

MOLECULAR MODELING OF GAS OIL HYDRODESULFURIZATION

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ABSTRACT

The hydrodesulfurization (HDS) process chemistry and reaction network have been modeled at the molecular level. The following sulfur compound types have been considered: mercaptans, sulfides, disulfides, thiophenes (T), benzothiophenes (BT), dibenzothiophenes (DBT), and their alkyl and hydrogenated derivatives. The steric and electronic effects of the alkyl side chain of thiophenic compounds (T, BT, and DBT) are taken into account. The dual-site mechanism - σ site for direct desulfurization and τ site for hydrogenation on catalyst surface - is incorporated; the corresponding dual-site LHHW formalism is constructed to describe the complex kinetics. A rigorous molecular model for gas oil HDS is thus developed fast and successfully by aid of the Kinetic Modeler's Toolbox (KMT). The model matches pilot plant data very well and can be used to optimize the HDS process.

KEYWORDS: Hydrodesulfurization (HDS), Molecular Modeling, Kinetic Modeling

INTRODUCTION

Hydrodesulfurization (HDS) has been one of the most important oil refining processes. The process chemistry has been studied extensively over the past two decades [1-3]. However, with more and more stringent environmental regulations, our interests in HDS process have been renewed. Low sulfur specifications caused the refiners to look at the hydrotreating options and thus more rigorous models are desired to better improve the process. In this paper, a practical molecular level modeling of HDS process is introduced and developed, which is part of a much wider effort aiming at automated molecule-based kinetic modeling of gas oil hydroprocessing [4].

MODEL DEVELOPMENT

Classification of Sulfur Compounds

The petroleum feedstock contains the following sulfur compound types: mercaptans, sulfides, disulfides, thiophenes (T), benzothiophenes (BT), dibenzothiophenes (DBT), and their alkyl and hydrogenated derivatives. HDS reactivity depends critically on the molecular size and structure of the sulfur compounds. The mercaptans, sulfides and disulfides have, generally, fast kinetics compared with the thiophenic compounds (T, BT, and DBT as shown in Figure 1). The substituent groups adjacent to the S atom on thiophenic compounds generally retard HDS. While methyl groups distant from the S atom generally increase HDS activity - an effect attributed to increased electron density on the S atom - those adjacent to the S atom decrease reactivity due to steric effect [2].

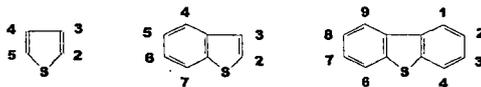


Figure 1. Thiophenes (T), Benzothiophenes (BT), and Dibenzothiophenes (DBT).

Those significant positions on T, BT, and DBT are identified as listed in Table 1. For example, it has been found that 4,6-dimethyldibenzothiophene (4,6-DMDBT) remains intact until the final stages of HDS of a light oil. The substituent groups on the significant and non-significant positions have different steric and electronic effects on HDS reactivities. As shown in Table 1, for example, we need at least two monomethyl, three dimethyl, and three trimethyl-substituted molecular structures to account for this position difference for alkyl-DBTs up to C3.

Table 1: The significant positions of thiophenic compounds.

Sulfur	Significant Position	Non-significant	Factor* (steric+electronic)	Representative Structures
T	2, 5	3, 4	$f_{1,T} \ll f_{2,T}$	2C1, 3C2, 2C3, 1C4
BT	2 (3, 7)	4, 5, 6	$f_{1,BT} \ll f_{2,BT}$	2C1, 2C2, 2C3, 2C4
DBT	4, 6	1, 2, 3, 7, 8, 9	$f_{1,DBT} \ll f_{2,DBT}$	2C1, 3C2, 3C3

* Subscript 1 denotes there is an alkyl chain at a significant position; 2 for non-significant position.

Reaction Pathways and Network

The following reaction pathways shown in Figure 2 are used to describe the HDS chemistry. The mercaptans, sulfides, and disulfides can be easily desulfurized. The T, BT, DBT and their alkyl

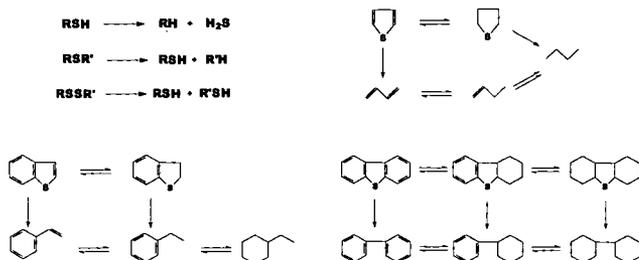


Figure 2. HDS reaction pathways and network.

derivatives can go through either the hydrogenation reaction at the τ site or the direct desulfurization reaction at the σ site on the catalyst surface [3].

Reaction Kinetics

Table 2 shows the rate laws used to model HDS kinetics. The classical dual-site mechanism - σ site for direct desulfurization and τ site for hydrogenation on catalyst surface in HDS process - is utilized to implement the corresponding dual-site LHHW formalism. This rate law is derived from the model compound studies by assuming the rate-determining surface reaction step between adsorbed reactants and two competitively adsorbed hydrogen atoms for both types of reaction [5].

Table 2: HDS rate law.

$$r = \frac{f_{\sigma} k K_{A,\sigma} K_{H_2,\sigma} [A] [H_2]}{(1 + \sum_i K_{i,\sigma} [I] + \sqrt{K_{H_2,\sigma} [H_2]})^n} + \frac{f_{\tau} k_{\tau} K_{A,\tau} K_{H_2,\tau} [A] [H_2] - [B]/K}{(1 + \sum_i K_{i,\tau} [I] + \sqrt{K_{H_2,\tau} [H_2]})^n}$$

Where r is reaction rate, $[I]$ is concentration of component, k is rate constant, K_i is adsorption constant of component, K is equilibrium constant and n is the exponent of inhibition term (3 for HDS).

The two global factors (f_{σ} and f_{τ}) are introduced to account for the total steric and electronic effects of substituents on thiophenic compounds at both σ and τ sites.

RESULTS AND DISCUSSION

A detailed molecular level kinetic model for HDS of light gas oil has been developed using the Kinetic Modeler's Toolbox (KMT) - a software package that automates the kinetic modeling of industrial complex processes [4]. The complete reaction model was built automatically in only 2 CPU seconds and solves very fast in less than 2 CPU seconds on an Intel Pentium II 333Mhz machine.

The current version of the model containing 243 species and 437 reactions was tuned to pilot plant data and the parity plot (Figure 3) shows the model matches the experimental data very well and can do a good job even in very low sulfur levels (<50ppm). The parity guarantees the model follows the right trends of the molecular conversions in the process stream and the developed model can certainly provide the quantitative insights to improve the HDS process.

CONCLUSIONS

The automated molecule-based kinetic modeling strategy was successfully extended to build rigorous HDS model as part of the effort to model gas oil hydroprocessing [4]. To rigorously model the HDS chemistry, it is necessary to incorporate at least all the representative molecular structures with substituents at both significant and non-significant positions. It is also very important to incorporate dual-site mechanism and implement the corresponding LHHW formalism to take into account the inhibitions of various compounds in the process stream (especially the H₂S inhibition at σ sites). The developed HDS Model matches the pilot-plant data very well and can be used to optimize the low sulfur hydrotreating process quantitatively.

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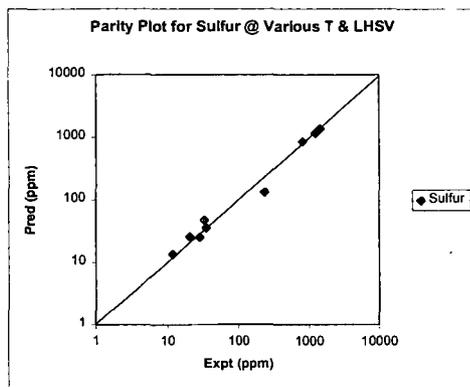


Figure 3. Parity plot of HDS model.