



## Full Length Article

## Thermodynamic analysis of diesel hydrotreating reactions

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## ABSTRACT

Thermodynamic analysis of diesel hydrotreating reactions—Hydrodesulfurization (HDS), Hydrodenitrogenation (HDN) and Hydrodearomatization (HDA)—were studied by Gibbs free energy minimization to understand the effect of process variables such as temperature (200–600 °C), pressure (10–80 bar(a)) and H<sub>2</sub>/oil ratio (stoichiometric ratio – 5 times of stoichiometric ratio) on the product distribution. Dibenzothiophene (DBT), naphthalene and pyridine were considered as representative compounds to study the HDS, HDA and HDN reactions respectively and the reactions were studied in both gas phase and two phase (gas–liquid). It was found that the HDN reaction has no thermodynamic limitation while HDA reaction has significant thermodynamic limitation at low pressures and high temperatures. Higher H<sub>2</sub> concentration favors the HDA equilibria but not very significantly. Overall HDS reaction has no thermodynamic limitation but for refractory sulfur compounds like DBT and alkyl substituted DBTs, the preference for individual reaction pathways—Direct Desulfurization (DDS) and Hydrogenation (HYD)—changes with change in process variables. It was shown that while the selection of operating temperature and H<sub>2</sub> concentration for a commercial diesel hydrotreating reactor are governed by the reaction kinetics, the reactor pressure is mostly governed by the HDA reaction equilibria.

## 1. Introduction

Diesel hydrotreaters are one of the most common units in a refinery and its importance is increasing day by day with the processing of heavier feedstocks with higher sulfur, nitrogen and aromatic content on the one hand and more stringent emission norms coming into force on the other hand [1]. Main reactions that take place in diesel hydrotreating are Hydrodesulfurization (HDS), Hydrodenitrogenation (HDN) and Hydrodearomatization (HDA) [2]. Industrial diesel hydrotreating reactors usually operate between 40–70 bar(g) and at 300–400 °C. For a particular unit, the pressure slightly increases from Start of Run (SOR) to End of Run (EOR), usually by 2–3 bar, in order to compensate for the pressure drop in reactors because of fouling of catalyst. However, the reactor operating temperature is slowly increased from SOR to EOR by as much as 40–50 °C in order to compensate for the progressive deactivation of the catalyst [3]. It is also a standard practice to maintain around three times the stoichiometric requirement of H<sub>2</sub> in the reactor [4]. Pilot plant studies carried out at higher stoichiometric ratios suggest that higher sulfur removal can be achieved by increasing the hydrogen to oil molar ratio up to ~11 [5]. However, the differential increase in sulfur removal at stoichiometric ratios higher than 3 is quite marginal and has not been adopted commercially because of the substantially higher capital and operating expenses involved in

maintaining a higher hydrogen to oil ratio.

Diesel hydrotreating is a mature technology and a lot of research has been done regarding the selection of catalyst and reactor for this process. However, little work is available in open literature that discusses the diesel hydrotreating reactions from a thermodynamic perspective. This is mainly because of the lack of accurate thermochemical data like standard heat of formation, activity coefficients etc. of the different species that take part in these reactions [6]. Moreover, the works that are published till date on HDS, HDN and HDA reaction equilibria pertaining to diesel hydrotreating have reported mostly the gas-phase equilibrium constants of these reactions at some particular temperature and pressure conditions and thus, do not provide the holistic picture from a thermodynamic perspective throughout the entire operating range of a commercial diesel hydrotreating reactor. The different conditions reported for reactions most relevant to diesel hydrotreating are given in Table 1.

Here, we have used Aspen Plus (v9.0) to study HDS, HDN and HDA reaction with representative compounds in order to gain insight into the equilibrium conversion of these reactions around the entire range of temperature, pressure and stoichiometric ratio used in operating an industrial hydrotreating reactor. Temperature effects have been studied between 200 °C and 600 °C which covers the optimum temperature range of 300–400 °C. Similarly, pressure effects have been studied

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### Nomenclature

$x_{H_2}$	mole fraction of hydrogen in liquid phase
$y_{H_2}$	mole fraction of hydrogen in vapor phase
$p_{H_2}$	partial pressure of hydrogen
$\log_{10}K_{eq}$	logarithm (base 10) of equilibrium constant

between 10 bar(a) and 80 bar(a), which also covers the optimum pressure range of 40–70 bar(g). The effect of reactant concentration has also been studied by varying the ratio of  $H_2$  to representative compound from stoichiometric ratio to five times the stoichiometric ratio. Although the equilibrium conversion is unique for each reaction yet, earlier studies have shown that they follow similar trend for the same type of reaction [7–11]. Hence, study with representative compounds is helpful in understanding the thermodynamic behavior of the same class of reaction. This study is also of particular importance from the point of view that the representative compounds considered are in liquid state for a considerable range of the reaction conditions studied, thus, giving insight into the equilibrium conversion of two-phase (gas–liquid) systems, which have not been studied in detail before.

The equilibrium composition of a reaction system can be accurately specified by Gibbs free energy minimization method [15]. The RGibbs reactor model of Aspen Plus (v9.0) is based on this method and can be used to carry out the thermodynamic analysis of reactions. In RGibbs reactor, the calculation varies the number of moles of each species in each phase subject to stoichiometric constraints, reaction pressure and temperature to find a solution that minimizes the total Gibbs free

energy of the system. Thermodynamic analysis of dry reforming of  $CH_4$  with  $CO_2$  has already been carried out in Aspen Plus and verified with experimental results [16] thus signifying that this tool has adequate capabilities to carry out thermodynamic analysis. We have also verified the result of Aspen Plus with results obtained from first principle for a typical hydrotreating reaction (HDA of toluene to methylcyclohexane) in order to ensure that the numerical algorithm of Aspen Plus is accurate for a system like ours.

To carry out thermodynamic studies, an appropriate property method is required that can satisfactorily provide the rigorous thermodynamic correlations. We have selected the Soave-Redlich-Kwong (SRK) equation of state for our purpose as it is capable of dealing with mixtures of hydrocarbon and hydrogen at elevated temperatures and pressures in both vapor and liquid phases with high accuracy [17–19]. The binary interaction parameters of Aspen Plus library have been used. Experimental data of vapor liquid equilibrium is available for hydrogen/tetralin system at elevated temperatures and pressures [20]. The experimentally obtained vapor and liquid mole fraction of hydrogen at different temperatures and pressures were compared with those obtained from Aspen Plus using SRK equation of state and the values were found to match closely, with the maximum deviation being less than 5% (Table 2). This highlights the accuracy of the interaction parameters present in Aspen Plus library. For other systems, the validation could not be done due to lack of published experimental data. Du et al. [21] has carried out simulation of diesel hydrotreating process with real components which included all the reactants that have been used in this study, viz. dibenzothiophene, pyridine, naphthalene and hydrogen. In the simulation, the thermodynamic properties were calculated by SRK equation of state without any modification. The

**Table 1**

Temperature and pressure conditions at which thermodynamic equilibrium data of most relevant diesel hydrotreating reactions are reported.

Reference	Reaction reported	Temperature dependence reported	Pressure dependence reported
<b>HDS</b>			
Weisser and Landa [12]	HDS of thiophene	$\log_{10}K_{eq}$ values at T = 298–1000 K	–
Speight [10]	HDS of thiophene	$\log_{10}K_{eq}$ values at T = 298.16 K, 500 K, 700 K, 900 K	–
Devanneaux and Maurin [13]	HDS of thiophene and benzothiophene	$\log_{10}K_{eq}$ values at T = 400 °C	–
<b>HDN</b>			
Cocchetto and Satterfield [8]	HDN of pyridine, pyrrole, quinoline	$\log_{10}K_{eq}$ values at T = 298–1000 K	Pyridine/piperidine equilibrium at T = 100–550 °C at $p_{H_2} = 11$ atm, 100 atm
<b>HDA</b>			
Wilson [14]	HDA of naphthalene	$\log_{10}K_{eq}$ values at T = 588–769 K	–
Frye [7]	HDA of naphthalene	$\log_{10}K_{eq}$ values at 343 °C and 14.5 atm, 383 °C and 24.9 atm, 402 °C and 41.8 atm	–
	HDA of phenanthrene	$\log_{10}K_{eq}$ values at T = 588–769 K	–
	HDA of phenanthrene	$\log_{10}K_{eq}$ values at 346 °C and 15.9 atm, 429 °C and 78.9 atm	–
Frye and Weitkamp [11]	HDA of naphthalene	$\log_{10}K_{eq}$ values at 301.5 °C and 6.1 atm, 301 °C and 6.97 atm, 351 °C and 20.35 atm, 396 °C and 10.66 atm, 396.5 °C and 47.1 atm, 457 °C and 68.8 atm	–

1 atm = 101325 Pa.

**Table 2**

Comparison of vapor–liquid equilibrium data for hydrogen/tetralin.

Temperature (°C)	Pressure (atm)	$x_{H_2}$			$y_{H_2}$		
		Aspen Plus	Simnick et al. [20]	% Deviation	Aspen Plus	Simnick et al. [20]	% Deviation
268.7	20	0.0139	0.0143	-2.9	0.8121	0.8028	1.1
	30	0.0212	0.0221	-4.2	0.8748	0.8676	0.8
	50	0.0359	0.0373	-3.9	0.9255	0.9155	1.1
	100	0.0722	0.0732	-1.4	0.9637	0.9538	1.0
348.6	50	0.0448	0.0452	-0.9	0.7107	0.7066	0.6
	100	0.0935	0.0925	1.1	0.8532	0.8346	2.2
389.1	50	0.0488	0.0482	1.2	0.4905	0.4810	1.9
	100	0.1161	0.1170	-0.8	0.7118	0.7008	1.5

1 atm = 101325 Pa.

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