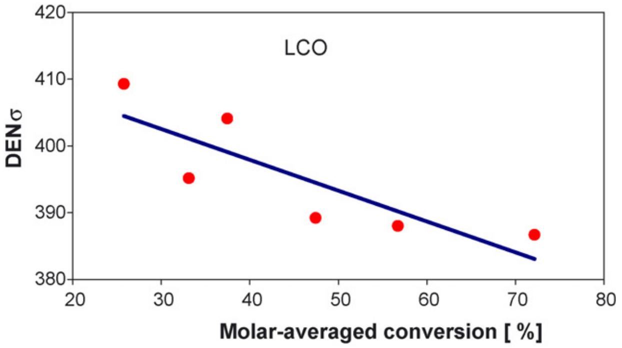

Fig. 2. DEN_σ at 330 °C as a function of the molar-averaged conversion of LCO. Line: Correlation obtained by least square fitting from the calculated DEN_σ. Molar H_2/LCO = 2.8.

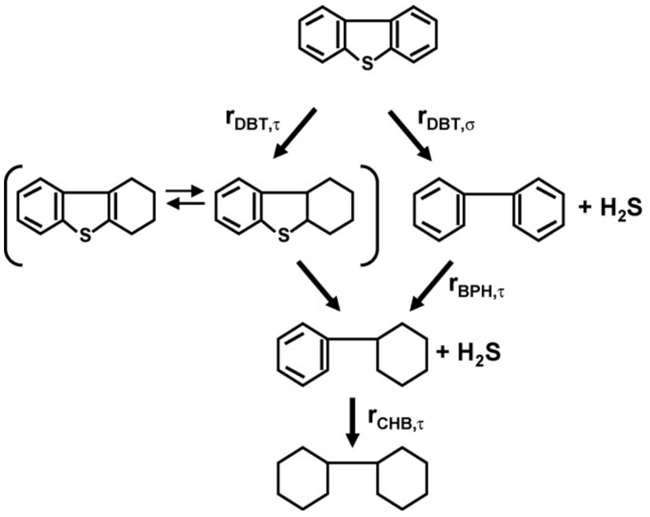

Fig. 3. Reaction network for the HDS of dibenzothiophene (DBT) into biphenyl (BPH), cyclohexylbenzene (CHB) and bicyclohexyl (BCH) [5,11].

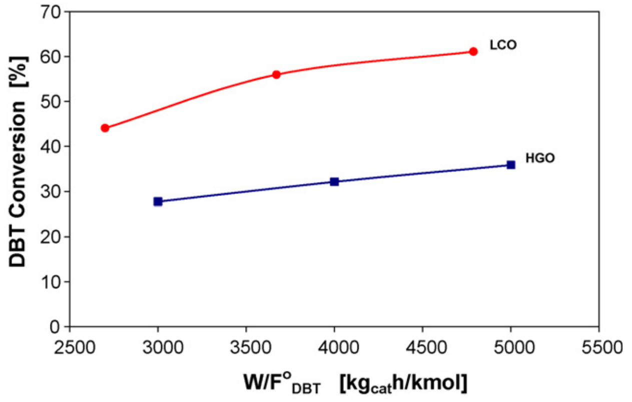

Fig. 4. Total conversion of DBT as a function of DBT-space time, W/F^0_{DBT}, in the HDS of LCO and HGO over a CoMo/Al$_2$O$_3$ catalyst. Experimental conditions: $T = 330$ °C, $P = 65$ bar, molar H$_2$/HC = 2.8.

parent molecule, DBT, BPH, CHB by accounting for the electronic and steric hindrance effects exerted by the substituents, as shown below for the DBT family.

The structural contributions to the adsorption equilibrium constants of the substituted DBT on the σ-sites are given in Table 3, to the DDS rate coefficients in Table 4. The contribution of steric hindrance is only felt for the substituents in the positions 4 and 6, surrounding the S-atom.

Table 3
Structural contributions to the adsorption equilibrium constants of substituted DBT on the σ–sites

DBT	$K_{DBT,\sigma}$
1-MeDBT	$K_{DBT,\sigma}(1;0;0) = K_{DBT,\sigma}K^{sDBT}_{EL,\sigma}(m;0;0)$
2-MeDBT	$K_{DBT,\sigma}(2;0;0) = K_{DBT,\sigma}K^{sDBT}_{EL,\sigma}(m;0;0)$
3-MeDBT	$K_{DBT,\sigma}(3;0;0) = K_{DBT,\sigma}K^{sDBT}_{EL,\sigma}(m;0;0)$
4-MeDBT	$K_{DBT,\sigma}(4;0;0) = K_{DBT,\sigma}K^{sDBT}_{EL,\sigma}(m;0;0)K^{sDBT}_{ST,\sigma}(4;0;0)$
1,2-DiMeDBT	$K_{DBT,\sigma}(1;2;0) = K_{DBT,\sigma}K^{sDBT}_{EL,\sigma}(m;n;0)$
4,6-DiMeDBT	$K_{DBT,\sigma}(4;6;0) = K_{DBT,\sigma}K^{sDBT}_{EL,\sigma}(m;n;0)K^{sDBT}_{ST,\sigma}(4;6;0)$
1,2,6-TriMeDBT	$K_{DBT,\sigma}(1;2;6) = K_{DBT,\sigma}K^{sDBT}_{EL,\sigma}(m;n;p)K^{sDBT}_{ST,\sigma}(6;0;0)$

Table 4
Structural contributions to the rate coefficients of the substituted DBT in DDS

DBT	$k_{DBT,\sigma}$
1-MeDBT	$k_{DBT,\sigma}(1;0;0) = k_{DBT,\sigma}k^{sDBT}_{EL,\sigma}(m;0;0)$
2-MeDBT	$k_{DBT,\sigma}(2;0;0) = k_{DBT,\sigma}k^{sDBT}_{EL,\sigma}(m;0;0)$
3-MeDBT	$k_{DBT,\sigma}(3;0;0) = k_{DBT,\sigma}k^{sDBT}_{EL,\sigma}(m;0;0)$
4-MeDBT	$k_{DBT,\sigma}(4;0;0) = k_{DBT,\sigma}k^{sDBT}_{EL,\sigma}(m;0;0)k^{sDBT}_{ST,\sigma}(4;0;0)$
1,2-DiMeDBT	$k_{DBT,\sigma}(1;2;0) = k_{DBT,\sigma}k^{sDBT}_{EL,\sigma}(m;n;0)$
4,6-DiMeDBT	$k_{DBT,\sigma}(4;6;0) = k_{DBT,\sigma}k^{sDBT}_{EL,\sigma}(m;n;0)k^{sDBT}_{ST,\sigma}(4;6;0)$
1,2,6-TriMeDBT	$k_{DBT,\sigma}(1;2;6) = k_{DBT,\sigma}k^{sDBT}_{EL,\sigma}(m;n;p)k^{sDBT}_{ST,\sigma}(6;0;0)$

Table 5
Structural contributions to the adsorption equilibrium constants of (s)DBT on τ-sites

$K_{DBT,\tau}$	DBT
$K_{DBT,\tau}(m;0;0) = K_{DBT,\tau}K^{sDBT}_{EL+ST,\sigma}(m;0;0)$	MeDBT
$K_{DBT,\tau}(m;n;0) = K_{DBT,\tau}K^{sDBT}_{EL+ST,\tau}(m;n;0)$	DiMeDBT
$K_{DBT,\tau}(m;n;p) = K_{DBT,\tau}K^{sDBT}_{EL+ST,\tau}(m;n;p)$	TriMeDBT

In the hydrogenation steps, in which the reacting molecule is adsorbed in a flat way on τ-sites, the electronic effect and the steric hindrance effect are combined into 1 structural contribution, as shown in Table 5 for the (s)DBT adsorption equilibrium constants and in Table 6 for the hydrogenation rate coefficient. With this approach the number of parameters for the HDS of DBT and all (s)DBT is reduced to 93.

Numerical values for the structural contributions for the (s)DBT, determined by Vanrysselberghe and Froment [11] from experimental work on the kinetics of HDS of DBT and various (s)DBT are given in Table 7.

This approach will now be applied to the kinetic modeling of the HDS of the LCO and HGO dealt with in the present work, but in the absence of own specific experimentation on the kinetics of HDS of pure (s)DBT components, normally required to determine the structural contributions.

Table 6
Structural contributions to the rate coefficients for the hydrogenation of substituted DBT

$k_{DBT,\tau}$	DBT
$k_{DBT,\tau}(m;0;0) = k_{DBT,\tau}k^{sDBT}_{EL+ST,\sigma}(m;0;0)$	MeDBT
$k_{DBT,\tau}(m;n;0) = k_{DBT,\tau}k^{sDBT}_{EL+ST,\tau}(m;n;0)$	DiMeDBT
$k_{DBT,\tau}(m;n;p) = k_{DBT,\tau}k^{sDBT}_{EL+ST,\tau}(m;n;p)$	TriMeDBT

Table 7
Numerical values for the structural contributions for (s)DBT

Hydrogenolysis (DDS)[a]	Hydrogenation
$K_{ST,\sigma}(4;0;0) = 0.310$	$K_{EL+ST,\tau}(m;0;0) = 1.04$
$K_{ST,\sigma}(4;6;0) = 0.238$	$K_{EL+ST,\tau}(m;n;0) = 1.11$
$k_{ST,\sigma}(4;0;0) = 0.588$	$k_{EL+ST,\tau}(m;0;0) = 6.05$
$k_{ST,\sigma}(4;6;0) = 0.050$	$k_{EL+ST,\tau}(m;n;0) = 6.07$

[a] $k_{EL,\sigma}$ and $K_{EL,\sigma} = 1$ for all m; n; p.

Based upon the network of Fig. 3 the expressions for the total conversion of DBT, x_{DBT}, for the conversion of DBT into biphenyl, x_{BPH} and for the conversion of DBT into cyclohexylbenzene, x_{CHB}, in LCO and HGO can be written for HDS in a completely mixed reactor:

$$x_{\mathrm{DBT}} = \frac{W}{F^0_{\mathrm{DBT}}} C_{\mathrm{DBT}} C_{\mathrm{H}_2} \left[\frac{k_{\mathrm{DBT},\sigma} K_{\mathrm{DBT},\sigma} K_{\mathrm{H},\sigma}}{\mathrm{DEN}_\sigma} + \frac{k_{\mathrm{DBT},\tau} K_{\mathrm{DBT},\tau} K_{\mathrm{H},\tau}}{\mathrm{DEN}_\tau} \right] \tag{5}$$

The first term in the right hand side of the equation relates to the hydrogenolysis and the second and third to hydrogenation

$$x_{\mathrm{BPH}} = \frac{W}{F^0_{\mathrm{DBT}}} C_{\mathrm{H}_2} \left[\frac{k_{\mathrm{DBT},\sigma} K_{\mathrm{DBT},\sigma} K_{\mathrm{H},\sigma} C_{\mathrm{DBT}}}{\mathrm{DEN}_\sigma} - \frac{k_{\mathrm{BPH},\tau} K_{\mathrm{BPH},\tau} K_{\mathrm{H},\tau} C_{\mathrm{BPH}}}{\mathrm{DEN}_\tau} \right] \tag{6}$$

$$x_{\mathrm{CHB}} = \frac{W}{F^0_{\mathrm{DBT}}} C_{\mathrm{H}_2} \left[\frac{k_{\mathrm{DBT},\tau} K_{\mathrm{DBT},\tau} K_{\mathrm{H},\tau} C_{\mathrm{DBT}}}{\mathrm{DEN}_\tau} + \frac{k_{\mathrm{BPH},\tau} K_{\mathrm{BPH},\tau} K_{\mathrm{H},\tau} C_{\mathrm{BPH}}}{\mathrm{DEN}_\tau} - \frac{k_{\mathrm{CHB},\tau} K_{\mathrm{CHB},\tau} K_{\mathrm{H},\tau} C_{\mathrm{CHB}}}{\mathrm{DEN}_\tau} \right] \tag{7}$$

with

$$\begin{aligned} \mathrm{DEN}_\sigma &= \left(1 + \sum_i K_{i,\sigma} C_i + \sqrt{K_{\mathrm{H},\sigma} C_{\mathrm{H}_2}} \right)^3 \\ \mathrm{DEN}_\tau &= \left(1 + \sum_i K_{i,\tau} C_i + \sqrt{K_{\mathrm{H},\tau} C_{\mathrm{H}_2}} \right)^3 \end{aligned} \tag{8}$$

and, assuming constant liquid density:

$$C_{\mathrm{DBT}} = C^0_{\mathrm{DBT}}(1 - x_{\mathrm{DBT}}), \quad C_{\mathrm{BPH}} = C^0_{\mathrm{DBT}} x_{\mathrm{BPH}}, \quad C_{\mathrm{CHB}} = C^0_{\mathrm{DBT}} x_{\mathrm{CHB}}$$

The concentration of hydrogen in the liquid phase (C_{H_2}) was obtained from correlations for the solubility of hydrogen in petroleum fractions proposed by Riazi and Vera [12] and by Korsten and Hoffmann [13].

The functional forms of the denominators represented by DEN_σ and DEN_τ are identical to those determined in the study of the HDS of the model components DBT [11], 4-MeDBT, and 4,6-DiMeDBT [14].

In the HDS of LCO or HGO the denominators DEN_σ and DEN_τ contain the concentrations of all adsorbing species of the LCO or HGO, multiplied by their respective adsorption equilibrium constant. Not all adsorbing species are identified, however, so that the denominators DEN_σ and DEN_τ cannot be explicited the way it is done for simple mixtures. The denominators DEN_σ and DEN_τ depend upon the mixture composition and the temperature in the completely mixed reactor. A molar-averaged conversion was used to express the variation of the liquid composition and the denominators DEN_σ and DEN_τ [2].

Table 8
Rate and adsorption parameters utilized in the modeling of the HDS of the HGO and LCO

Parameter	Units
$k_{\mathrm{DBT},\sigma} = 2.44336 \times 10^{10} \exp\left[\frac{-122.770\times10^3}{R_{\mathrm{gas}}T}\right]$	kmol/kg$_{\mathrm{cat}}$ h
$K_{\mathrm{H},\sigma} = 3.36312 \times 10^{-11} \exp\left[\frac{113.232\times10^3}{R_{\mathrm{gas}}T}\right]$	m^3/kmol
$K_{\mathrm{DBT},\sigma} = 7.56868 \times 10^{1}$	m^3/kmol
$k_{\mathrm{DBT},\tau} = 2.86757 \times 10^{16} \exp\left[\frac{-186.190\times10^3}{R_{\mathrm{gas}}T}\right]$	kmol/kg$_{\mathrm{cat}}$ h
$k_{\mathrm{BPH},\tau} = 3.4112 \times 10^{23} \exp\left[\frac{255.714\times10^3}{R_{\mathrm{gas}}T}\right]$	kmol/kg$_{\mathrm{cat}}$ h
$K_{\mathrm{H},\tau} = 1.40255 \times 10^{-15} \exp\left[\frac{142.693\times10^3}{R_{\mathrm{gas}}T}\right]$	m^3/kmol
$K_{\mathrm{DBT},\tau} = 2.50395 \times 10^{-7} \exp\left[\frac{76.840\times10^3}{R_{\mathrm{gas}}T}\right]$	m^3/kmol
$K_{\mathrm{BPH},\tau} = 4.96685 \times 10^{-4} \exp\left[\frac{37.899\times10^3}{R_{\mathrm{gas}}T}\right]$	m^3/kmol
$k_{\mathrm{CHB},\tau} K_{\mathrm{CHB},\tau}(573K) = 3.38631 \times 10^{-1}$	m^3/kg$_{\mathrm{cat}}$ h

Taken from Vanrysselberghe and Froment [11].

The denominators appearing in Eqs. (5)–(8) can be calculated when kinetic equations are available for model components for which the products $(k_i K_i K_{\mathrm{H}})_\sigma$ and $(k_i K_i K_{\mathrm{H}})_\tau$ appearing in the numerators are known.

Table 8 shows the expressions derived by Vanrysselberghe and Froment [2,11] for the parameters k_{DBT_σ}, k_{DBT_τ}, K_{DBT_σ}, K_{DBT_τ}, k_{BPH_σ} and K_{BPH_τ} in the numerator of Eqs. (5)–(7) from their experimentation on HDS of pure DBT at temperatures in the same interval as used here (i.e. 290–330 °C) and on a very similar CoMo/Al$_2$O$_3$ catalyst, characterized in Table 1. The above products of parameters $k_{\mathrm{DBT}_\sigma} K_{\mathrm{DBT}_\sigma} K_{\mathrm{H}_2}$ for the hydrogenolysis of dibenzothiophene and $k_{\mathrm{DBT}_\tau} K_{\mathrm{DBT}_\tau} K_{\mathrm{H}_2}$ for its hydrogenation do not depend on the mixture composition, only on the catalyst and because of the similarity of both catalysts these products were accepted in the present work. This opened the way to the calculation of DEN_σ and DEN_τ.

2.5. Determination of the denominators DEN_σ and DEN_τ

Relating the rates of substituted (di)benzothiophenes in the LCO or HGO to those of the unsubstituted parent molecule (DBT), requires the knowledge of both denominators DEN_σ and DEN_τ. These values differ for each experiment, because of the evolution in the composition of the reaction mixture.

The parameters DEN_σ and DEN_τ are obtained by minimization of the sum of squares of residuals of the DBT conversions in one experiment j

$$S = \sum_{i=1}^{i=3} (x_{ij} - \hat{x}_{ij})^2 \xrightarrow{\mathrm{DEN}_\sigma \text{ and } \mathrm{DEN}_\tau} \min \tag{9}$$

in which x_{ij} is the observed and $\hat{x}_{ij}$ the predicted value of the dependent variable, i.e. the total conversion of DBT (x_{DBT}), the conversion of DBT into BPH (x_{BPH}) and the conversion of DBT into cyclohexylbenzene (x_{CHB}) in experiment j. The number of experiments (n_{exp}) per temperature was 7 for LCO and 3 for the HGO.

Table 9
Parameter estimates, 95% confidence intervals and *t*-values at 330 °C for light cycle oil; H_2/LCO = 2.8

	Parameter estimate	Lower limit	Upper limit	*t*-Value
DEN_σ	386.7	360.9	412.4	31.4
DEN_τ	11.0	9.0	13.0	11.5

3. Application to LCO

3.1. DEN_σ and DEN_τ for light cycle oil

Table 9 shows the estimates of DEN_σ and DEN_τ their 95% confidence interval and the *t*-values for a conversion obtained at 330 °C, $W/F^0_{DBT} = 6000\,kg_{cat}\,h/kmol$ and a molar ratio H_2/LCO of 2.8. The accuracy of the estimates is quite satisfactory, although only 3 responses were used. It could be improved further by considering more responses, e.g. those related to benzothiophene and its products, provided that the rate coefficients and adsorption equilibrium constants appearing in the numerator are available.

3.2. DEN_σ and DEN_τ as a function of the molar-averaged conversion for LCO

The values of the unknown DEN_σ and DEN_τ were estimated for each LCO experiment. The variation of DEN_σ and DEN_τ with the mixture composition at 330 °C is shown in Figs. 4 and 5. The mixture composition is expressed in terms of a molar-averaged conversion of the selected components, e.g. in the HDS of LCO

$$\bar{x} = \frac{1}{\sum_{i=1}^{8} y_i^{LCO}} \sum_{i=1}^{8} x_i y_i^{LCO} \tag{10}$$

with x_i the conversions of a set of the identified sulfur components in the LCO and reaction products DBT, 4-MeDBT, 3-MeDBT, 3-ethylDBT, 4,6-DiMeDBT, 3,6-DiMeDBT, 2,8-DiMeDBT, 4,9-DiMeNaphtho[2,3-*b*]thiophene, and y_i^{LCO} the corresponding mole fractions in the LCO.

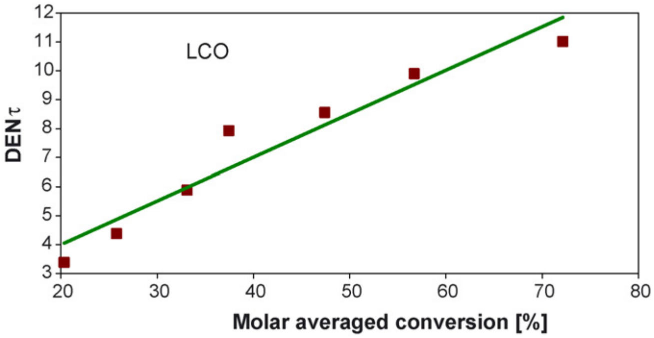

Fig. 5. DEN_τ at 330 °C as a function of the molar-averaged conversion of LCO. Line: Correlation obtained by least square fitting from the calculated DEN_τ. H_2/LCO = 2.8.

The order of magnitude and the trends are the same as those observed by Vanrysselberghe and Froment [2] for a different LCO, in spite of a slightly different definition of the average conversion. DEN_σ decreases because the number of S-components decreases with increasing conversion and their products are likely to be less strongly adsorbed. DEN_τ increases because the number of the products that are subject to hydrogenation increases with the conversion of the S-compounds.

3.3. Comparison of calculated and experimental conversions in the HDS of LCO

Fig. 6 shows an excellent fit between the calculated conversions for DBT, the conversion of DBT into biphenyl and the conversion of DBT into cyclohexylbenzene based upon rate equations containing the DEN_σ and DEN_τ values given in Figs. 4 and 5 and the products in the numerator calculated from Table 8.

Accounting for the structural contributions given in Table 7 for the family of (s)DBT it now becomes possible to predict the evolution of its members, e.g. 3-MeDBT, 4-MeDBT 4,6-diMeDBT, 3,6-diMeDBT and 2,8-diMeDBT for various operating conditions in the HDS of LCO. Fig. 7 shows an excellent agreement between the calculated and experimental rates of conversion of these components for a wide range of conversions.

4. Application to HGO

4.1. Estimation of DEN_σ and DEN_τ

The DEN_σ and DEN_τ were estimated from the total conversions of DBT, the conversions of DBT into BPH and the conversions of DBT into CHB for a number of space times in the range 3000–5000 kg_{cat} h/kmol in the same way as done for LCO. The products of rate and adsorption constants of the key components in the numerator were taken from the work of Vanrysselberghe and Froment [11] on LCO and are given in Table 8. The C_{H_2} was calculated specifically for HGO.

Table 10 shows the estimates of DEN_σ and DEN_τ their corresponding 95% confidence intervals and the *t*-values at 330 °C, H_2/HGO = 2.8 and a space time $W/F^0_{DBT} = 3000\,kg_{cat}\,h/kmol$.

4.2. DEN_σ and DEN_τ as a function of the molar-averaged conversion for HGO

The variation of DEN_σ and DEN_τ with the mixture composition at 330 °C is shown in Figs. 8 and 9, respectively. The straight line was obtained by least square fitting of the calculated DEN_σ. The mixture composition is expressed in terms of a molar-averaged conversion of selected components, as defined above in (10).

The trends are the same as those for LCO. The DEN values differ because the compositions of LCO and HGO are very different, but they are of the same order of magnitude.

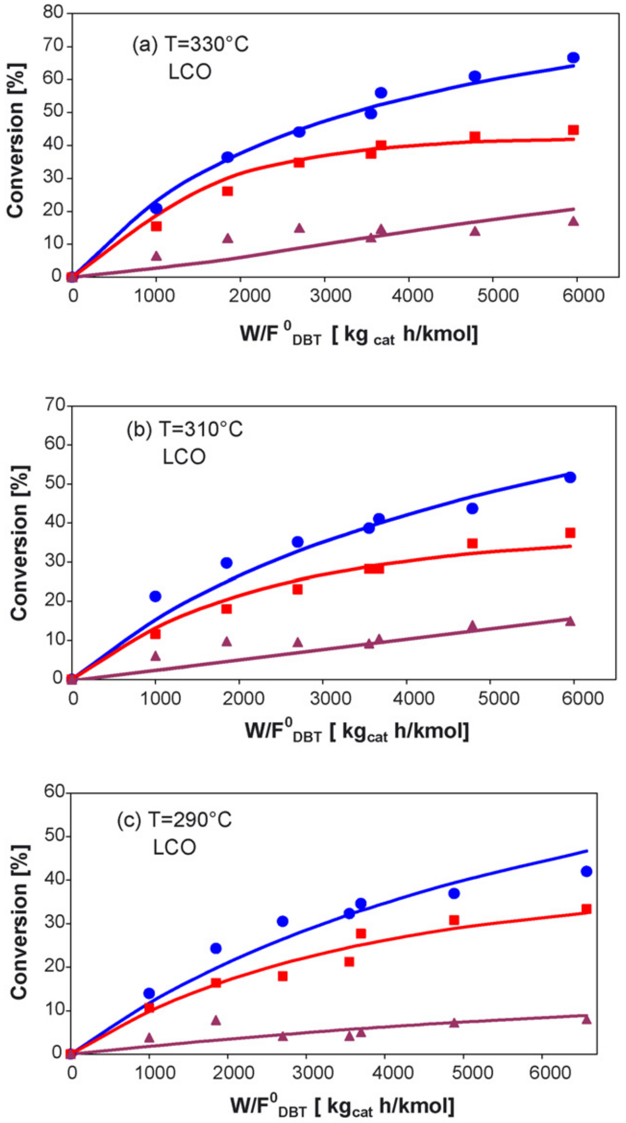

Fig. 6. Comparison of experimental and calculated conversions as a function of W/F^0_{DBT} at H_2/LCO = 2.8 molar ratio. (a) 330 °C, (b) 310 °C, (c) 290 °C. (●) Total conversion of DBT. (■) Conversion of DBT into biphenyl. (▲) Conversion of DBT into CHB. Full curves: calculated. Symbols: experimental.

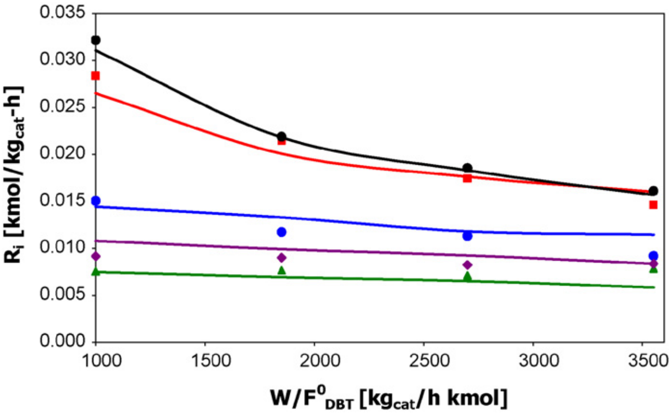

Fig. 7. Comparison of experimental and calculated R_i as a function of W/F^0_{DBT} for various (s)DBT at 330 °C. P = 65 bar, H_2/LCO = 2.8 molar ratio. (●) 4-MeDBT. (■) 3-MeDBT. (▲) 4,6-DiMeDBT. (◆) 3,6-DiMeDBT. (●) 2,8-DiMeDBT. Full curves: calculated. Symbols: experimental.

Table 10
Parameter estimates, 95% confidence intervals and t-values at 330 °C, H_2/HGO = 2.8 and $W/F^0_{DBT} = 3000\,kg_{cat}\,h/kmol$ for heavy gas oil

	Parameter estimate	Lower limit	Upper limit	t-Value
DEN_σ	591.8	550.8	632.8	34.1
DEN_τ	3.6	2.9	4.4	11.3

4.3. Comparison of calculated and experimental conversions in the HDS of HGO

With the completed kinetic model now available it becomes possible to compare also for HGO the calculated conversions for DBT, the conversion of DBT into biphenyl and the conversion of DBT into cyclohexylbenzene with the experimental data at 330, 310 and 290 °C and for a molar ratio H_2/HGO = 7.2 (Fig. 10). Again the observed and calculated conversions are in excellent agreement.

4.4. Effect of the molar H_2/HGO ratio in the HDS of HGO

Fig. 11 shows how with DEN_σ and DEN_τ estimated at T = 330 °C and P = 65 bar the calculated conversion for DBT, the conversion of DBT into biphenyl and the conversion of DBT into cyclohexylbenzene as a function of the molar H_2/HGO

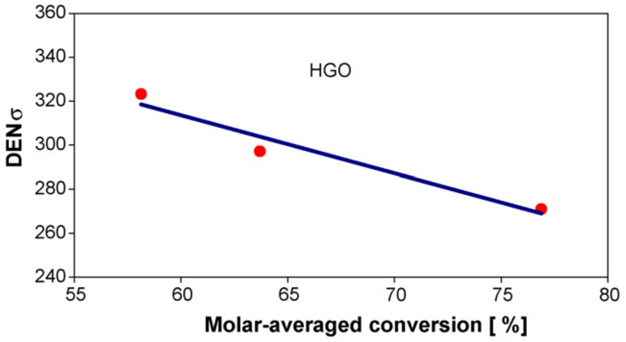

Fig. 8. DEN_σ at 330 °C and a molar ratio H_2/HGO = 7.2 as a function of the molar-averaged conversion of HGO. Line: Correlation obtained by least square fitting from the calculated DEN_σ.

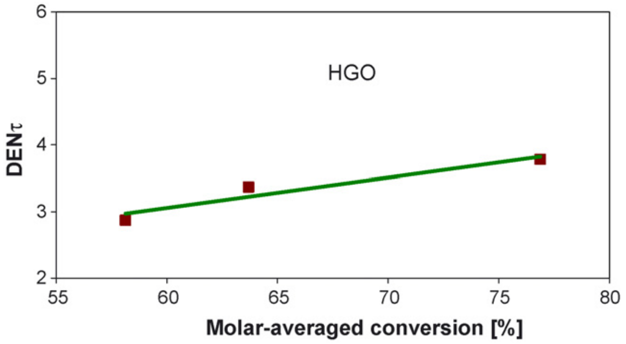

Fig. 9. DEN_τ at 330 °C and molar ratio H_2/HGO = 7.2 as a function of the molar-averaged conversion of HGO. Line: Correlation obtained by least square fitting from the calculated DEN_τ.

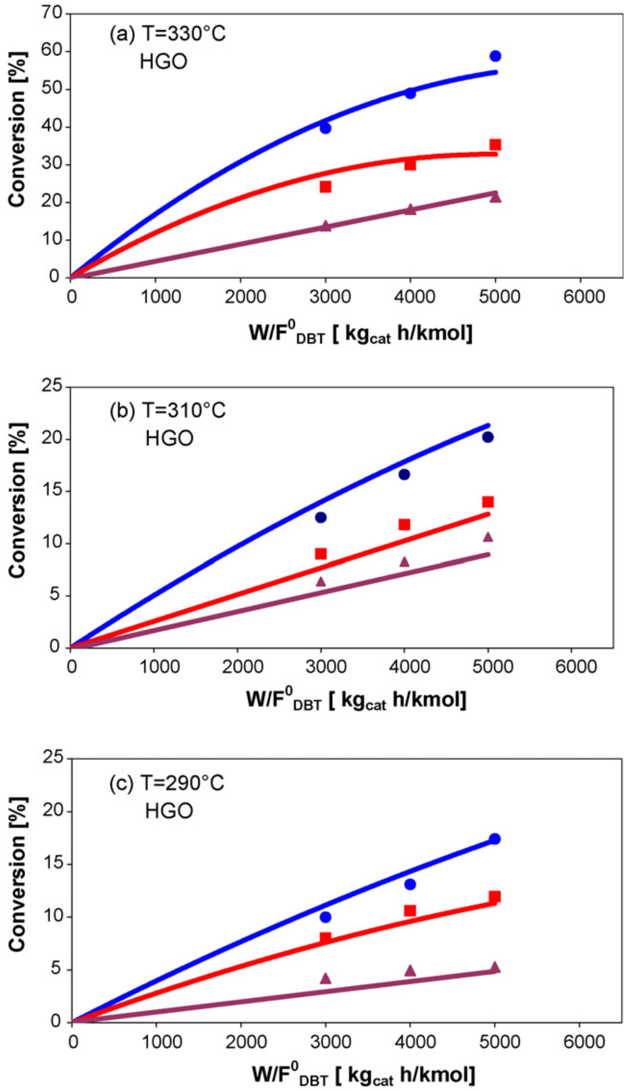

Fig. 10. Comparison of experimental and calculated conversions as a function of W/F^0_{DBT} at H_2/HGO = 7.2. (a) 330 °C, (b) 310 °C, (c) 290 °C. (●) Total conversion of DBT. (■) Conversion of DBT into Biphenyl. (▲) Conversion of DBT into CHB. Full curves: calculated. Symbols: experimental.

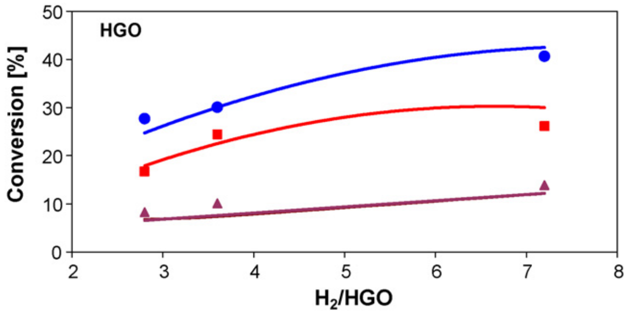

Fig. 11. Comparison of experimental and calculated conversions as a function of H_2/HGO. (●) Total conversion of DBT. (■) Conversion of DBT into biphenyl. (▲) Conversion of DBT into CHB. Experimental conditions: $W/F^0_{DBT} = 3000\,kg_{cat}\,h/kmol$, $T = 330$ °C and $P = 65$ bar. Full curves: calculated. Symbols: experimental.

Table 11
Comparison of experimental and calculated rates of (s)DBT conversion in the HDS of HGO as a function of W/F^0_{DBT}

Rates ($\times 10^4$ kmol/kg_{cat} h)				W/F^0_{DBT}
4-MeDBT		4,6-DiMeDBT		
Experimental	Calculated	Experimental	Calculated	
44	44	36	35	4000
37	41	33	34	5000
40	39	37	33	6000

Conditions: 310 °C. $P = 65$ bar, H_2/HGO = 7.2 molar ratio.

ratio agree with the experimental data at $W/(F^0_{DBT}) = 3000$, a higher molar H_2/HGO ratio leads to higher conversions.

As for LCO and accounting for the structural contributions given in Table 7 for the family of (s)DBT it now becomes possible to predict the evolution of, e.g. 4,6-diMeDBT and other components for various operating conditions in the HDS of HGO. Table 11 shows the experimental and calculated rates of (s)DBT conversion in the HDS of HGO.

5. Conclusion

The present paper illustrates the power of a fundamental approach for the kinetic modeling of the HDS of complex mixtures.

The parameters $k_{DBT_\sigma}K_{DBT_\sigma}K_{H_2}$ and $k_{DBT_\tau}K_{DBT_\tau}K_{H_2}$ determined by Vanrysselberghe and Froment [2,11] for the DDS and hydrogenation of dibenzothiophene and $k_{BPH,\tau}$, $K_{BPH,\tau}$, $K_{H,\tau}$ and k_{CHB_τ}, K_{CHB_τ}, K_{H_τ} determined for the hydrogenation into BPH and CHB can be used in the kinetic modeling of the HDS of LCO and HGO or any other complex mixture upon a similar $CoMo/Al_2O_3$ catalyst. From a small number of experimental data numerical values of the denominators DEN_σ and DEN_τ at various conversions can then be obtained so that in combination with the structural contribution approach complete kinetic equations become available for a family of S-components. The model accurately reproduces the observed total conversion of DBT, as well as the conversions of DBT into biphenyl and into cyclohexylbenzene as a function of temperature for oil fractions as different in composition as LCO and HGO.

Refineries are continuously confronted with the adaptation of the operating conditions of their hydrodesulfurization units as crudes with different characteristics are being processed. These adaptations are presently guided by extensive and costly pilot plant experimentation. The lessons learned from the application of the structural contributions approach to real oil fractions presented here opens perspectives for the prediction of the HDS of oil fractions based upon realistic kinetic models without having to resort to extensive experimentation. Provided the catalyst is not changed the approach necessitates only a limited number of experiments aiming at the determination of the denominators of the kinetic equations. It is to be expected that in the future catalogs of the feed invariant elements of the rate equations will be established for a number of commercial catalysts so that the approach illustrated here can be routinely applied.

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