Available online at www.sciencedirect.com

ScienceDirect

Catalysis Today 127 (2007) 99–102

CATALYSIS TODAY

www.elsevier.com/locate/cattod

The effects of gas-to-oil rate in ultra low sulfur diesel hydrotreating

George Hoekstra *

BP Products North America, Naperville, IL, United States

Abstract

Hydrotreating has become a critical refining process as fuel sulfur specifications are tightened around the world. Recently, refiners in the United States have been learning how to optimize the performance of ultra low sulfur diesel (ulsd) hydrotreaters. The gas-to-oil feed rate ratio is known to be an important variable in this respect. It is well known that the gas-to-oil rate must be kept high enough to maintain the desired hydrogen partial pressure through the hydrotreating reactor, and to minimize the inhibiting effect of hydrogen sulfide. A lesser-known effect is the effect of gas-to-oil rate on the vapor–liquid equilibrium in the reactor. Changing the gas-to-oil rate alters the distribution of reactants between vapor and liquid in a way that changes the relative reaction rates of different sulfur compounds. This paper presents some pilot plant data and analysis showing this effect of phase equilibrium in deep diesel desulfurization. The effect can be modeled using the Frye–Mosby equation, which accounts for the effects of feed vaporization and phase equilibrium on the reaction rates of individual sulfur compounds in a trickle bed hydrotreater.

Keywords: Gas-to-oil rate; Ultra low sulfur diesel (ulsd); Hydrotreating

---

1. Theory

In a trickle bed hydrotreater, the sulfur-containing reactants are distributed between the liquid and vapor phases. If the phases are in equilibrium, then the compositions of the liquid and vapor can be described by a phase equilibrium relationship. If we assume that Raoult's law applies, then the following equations describe the relationships between the liquid phase mole fractions, (x_s) the vapor phase mole fractions (y_s) and the partial pressures, (P_s), of the sulfur compounds.

$$y_s = \frac{P_s}{P_{\text{total}}} = \frac{P_s^0 x_s}{P_{\text{total}}} \qquad (1)$$

where y_s is mole fraction of a sulfur compound in the vapor phase, P_s the partial pressure of the sulfur compound, P_s^0 the vapor pressure of the sulfur compound, x_s the mole fraction of the sulfur compound in the liquid phase, and P_{total} is the total pressure.

In 1967, Frye and Mosby [1] published the following equation for first-order hydrodesulfurization of a sulfur compound reacting under these conditions:

$$\ln\frac{X_s^0}{X_s} = \frac{k_s P_s^0 P_h L}{(1 - a + (a + H/M)P_s^0/P_{\text{total}})(1 + \sum B_j P_j)^n} \qquad (2)$$

where a is mole fraction of feed liquid vaporized at reactor inlet, B_j the adsorption equilibrium constant of non-reacting compound j, H the molar feed rate of gas, k_s the volumetric reaction rate constant for the sulfur compound, L the reactor length, M the molar feed rate of oil, n a constant which depends on reaction mechanism, P_h the hydrogen partial pressure, P_j the partial pressure of non-reacting compound j, P_{total} the total pressure, X_s^0 the mole fraction of a single sulfur compound in feed liquid, and X_s is the mole fraction of the single sulfur compound in product liquid.

This equation was derived from a differential mass balance on an individual sulfur compound reacting in the flowing liquid–vapor mixture. The assumptions are:

- plug flow of liquid and vapor;
- phase equilibrium is maintained throughout the reactor;
- Raoult's law describes the phase equilibrium;
- Langmuir–Hinshelwood concepts describe adsorption of reactants and inhibitors;
- the reaction rate is limited by first-order surface kinetics;
- negligible pressure drop throughout the reactor;

---

* Tel.: +1 630 330 8159; fax: +1 630 420 4507.
E-mail address: hoekstgr@bp.com.

0920-5861/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2007.05.001

- constant molar ratio of hydrogen to oil;
- constant temperature;
- constant percentage feed vaporization;
- constant hydrogen partial pressure.

The right hand side of the equation can be written as the product of two factors:

$$\ln\frac{X_{\mathrm{s}}^0}{X_{\mathrm{s}}} = V_{\mathrm{s}}\frac{k_{\mathrm{s}}P_{\mathrm{h}}L}{(1+\sum B_iP_i)^n}$$

where

$$V_{\mathrm{s}} = \frac{P_{\mathrm{s}}^0}{1-a+(a+H/M)P_{\mathrm{s}}^0/P_{\mathrm{total}}}$$

The factor V_{s} takes on a different value for each sulfur compound in the feed, depending on its volatility (P_{s}^0). V_{s} represents a thermodynamic effect of phase equilibrium on the partial pressure of the sulfur compound. Its value depends on the fractional vaporization of the feed (*a*), the hydrogen to oil molar flow ratio (*H*/*M*), the total pressure P_{total}, and the vapor pressure of the compound (P_{s}^0). These are the variables that affect the partial pressure of that compound under conditions of vapor–liquid equilibrium.

For the special case where the fractional feed vaporization (*a*) is 1 (all vapor phase condition), this factor reduces to

$$V_{\mathrm{s}} = \frac{P_{\mathrm{total}}}{1+H/M}$$

The vapor pressure cancels out of the equation. When the feed is fully vaporized, the vapor pressures of the reactants are no longer important in determining their partial pressures in the reactor.

2. Effects of gas-to-oil rate and feed vaporization in diesel hydrotreating

At low gas-to-oil rates, changing the gas-to-oil rate alters the partial pressures of hydrogen and hydrogen sulfide in the hydrotreating reactor. These are primary effects that are usually considered in process design. The gas-to-oil rate is often specified at a minimum of three or four times the expected hydrogen consumption to ensure adequate hydrogen supply through the reactor.

Even when the gas-to-oil rate exceeds this minimum level, it still has an important effect on desulfurization rates because it alters the phase equilibrium in the reactor. Diesel hydrotreaters usually operate with partially vaporized feed. The sulfur-containing reactants are distributed between the liquid and vapor phases as determined by their volatilities. Any process change that alters the phase equilibrium in the reactor alters the partial pressures, the reaction potentials and the reaction rates of the sulfur compounds.

This becomes especially important when processing a diesel feedstock to very low sulfur levels, as in ultra low sulfur diesel (ulsd) hydrotreating. In ulsd hydrotreating, the remaining sulfur compounds are all concentrated in the heavy end of the feed. The removal of these compounds becomes the limiting factor in meeting product sulfur specifications.

3. Experimental data

In a pilot plant, the gas-to-oil rate can be used as a variable to manipulate the feed vaporization at constant temperature and pressure. When the gas-to-oil rate (*H*/*M*) is increased, light hydrocarbons are stripped from the liquid, concentrating the critical high-boiling sulfur compounds in the liquid phase, and increasing their reaction rates. This is the effect that is accounted for by the factor V_{s}.

Fig. 1 shows results of a pilot plant hydrotreating experiment in which gas-to-oil rate was varied over the range from 150 to 1000 $\mathrm{nm^3/m^3}$ at constant temperature and pressure on a straight run diesel feed. The curve in Fig. 1 is a trend line drawn through the experimental data points. The data from this experiment are summarized in Table 1. Fig. 1 shows a sharp decrease in product sulfur with increased gas-to-oil rate. The product sulfur decreases from 84 ppm sulfur at a gas rate of 150 $\mathrm{nm^3/m^3}$ down to 3 ppm at 1000 $\mathrm{nm^3/m^3}$.

4. Interpretation of data

At first it may seem that Fig. 1 can be explained by the primary effects of gas-to-oil rate on the average hydrogen and hydrogen sulfide partial pressures in the reactor. However, calculations show that the gas-to-oil rates of this experiment are much too high for these effects to explain the result.

The strong sensitivity seen in Fig. 1 is caused by the effect of increased feed vaporization on the reaction rates of high-boiling dibenzothiophenes. The sulfur compounds in the product are all dibenzothiophenes with normal boiling points of 350–370 °C, near the heavy end of the feed.

Fig. 1 can be understood with reference to the Frye–Mosby equation, and the factor V_{s}, which is a multiplier on the apparent reactivity of each sulfur compound. To calculate V_{s} it is

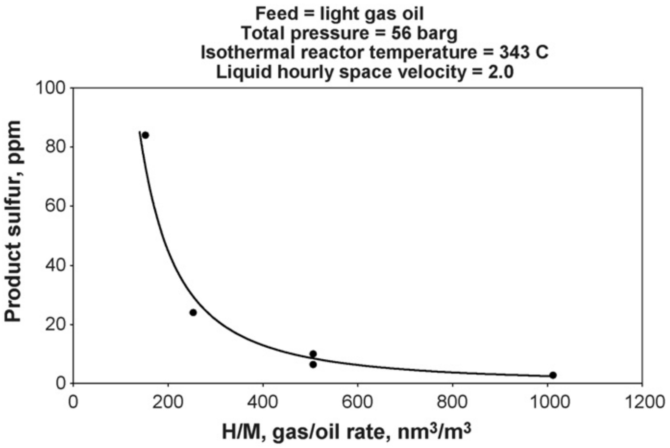

Fig. 1. Effect of gas/oil rate on product sulfur in diesel hydrotreating. Feed = light gas oil; total pressure = 56 bar; isothermal reactor temperature = 343 °C; and liquid hourly space velocity = 2.0.

Table 1
Summary of pilot plant experiment—effect of gas-to-oil rate on desulfurization

Pilot plant configuration	Isothermal once-through reactor, 20 cc's catalyst diluted 4 to 1 with 20 mesh silicon carbide, once-through pure H2 feed gas
Catalyst	Partially deactivated NiMo on alumina
Feed type	Straight run light gas oil
Feed specific gravity	0.857
Sulfur (ppm)	8000
Nitrogen (ppm)	123
Hydrogen (wt.%)	12.84
Carbon (wt.%)	85.33
Aromatics (wt.%)	31.1
Feed IBP (°C) (D-2887)	152
10	240
20	267
30	282
40	296
50	308
60	322
70	338
80	356
90	377
FBP	424
Reactor pressure (bar)	56
Reactor temperature (°C)	343
Volumetric space velocity (h^{-1})	2.0
Hydrogen consumption (nm^3/m^3)	50

Gas-to-oil rate (nm^3/m^3)	Product sulfur (ppm)
Product sulfur vs. gas-to-oil rate data	
150	84
250	24
500	7
1000	3
500 (repeat)	10

necessary to know the partial vaporization of the feed and the vapor pressures of the sulfur compounds at reactor conditions. Table 2 presents the calculated feed vaporization as a function of gas-to-oil rate for this experiment. Increasing the gas-to-oil rate at constant temperature and pressure causes an increase in feed vaporization from 10% vaporization at the lowest gas-to-oil rate to 65% vaporization at the highest gas-to-oil rate.

The factor V_s is now calculated to estimate the effect of this increased vaporization on the conversion of individual sulfur compounds. Table 2 summarizes the calculation for two particular sulfur compounds. They are benzothiophene, with a normal boiling point of 220 °C, near the light end of the feed, and 4,6-dimethyl dibenzothiophene, with a normal boiling point of 370 °C, near the heavy end of the feed. The vapor pressures of these compounds at the reactor temperature are 12 and 0.8 bar, respectively.

Table 2 reflects the influence of increased gas-to-oil rate on the composition of the liquid in the reactor. As the gas-to-oil rate is increased, light ends are stripped from the liquid. The liquid gets heavier; that is, the liquid mole fractions of heavy reactants like 4,6-dimethyldibenzothiophene increase and the liquid mole fractions of light reactants like benzothiophene decrease. The partial pressures and the reaction rates of these reactants move in proportion with their liquid mole fractions. Therefore, the effect of increased feed vaporization is to increase the reaction rates of heavy sulfur compounds, and decrease the reaction rates of light sulfur compounds.

In ulsd hydrotreating, all of the remaining sulfur is of the heavy type. The net effect of increased gas-to-oil rate then approaches the increased reactivity represented by the heavy sulfur curve. This effect continues to play out as gas-to-oil rate is increased far beyond the level normally considered optimal for diesel hydrotreating. At the conditions of this pilot plant experiment, the vaporization effect nearly doubled the apparent overall reaction rate. At some ulsd operating conditions, the effect can more than triple the apparent overall reaction rate.

5. Significance

In diesel hydrotreating, it is well known that gas-to-oil rate must be kept high enough to maintain the desired hydrogen and hydrogen sulfide partial pressures through the reactor. For this reason, it is usually recommended that gas-to-oil rate should be kept at a minimum of three to four times the hydrogen consumption. In ulsd hydrotreating, there is a significant additional incentive for increased gas-to-oil rate. This is because of the effect of phase equilibrium on the reaction rates of high-boiling sulfur compounds. This becomes very important as unit designs and operating conditions are modified to meet ultra low sulfur diesel specifications. Consequently, the optimal gas-to-oil rate for ultra low sulfur

Table 2
Calculation of V_s for a light and a heavy sulfur compound

Gas-to-oil rate (H/M) (nm^3/m^3)	Gas-to-oil rate (H/M) (mole/mole)	Vaporization of feed (a) (mole fraction)	Vaporization factor of sulfur compounds $(V_s) = \frac{P_s^0}{1-a+(a+H/M)P_s^0/P_{ttotal}}$	
			Benzothiophene ($P_s^0 = 12\,\text{bar}$)	4,6-Dimethyl dibenzothiophene ($P_s^0 = 0.8\,\text{bar}$)
150	1.7	0.10	9.4	0.86
250	2.8	0.19	8.3	0.94
500	5.6	0.37	6.3	1.1
1000	11.2	0.65	4.2	1.5

diesel hydrotreating may be much higher than is typically used today.

Acknowledgements

Chemical Process Research Institute (CPERI) performed the experiments in Thessaloniki, Greece, under a contract with BP Products North America. Thank you to Professor Iacovos Vasalos, Stelios Vousvoukis, and the entire CPERI team for their outstanding work.

Reference

[1] C.G. Frye, J.F. Mosby, Chem. Eng. Progr. 6 (9) (1967) 66.