# Part A- Hydrotreating of a Mixture of FCC & Coke Gas Oil, 45:55 respectively in Fixed- Bed Down Flow Reactor with NiO-MoO₃-WO₃ [F-5] Catalyst for Diesel and Gasoline Pool

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## Abstract

Hydrotreating of a mixture of FCC and Coke gas oil, 45:55 respectively was investigated by using FH-5 catalyst to reduce its sulfur, nitrogen content, saturate of unsaturated hydrocarbon for diesel and gasoline pool. The experiments were performed in an adiabatic fixed- bed down flow reactor under operation conditions of 4.0 - 6.0 MPa of pressure, 300 - 450 $m^3/m^3$ of, hydrogen to gas oil ratio, 2 5 - 3.5 $h^{-1}$ of LHSV and 300 - 380 °C of temperature, by diluting the catalyst with inert ceramics in increasing order. About 97% of sulfur, 80% of total nitrogen, 93% of basic nitrogen, and 95% of hydrocarbon saturation can be achieved. If this product is used to produce gasoline or diesel fuel directly, the amount of sulfur in the final product should be about 110 ppm and that of nitrogen 141 ppm, which increasing its blending ratio to fuel pool.

*Keywords:* Hydrotreating; gasoil; reactor, NiO-MoO₃-WO₃ catalyst.

## 1. Introduction

In many developing regions the buses, trains, and taxes are the principal means of transportation and they use diesel fuel. The consumption of middle distillate fuels in some developing countries was expected to increase approximately by 5% yearly since 2000 [1]. More than 30% of gasoline pool comes from FCC unit, while at the same time; it is responsible for 90% sulfur in gasoline pool [2,3]. Recently auto / oil studies indicated that, reducing sulfur in gasoline would lower the emission of hydrocarbons, NOx and CO [4]. Future environmental regulation requires refiners to produce catalytic cracking gasoline with 30 ppm while diesel fuel with 50 ppm of sulfur in year 2005 [3, 5]. Reduction of gasoline and diesel sul-

fur can be achieved by hydrotreating the feedstock of FCC gasoline and diesel or desulfurizing the products [gasoline & diesel] in industrial processes such as both hydrotreating and hydrocracking simultaneously [2]. Recent study shows that the amount of sulfur content in the FCC gasoline is about tenth of the sulfur in the non- hydrotreated feed, while about twentieth in hydrotreated feedstock's [2 ]Deep hydrotreating implies severity operation conditions such as low LHSV, higher reaction temperature, and higher operating pressure, which improved products qualities while at same time, accelerated the catalysts deactivation. The bulk of the desulfurisation (approximately 95%) was carried out in the first half of the catalyst bed the remaining half of the catalyst is severely in-

hibited by the significant quantities of $H_2S$, which is released by the reactions.[3]

### The Aim of this Study

1. To improve the properties of FCC & coke gas oil by hydrotreating under typical industrial operation conditions. In addition, determine the overall reaction order and activation energy for further investigation such as reactor design.

2. To study the effect of diluting the catalyst with inert ceramics in increasing order on the reactor performance, and the rate of hydrotreating.

## 2. Material and Methods

Hydrogen. The hydrogen used in this investigation was 99.5% pure, supplied by Shanghai Shi Wu jing Chemical Factory.Nitrogen. The nitrogen used in this investigation was 99.5% pure, supplied by Shanghai Shi Wujing Chemical Factory. Styrene. The styrene used in this investigation was supplied by Shanghai refinery [Jing Shan] Factory. Gas oil The gas oil used in this investigation was a mixture of FCC & coke gas oil; 45:55 respectively supplied by Shanghai refinery [Jing Shan] Factory.

### Catalyst

Catalys [FH-5 [[NiO-MoO$_3$-WO$_3$-additives supports on $\gamma$ -Al$_2$O$_3$/SiO$_2$] spherical] was commercial catalysts, widely used in P. R. China for Petroleum & petroleum distillate hydrotreating [3]. Table (2.1) shows its properties.

The reactor tube used in this work is made of steel and has an internal diameter of 25mm, outside diameter of 34 mm and a height of 1.60 m. Figure (2.1) shows schematic diagram of experimental apparatus for down flow hydrotreating reactor of gas oil and Figure (2.2). Shows the catalyst loading inside the reactor.
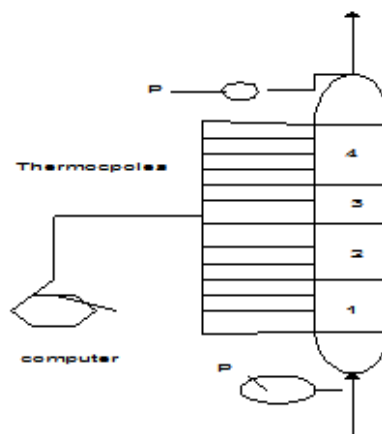


**Figure 2.2:** Catalyst loading inside the down flow reactor.

### Reactor loading by catalyst

The catalysts have been diluted with ceramics in different ratio such as: Part 1 of the catalyst bed at the inlet of the reactor contains 24 g Catalyst mixed homogeneously with 143.1 g ceramics. Part 2 after part.1 contain 48 g catalyst plus 100.8 g ceramics. Part 3 contain 72 g catalyst plus 79.2 g ceramics. Part 4 at reactor outlet contain 96 g catalyst plus 52.8 g ceramics. The overall catalyst bed length was 100.00m.The bed, settled in the middle of the reactor height, contained ten equidistant internal thermocouples.

### Catalyst Preparations and Hydrotreating procedure

The catalyst was dried by circulation of nitrogen first at a pressure of 2.0 MPa and temperature of $250^oC$ for 4 hrs, then at 1.5 MPa and temperature of $250^oC$ for 4 hrs. The sulfiding step has been performed [wet] using straight run gas oil plus $CS_2$ [$CS_2$ was 14% wt of catalyst] under a pressure of 5.0 MPa, temperature of $200^oC$, LHSV of 2.5h$^{-1}$ and hydrogen / gas oil ratio of 350 m$^3$/m$^3$ for 24 hrs.

### Methods of Analysis

1. Total sulfur was analyzed by using Chinese Petroleum Test Method. SH/T 02533

2. Bromine number was analyzed by using ASTM D1159

**Table 2.1:** The properties of catalyst

| Catalyst | FH-5 [[NiO-MoO$_3$-WO$_3$-additives supported on γ-Al$_2$O$_3$/SiO$_2$]] |
|---|---|
| Total surface area m$^2$/g | 140.85 |
| Pore volume ml/g | 0.3280 |
| Surface area of middle diameter D=1.0-100nm [B.J.H] m$^2$/g | 181.59 |
| Volume of pores middle diameter, D=1.0-100nm [B.J.H] ml/g | 0.3253 |
| Me n diameter D, [B.E.T nm | 9.316 |
| Mean diameter, D [B.J.H] nm | 5.744 |
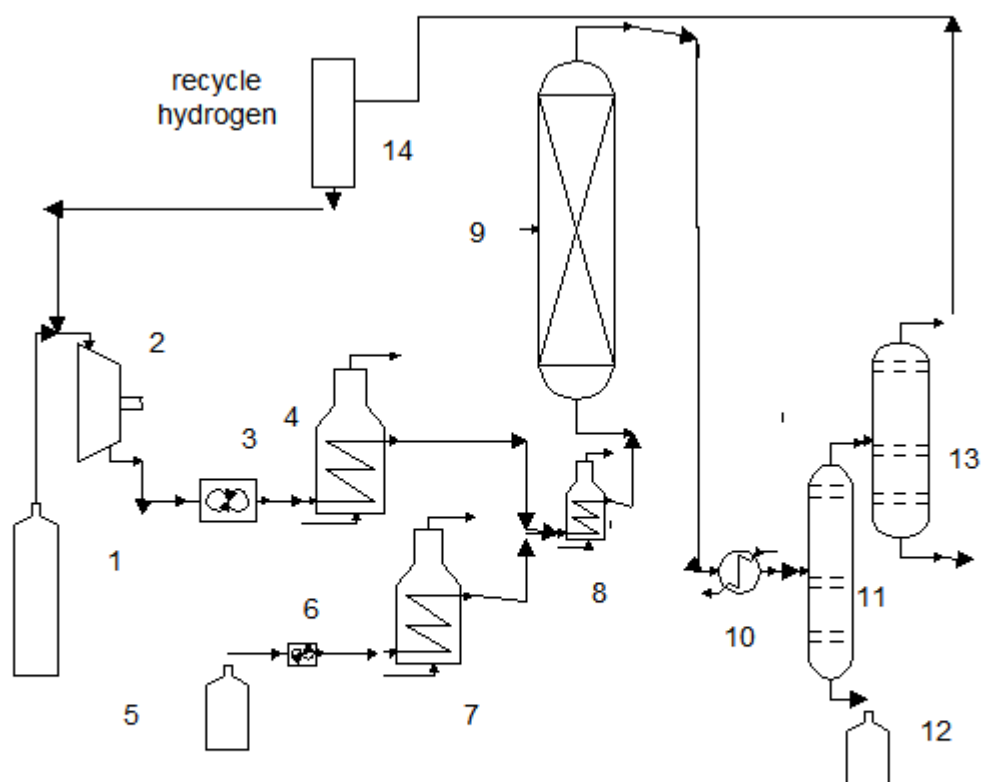


1-Hydrogen cylinder, 2-Compressor, 3-Gas flow meter, 4-Gas heater, 5-Gas oil tank, 6-Liquid flow meter, 7-Gas oil heater, 8-Gas-liquid heater, 9-Reactor, 10-Heat exchanger [cooler],11-Liquid-gas separator, 13- gas liquid separator, 14-Separater of H$_2$S & others gases

**Figure 2.1:** down flow gas oil hydrotreating flow sheet diagram

3. Total nitrogen was analyzed by using Chinese Petroleum Test Method. SH/T 0657

4. Basic nitrogen was analyzed by using Chinese Petroleum Test Method SH/T 0162

5. Cetane number was analyzed by using ASTM D976

6. Boilling point was analyzed by using ASTM D86

**Hydrotreating Kinetics**

Total sulfur and nitrogen in power law rate equation were used to determine the overall reaction order for HDS, HDN, and hydrocarbon saturation. By using the integrated equation for the nth, order namely [2,3] ,

$$(C_o)^{1-n} - (C_i)^{1-n} = (n-1)\frac{k_n}{LHSV} \qquad (2.1)$$

The experimental data were used to solve equation. (2.1) By using statistical module non-linear estimation, then activation energies were calculated from Arrhenius equation namely,

$$k = Ae^{(-E_A/RT)} \qquad (2.2)$$

or

$$lnk = -\frac{E_A}{R}\left(\frac{1}{T} - \frac{1}{T_a}\right) + lnk_o \qquad (2.3)$$

Where

    A=frequency factor or Arrhenius constant,

    $E_A$=activation energy,

    Ta = mid-temperature for temperature range considered,

    $k_o = Ae^{(-E/RT_a)}$

$E_A/R$ was evaluated from the slope of a plot of ln k versus (1/T-1/Ta), the intercept ln ko is evaluated at (1/T-1/Ta) = 0 and A was calculated from the definition of ko. Where C is concentration of reactant, kn the apparent intrinsic rate constant, LHSV is the liquid hourly space velocity, Ci is the concentration of reactant at inlet, and Co is the concentration of reactant at outlet, R is real gas constant [8.314 kJ/kmol. K] And T is absolute temperature in K

# 3. Results, and Discussion

**Effect of Reaction Temperature on Product Quality**

Table 2 and Figures (3.32) & (3.33) show the effects of reaction temperature on product density, percentage conversion of sulfur, hydrocarbon saturation, and nitrogen. According to experimental data, increasing reaction temperature will decrease the product density, IBP, sulfur, unsaturated hydrocarbons, and nitrogen compounds, as the results this is improvement in product quality, possible since high reaction temperature will increase the activity of the catalyst. These results are in agreement with
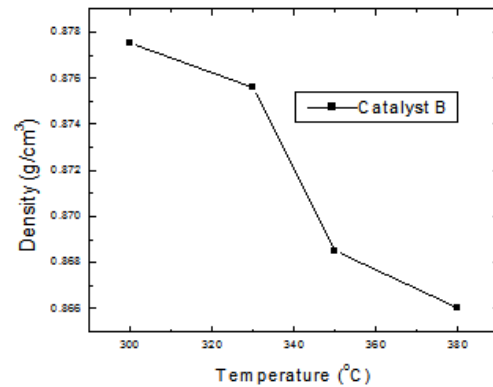


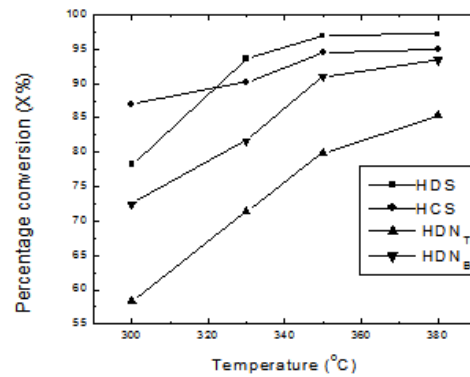Figure 3.32 : Effect of reaction temperature on product density



Figure 3.33: Effect of reaction temperature on percentage HDS, HCS & HDN

**Table 3.1:** Effect of reaction temperature on product quality

| Exp. No | Feed | 111G1 | 111G1 | 211G | 2112T380 |
|---|---|---|---|---|---|
| P, MPa | | 6 | 6 | 6 | 6 |
| T, ºC | | 300 | 330 | 350 | 380 |
| R, m³/m³ | | 350 | 350 | 350 | 350 |
| LHSV h⁻¹ | | 2.5 | 2.5 | 2.5 | 2.5 |
| D, g/cm³ | 0.8924 | 0.8775 | 0.8756 | 0.8685 | 0.8633 |
| S, % (ppm) | 0.39 | [848] | [250] | [119] | [92] |
| Br, gBr/100g | 21.5 | 2.8 | 2.1 | 1.4 | 1.1 |
| $N_T$ , ppm | 749 | 312 | 214 | 150 | 141 |
| $N_B$ , ppm | 273 | 75 | 50 | 36 | 18 |
| IBP, ºC | 205 | 186 | 185 | 120 | 110 |
| 10% | 227 | 217 | 215 | 211 | 209 |
| 20% | 239.5 | 229 | 229 | 225 | 223 |
| 30% | 251.5 | 243 | 243 | 239 | 239 |
| 40% | 269.5 | 259.5 | 256.5 | 253 | 253 |
| 50% | 283.5 | 276.5 | 268.5 | 269 | 269 |
| 60% | 301.5 | 297 | 292.5 | 284 | 284 |
| 70% | 317 | 316.5 | 308.5 | 303 | 303 |
| 80% | 335 | 328 | 325 | 319 | 319 |
| 90% | 345 | 344 | 340.5 | 336 | 336 |
| 100% | >350 | >350 | >350 | >350 | >350 |

Jorge et al., [1999] [1] and. our earlier works [3] . About 97% of sulfur, 80% of total nitrogen, and 93% of basic nitrogen can be removed and 95% of hydrocarbon saturation can be achieved. If this product is used to produce gasoline or diesel fuel directly, the amount of sulfur in the final product should be about 110 ppm and that of nitrogen 141 ppm. In addition, if this product is used as a feedstock for FCC gasoline the sulfur in the final product should be in the range of 6-10 ppm.

**Effect of Reaction Pressure on Product Quality**

Table 4, figures (3.34) & (3.35) show the effect of pressure on product qualities. According to the data by increasing the reaction pressure the product density, IBP, sulfur, unsaturated hydrocarbons and nitrogen compounds will decrease,
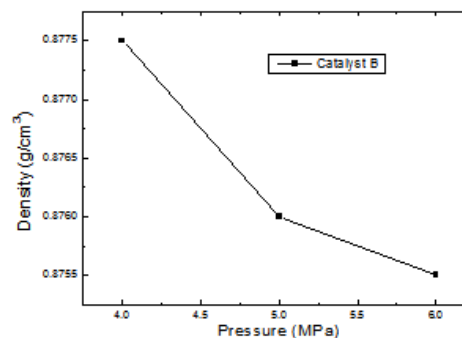


Figure 3.34:Effect of pressure on product Density

**Table 3.2:** Effect of reaction pressure on product quality

| Exp. No | Feed | 117RP4 | P5 | 211G |
|---|---|---|---|---|
| P MPa | | 4 | 5 | 6 |
| R m³/m³ | | 350 | 350 | 350 |
| T °C | | 350 | 350 | 350 |
| LHSV h⁻¹ | | 2.5 | 2.5 | 2.5 |
| D g/cm³ | 0.8924 | 0.8775 | 0.8760 | 0.8750 |
| S % [ppm] | 0.39 | 0.1 | [564] | [119] |
| Br gBr/100g | 21.5 | 4.8 | 3.2 | 1.2 |
| N$_T$ ppm | 749 | 350 | 310 | 150 |
| N$_B$ ppm | 273 | 66 | 60 | 20 |
| IBP°C | 205 | 187 | 174 | 120 |
| 10% | 227 | 218 | 222 | 211 |
| 20% | 239.5 | 229 | 236 | 225 |
| 30% | 251.5 | 243 | 248 | 239 |
| 40% | 269.5 | 259.5 | 261.5 | 253 |
| 50% | 283.5 | 276.5 | 279 | 269 |
| 60% | 301.5 | 292.5 | 294.5 | 284 |
| 70% | 317 | 308.5 | 312 | 303 |
| 80% | 335 | 325 | 327 | 319 |
| 90% | 345 | 340.5 | 343.5 | 336 |
| 100% | >350 | >350 | >350 | >350 |

Which indicated that improvement of product quality as pressure increased, possible due to better contact between hydrogen, hydrocarbon and the catalyst at high pressure? Similar results observed by others [1,7,10-12].

### Effect of LHSV on Product Quality

Table 5, Figures (3.36) & (3.37) shows the effect of LHSV on product density, percentage conversion of sulfur and nitrogen compounds and hydrocarbon saturation respectively, according to the data decreasing LHSV will improve product quality, by decrease product density, sulfur, nitrogen content, IBP and increase the rate of hydrocarbon saturation. The same observation reported by Jamal and Ali [7].
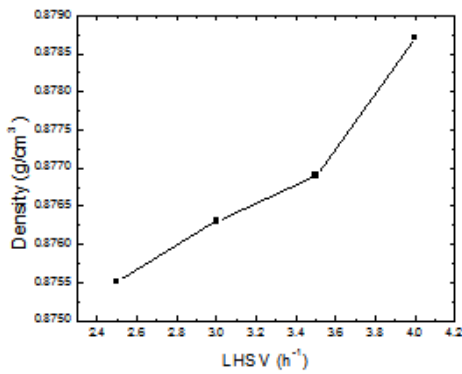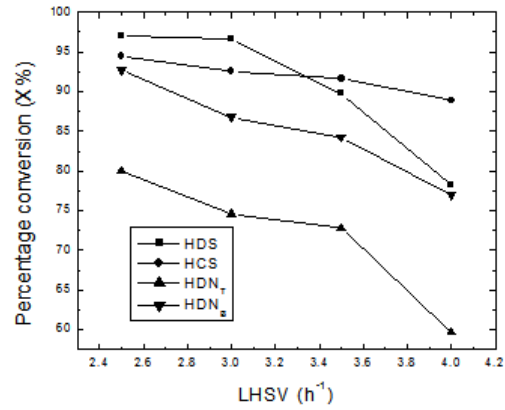


Figure 3.37: Effect of LHSV on HDS,HCS & HDN

### Effect of Ratio of Hydrogen / Gas oil on Product Quality

Table 6 and Figures (3.38) & (3.39) show the effects of ratio of hydrogen to gas oil on product density, percentage conversion of
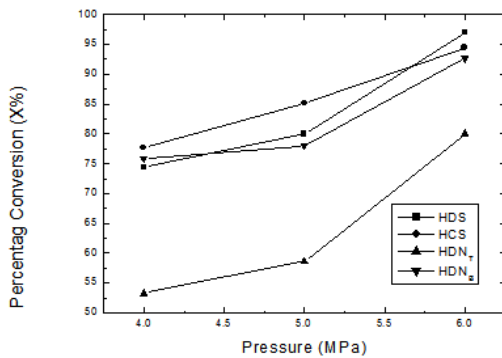


Figure 3.36: Effect of LHSV on product density



Figure 3.35:Effect of pressure on HDS, HCS & HDN

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**Table 3.3:** Effect of LHSV on product quality

| Exp. No | Feed | 111G1 | 111G | 111G1 | 211G |
|---|---|---|---|---|---|
| P, MPa | | 6 | 6 | 6 | 6 |
| T, oC | | 350 | 350 | 350 | 350 |
| R, m³/m³ | | 350 | 350 | 350 | 350 |
| LHSV h⁻¹ | | 2.5 | 3.0 | 3.5 | 4.0 |
| D, g/cm³ | 0.8924 | 0.8755 | 0.8763 | 0.8769 | 0.8787 |
| S % (ppm) | 0.39 | [119] | [133] | [183] | [230] |
| Br gBr/100g | 21.5 | 1.2 | 1.4 | 1.8 | 2.4 |
| $N_2$ ppm | 749 | 134 | 150 | 190 | 204 |
| $N_B$ ppm | 273 | 20 | 36 | 43 | 55 |
| IBP (oC) | 205 | 120 | 175 | 185 | 188 |
| 10% | 227 | 211 | 212 | 215 | 219 |
| 20% | 239.5 | 225 | 230 | 232 | 235 |
| 30% | 251.5 | 239 | 242 | 245 | 249 |
| 40% | 269.5 | 253 | 256.5 | 257.5 | 258.5 |
| 50% | 283.5 | 269 | 269.5 | 270.5 | 2271.5 |
| 60% | 301.5 | 284 | 293.5 | 295.5 | 296.0 |
| 70% | 317 | 303 | 308.5 | 310.5 | 311.5 |
| 80% | 335 | 319 | 325 | 325.5 | 326.5 |
| 90% | 345 | 336 | 340.5 | 341.5 | 342.5 |
| Final | >350 | >350 | >350 | >350 | >350 |
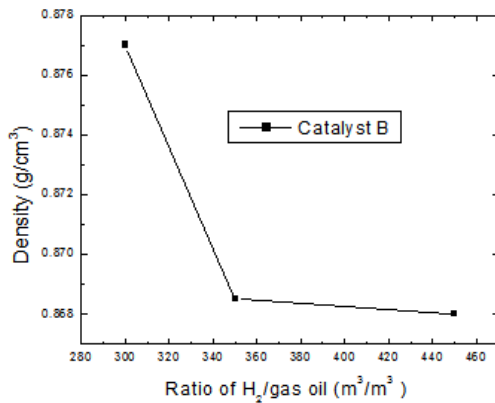
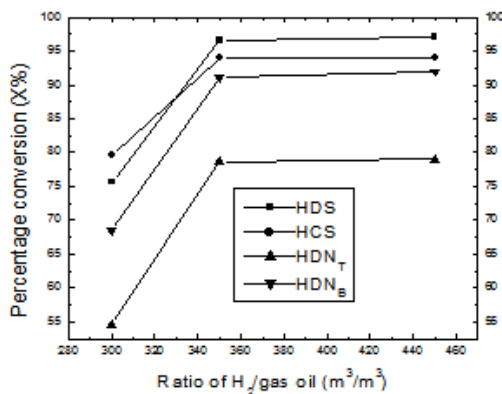Figure 3.38: Effect of ratio of hydrogen/gas oil on product density



Figure 3.39: Effect of ratio of $H_2$/gas oil on HDS, HCS &HDN

Sulfur, hydrocarbon saturation, and nitrogen compounds. According to the experimental data, increasing ratio of hydrogen to gas oil will increase the rate of HDS, HCS, and HDN while the product density & IBP will decrease possible due to increase in hydrogen partial pressure, which increase the rate of HT. As the result, the product quality is improved with increasing the ratio of hydrogen / gas oil. Similar results of improvement of product properties as a function of increasing ratio of hydrogen /gas oil was reported by Varg et al. [2]

### Hydrotreating Kinetics

Table 7 and Figure (3.40)-(3.44) show the reaction order, rate constant, activation energy and frequency factor of HDT reactions at down flow reactor with catalysts B. The activation energies using Arrhenius equation for HDS is 866.01 k J. /kmol, HCS is 336.78 k J. /kmol, HDNT is 553.28 and HDNB is 577.34 kJ. / k mol. The reaction order n for HDS is 1.47, for HCS is 1.35, for HDNT n is 1.59, and HDNB n is 1.37. These results agree with those reported in literature [1,7]. The results also indicated that the activation energy of HDS > HDNB >HDNT>HCS reaction which mean that the HDS reaction is more temperature sensitive than HDN reaction and HDN reaction is more than that of HCS reaction.

## 4. Conclusion

By increasing reaction temperature, pressure, and decreasing LHSV the rate of HDS, HDN and hydrocarbon saturation will increase, while the product density and IBP will decrease. . By diluting the catalyst with inert ceramics, the heat of reaction could be easily removed from catalyst and the LHSV can be increased due to increasing of liquid hold up and resident time. Also by diluting the catalyst with inert ceramics in this way, increasing the amount of catalyst from reactor inlet to the reactor out let we excepted that the order of hydrotreating reaction as follow saturation of unsaturated hydrocarbon followed by hydrodesulfurizaion reaction and finally hydrodenitrogenation reaction since reaction temperature of HDN >HDS>HCS The study of HDT of FCC & coke gas oil is very important for efficient design and simulation of commercial units, better understanding of catalyst behavior, and the effect of the process conditions. By hydrotreating FCC & coke gas oil, perhaps new and future specification of gasoline & diesel oil could be proposed.

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**Table 3.4:** Effect of hydrogen/gas oil on product quality

| Exp. No | Feed | R300 | 211G | R450 |
|---|---|---|---|---|
| P MPa | | 6 | 6 | 6 |
| T, °C | | 350 | 350 | 350 |
| R, m³/m³ | | 300 | 350 | 450 |
| LHSV h⁻¹ | | 2.5 | 2.5 | 2.5 |
| D, g/cm³ | 0.8924 | 0.8770 | 0.8755 | 0.8753 |
| S % (ppm) | 0.39 | 0.095 | [119] | [115] |
| Br gBr/100g | 21.5 | 4.4 | 1.2 | 1.3 |
| $N_T$ , ppm | 749 | 440 | 150 | 145 |
| $N_B$ ,ppm | 273 | 2 | 20 | 15 |
| IBP, °C | 205 | 186 | 120 | 172 |
| 10% | 227 | 217 | 211 | 221.5 |
| 20% | 239.5 | 230 | 225 | 234 |
| 30% | 251.5 | 246 | 239 | 248 |
| 40% | 269.5 | 260 | 253 | 261.5 |
| 50% | 283.5 | 279 | 269 | 279 |
| 60% | 301.5 | 299.5 | 284 | 294.5 |
| 70% | 317 | 312 | 303 | 312 |
| 80% | 335 | 327 | 319 | 327 |
| 90% | 345 | 341 | 336 | 343.5 |
| 100% | >350 | >350 | >350 | >350 |

**Table 3.5:** reaction order, rate constant, activation energy and frequency factor of HT reactions at down flow reactor with catalysts B

| Factor | n | At 300 °C, k | At 330 °C, k | At 350 °C, k | At 380 | $E_A$, kJ. / kmol | A |
|---|---|---|---|---|---|---|---|
| HDS | 1.47 | 8.68253 h⁻⁰·⁴⁷ | 21.18367 h⁻⁰·⁴⁷ | 34.41066 h⁻⁰·⁴⁷ | 39.89924 h⁻⁰·⁴⁷ | 866.00914 | 27.85096 h⁻⁰·⁴⁷ |
| HCS | 1.35 | 2.54085 h⁻⁰·³⁵ | 3.06813 h⁻⁰·³⁵ | 3.90818 h⁻⁰·³⁵ | 4.46737 h⁻⁰·³⁵ | 336.78133 | 3.68422 h⁻⁰·³⁵ |
| $HDN_T$ | 1.59 | 14.95157 h⁻⁰·⁵⁹ | 24.40510 h⁻⁰·⁵⁹ | 35.62379 h⁻⁰·⁵⁹ | 37.84717 h⁻⁰·⁵⁹ | 553.28362 | 30.0098 h⁻⁰·⁵⁹ |
| $HDN_B$ | 1.37 | 15.69452 h⁻⁰·³⁷ | 22.37957 h⁻⁰·³⁷ | 28.58144 h⁻⁰·³⁷ | 44.42357 h⁻⁰·³⁷ | 577.33943 | 29.46623 h⁻⁰·³⁷ |

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