

## Hydrotreating of a Mixture of FCC & Coke Gas Oil, 45:55 respectively in Fixed-Bed up Flow Reactor with NiO-WO<sub>3</sub>[RN-1] for Middle Distillate

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### Abstract

Hydrotreating of a mixture of FCC and coke gas oil, 45:55 respectively was investigated by using RN-1 catalyst to reduce its sulphur, nitrogen content, saturate of unsaturated hydrocarbon, and to improve the product quality. The experiments were performed in an adiabatic fixed - bed up flow reactor under operation conditions of 3.0 - 6.0 MPa of pressure, hydrogen to gas oil ratio of 300-450 m<sup>3</sup>/m<sup>3</sup>, and LHSV of 2.5 -3.5 h<sup>-1</sup> at the temperatures of 300-380 °C. The experimental data were used to determine overall apparent reaction orders and activation energies. From the results we can observed that. About 96% of sulphur, 84% of total nitrogen, and 97% of basic nitrogen and 95% of saturation of unsaturated removed; the amount of sulphur in the final product should be about 272 ppm and that of nitrogen 117 ppm, which indicated product improvement, and increasing ratio to middle distillate fuel.

*Keywords:* Fixed-bed reactor; gas oil hydrotreating; NiO-WO<sub>3</sub> catalyst.

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### 1. Introduction

The consumption of middle distillate fuels in some developing countries was expected to increase approximately by 5% yearly since 2000 [1]. In order to meet the increasing demand of middle distillate fuels, refiners have to blend significant fraction of cracked distillates from other secondary refinery processes, such as FCC, coking and visbreaking. Unfortunately the products of these processes and blends contained many impurities such as sulfur, nitrogen, metals etc. Hydrotreating is a process to catalytically stabilize petroleum products by converting unsaturated hydrocarbons e.g. olefins and gum-forming unstable diolefins to paraffin's, and /or remove objectionable ele-

ments such as sulfur, nitrogen, oxygen and traces of metals from products or feedstock by reacting them with hydrogen. [2,3].The gas oil hydrotreating is practiced to lower the level of poisons for catalytic reforming such as sulfur and nitrogen components [temporary poisons] and As, Pb and other metals [permanent poisons] [4].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 [5]. HDS reactions are exothermic; the heat of reaction is removed by recycling cooled hydrogen [5]. In addition, by dilution of catalysts, the heat of reaction can be absorbed by the diluents [6].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 inhibited by the significant quantities of  $H_2S$ , which is released by the reactions. 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 2-To study the effect of diluting the catalyst with inert ceramics in increasing order on the reactor performance, and the rate of hydrotreating.

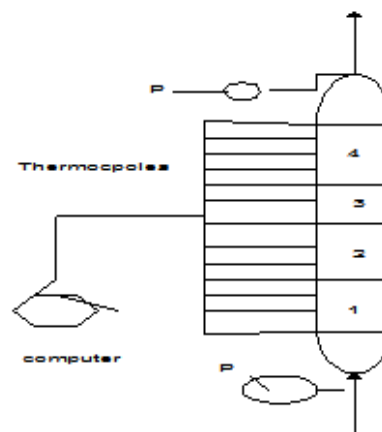
## 2. Material and Methods

### Materials

The hydrogen used in this investigation was 99.5% pure, supplied by Shanghai Shi Wu jing Chemical Factory.. The nitrogen used in this investigation was 99.5% pure, supplied by Shanghai Shi Wujing Chemical Factory.. The styrene used in this investigation was supplied by Shanghai refinery [Jing Shan] Factory. 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 .Catalysts [RN-1 [NiO-WO<sub>3</sub>/additive Supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>]] cylindrical trilbies in shape] was commercial catalyst, widely used in P. R. China for Petroleum & petroleum distillate hydrotreating [6] 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 1.60m. 214g of the catalysts have been diluted with ceramics in different ratio such as: Part 1 of the catalyst bed at the inlet of the reactor contain 21.4 g catalyst mixed homogeneously with 113.42 g ceramics, Part 2 after part.1 contain 42.8 g catalyst plus 89.88 g ceramics, part 3 contain 64.2 g catalyst plus 70.62 g ceramics and part 4 at reactor outlet contain 85.6 g catalyst plus 47.08 g ceramics. The overall catalyst bed length was 100.00 m. The bed, settled in the middle of the reactor height, contained ten equidistant internal thermocouples. Figure (2.1) shows schematic diagram of

experimental apparatus for up flow hydrotreating reactor of gas oil and Figure (2.2) Shows the catalyst loading inside the reactor.



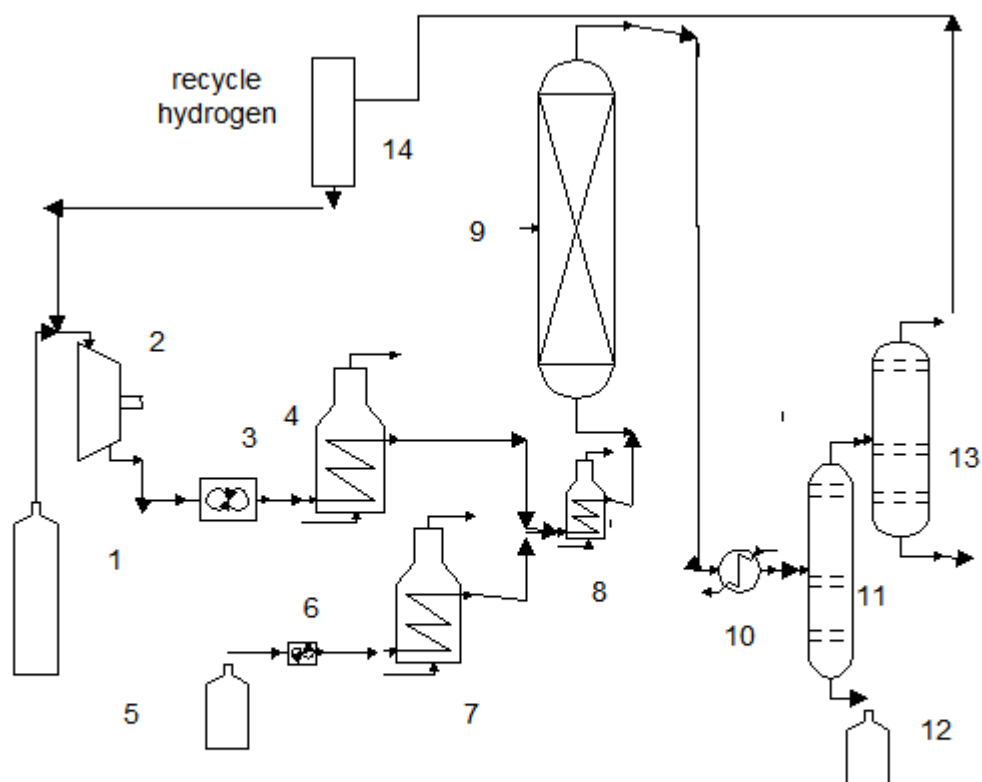
**Figure 2.2:** Catalyst loading inside the up flow reactor.

### 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°C for 4 hrs. The sulfiding step has been performed [wet] using straight run gas oil plus CS<sub>2</sub> [CS<sub>2</sub> was 14% wt of catalyst] under a pressure of 5.0 MPa, temperature of 200 °C, LHSV of 2.5h-1 and hydrogen / gas oil ratio of 350 m<sup>3</sup>/m<sup>3</sup> for 24 hrs. In order to avoid the coke due to high activity of the catalyst at the beginning, the straight run gas oil was used instead of the feedstock under the following operation conditions: Pressure of 6.0 MPa temperature of 350 °C, LHSV of 2.5-1h and hydrogen/gas oil ratio of 350 m<sup>3</sup>/m<sup>3</sup> for 6 hrs. The feedstock was preheated and mixed with preheated hydrogen at desired reactor inlet temperature and charged into the reactor. The product was cooled by heat exchanger before entering the separators; the gaseous phase was led to other separator where the H<sub>2</sub>S and other condensable gases were separated from recycle hydrogen. After 3 hrs steady state operation conditions, the liquid product was collected for 1h, the rate of inlet feedstock and the product were all measured in 1h interval.

**Table 2.1:** The catalyst properties

Catalyst	[RN-1 [NiO-WO <sub>3</sub> /additive, Supported on $\gamma$ -Al <sub>2</sub> O <sub>3</sub> ]]
Total surface area m <sup>2</sup> /g	130.13
Pore volume ml/g	0.2489
Surface area of middle diameter D=1.0-100nm [B.J.H] m <sup>2</sup> /g	174.26
Volume of pores middle diameter, D=1.0-100nm [B.J.H] ml/g	0.2502
Mean diameter D, [B.E.T nm	7.652
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<sub>2</sub>S & others gases

**Figure 2.1:** Up flows Gas oil hydrotreating flow sheet diagram



### Methods of Analysis

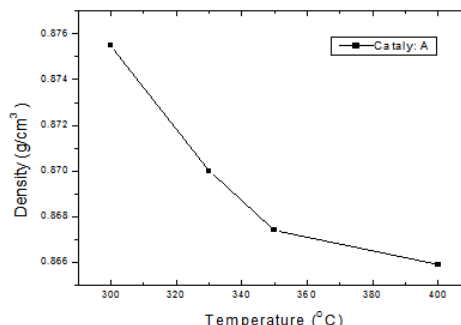
1. Total sulfur was analyzed by using Chinese Petroleum Test Method. SH/T 02533
2. Bromine number was analyzed by using ASTM D1159
3. Total nitrogen was analyzed by using Chinese Petroleum Test Method. SH/T 0657
4. Basic nitrogen was analyzed by using Chinese Petroleum Test Method SH/T 0162
5. Cetane number was analyzed by using ASTM D976
6. Boiling point was analyzed by using ASTM D86

### 3. Results, and Discussion

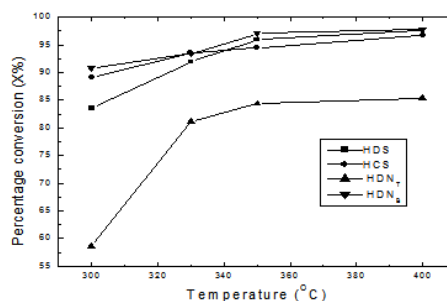
#### Effect of Reaction Temperature on Product Quality

Table (3.1) and Figures (3.1a) & (3.1b). show the effects of reaction temperature on product density, percentage conversion of sulfur, nitrogen, and hydrocarbon saturation. According to the experimental data increasing reaction, temperature will increase the percentage conversion of sulfur, nitrogen, saturation of unsaturated hydrocarbons and decrease the product density and boiling point; this is an indication of increasing the rate of HDS, HCS, and HDN with increasing of reaction temperature. The decrease of product density & IBP is also an indication of removal of impurities; possible since the activity of the catalyst increases at high reaction temperature also the viscosity decreases at high temperature. These results agree with those reported by Jorge et al.[7], Varga et al.[8] and our earlier works[6]. About 96% of sulfur, 84% of total nitrogen, and 97% of saturation of unsaturated hydrocarbon 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 272 ppm and that of nitrogen 117 ppm. Also if this product is used as a feedstock for FCC gasoline the sulfur in the final product should be in the range of 15-27 ppm, since the amount of sulfur content in FCC product is about 1/10 of the sulfur in un hydrotreated feed while about 1/20 in

hydrotreated feed [9]. At temperature of 350°C the amount of gasoline was about 10 % while at higher temperature 380°C the gasoline was 20 % of the product. The data indicated that the conversion of total nitrogen compounds is much lower than that of basic nitrogen compounds. For example at 350°C , the conversion of basic nitrogen compounds was about 97 % as compared to only 74 % for total nitrogen, which indicated that non basic nitrogen conversion is less than that of basic nitrogen at the same temperature 77% [Total nitrogen = basic nitrogen + non basic nitrogen] a similar results was reported by Shyamal et al.[10]. From the results we can observed that the rate of HDS>HCS>HDNB>HDNT which indicated that the removal of nitrogen component by HDT is more difficult than that of sulfur, also its not possible to remove all nitrogen and sulfur at this operation conditions [pressure,temperature, ratio and LHSV]



(a) Effect of reaction temperature on product density



(b) Effect of reaction temperature on precentage conversion of HDS, HDN & hydrocarbon saturation

Figure 3.1

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

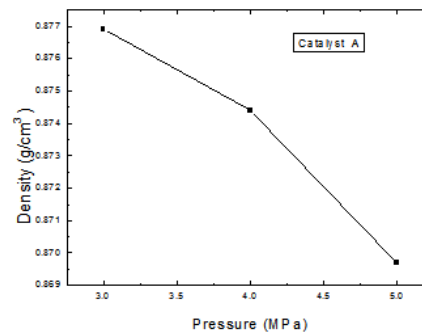
Sample NO	Feed	2051A	2053A	20430A	20511A1
P, MPa		6	6	6	6
T, °C		300	330	350	380
R, m <sup>3</sup> /m <sup>3</sup>		350	350	350	350
LHSV, h <sup>-1</sup>		2.5	2.5	2.5	2.5
D, g/cm <sup>3</sup>	0.8924	0.8755	0.87	0.8674	0.8659
S, % [ppm]	0.390	0.11	[545]	[273]	[91]
Br, gBr/100 g	21.5	2.4	1.4	1.2	1.1
N <sub>T</sub> , ppm	749	310	142	117	110
N <sub>B</sub> , ppm	273	25	18	8	6
IBP, °C	205	183.5	156	139.5	83.0
10%	227	218	211	211	135
20%	239.5	233	226	227	180
30%	251.5	242	240	238	210.5
40%	269.5	258	255	253.5	221
50%	283.5	274	271.5	268	236
60%	301.5	289.5	286	284.5	248
70%	317	308	304.5	303.5	262.5
80%	335	326.5	321.5	320.5	283
90%	345	341	338.5	337.5	306.5
100%	>350	>350	>350	>350	>350

**Effect of Reaction Pressure on Product Quality**

Table (3.2), Figures (3.3) & (3.4) show the effect of pressure on product density, percentage conversion of sulfur, nitrogen and hydrocarbon saturation. According to the data by increasing the reaction pressure the product density, IBP, sulfur, nitrogen, hydrocarbon saturation will decrease, possible due to increase in hydrogen partial pressure and its well known that high hydrogen partial pressure increases the rate of HDT. others [7,8,10] observed the same results.

**Effect of LHSV on Product Quality**

Table (3.3), Figures (3.5) & (3.6) show the effect of LHSV on product density, percentage conversion of sulfur, nitrogen compounds, and hydrocarbon saturation respectively. According to the data, decreasing LHSV will decrease product density, sulfur, nitrogen; saturation of unsaturated hydrocarbons, which mean improvement of product quality, acceptable since decreasing of LHSV means increasing resident time, and its well known that increasing resident time, will increase the rate of HDT. These results in agreement with



**Figure 3.2:** Effect of reaction pressure on product density

those reported by Varg et al.[8] and Jamal and Ali [11].

Table 3.2: Effect of reaction pressure on product quality

Sample NO	Feed	20558A	2054A2	2054A1	20430A
P, MPa		3	4	5	6
T, °C		350	350	350	350
R, m <sup>3</sup> /m <sup>3</sup>		350	350	350	350
LHSV, h <sup>-1</sup>		2.5	2.5	2.5	2.5
D, g/cm <sup>3</sup>	0.8924	0.8769	0.8744	0.8697	0.8674
S, % [ppm]	0.39	[765]	674	[572]	[273]
Br, gBr/100g	21.5	10.63	3.65	1.88	1.2
N <sub>T</sub> , ppm	749	431	250	150	117
N <sub>B</sub> , ppm	273	29	19	13	8
IBP, °C	205	169	168	118	139.5
10%	227	213.5	210	206	211
20%	239.5	227	225	223.5	227
30%	251.5	241	240.5	240	238
40%	269.5	254.5	258	251.5	253.5
50%	283.5	272.5	272	266.5	268
60%	301.5	289	288.5	282.5	284.5
70%	317	366.5	305.5	299.5	303.5
80%	335	322	321.5	316.5	320.5
90%	345	339	337	334.5	337.5
100%	>350	>350	>350	>350	>350

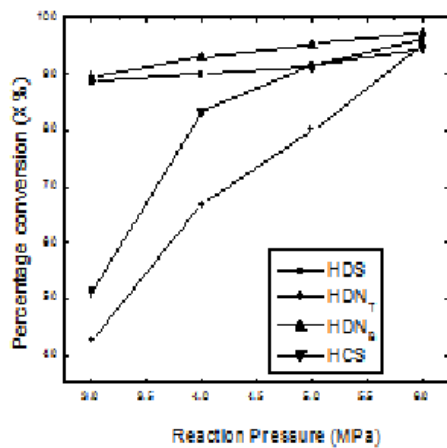


Figure 3.3: Effect of reaction pressure on percentage conversion of HDS, HDN & hydrocarbon saturation

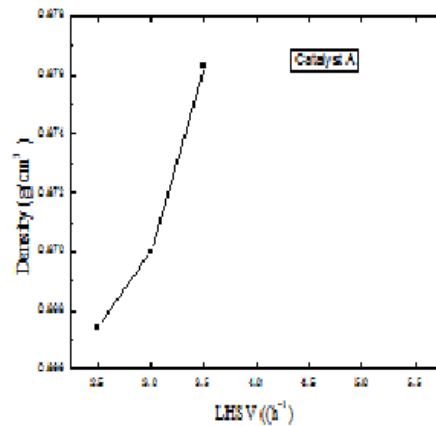


Figure 3.4: Effect of LHSV on product density

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

Table (3.4) and Figures (3.7) & (3.8) show the effect of ratio of hydrogen / gas

Table 3.3: Effect of LHSV on product quality

Sample NO	Feed	20430A	2053A	2059A24.5
P, MPa		6	6	6
T, °C		350	350	350
R, m <sup>3</sup> /m <sup>3</sup>		350	350	350
LHSV, h <sup>-1</sup>		2.5	3.0	3.5
D, g/cm <sup>3</sup>	0.8924	0.8674	0.87	0.8763
S, % [ppm]	0.39	[273]	[361]	[450]
Br,	21.5	1.2	1.6	2.1
gBr/100g				
N <sub>T</sub> , ppm	749	117	150	170
N <sub>B</sub> , ppm	273	8	14	18
IBP, °C	205	139.5	156	186
10%	227	211	211	217
20%	239.5	227	226	229
30%	251.5	238	240	243
40%	269.5	253.5	255	259
50%	283.5	268	271.5	276
60%	301.5	284.5	286	292
70%	317	303.5	304.5	308
80%	335	320.5	321.5	325
90%	345	337.5	338.5	340
100%	>350	>350	>350	>350

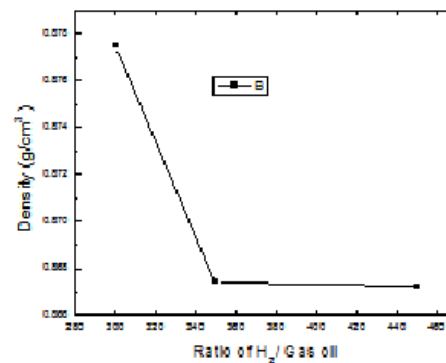
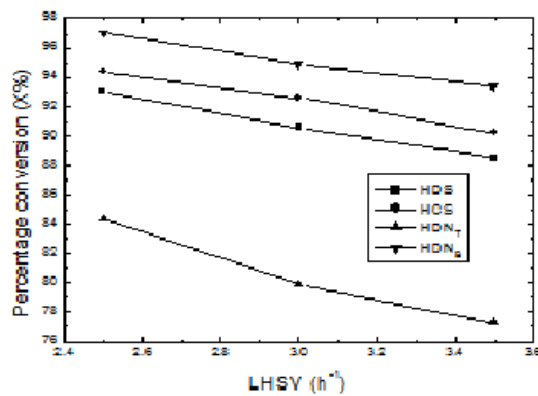


Figure 3.6: Effect of ratio of hydrogen / gas oil on product density

Figure 3.5: Effect of LHSV on percentage conversion for HDS, HCS and HDN



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

Sample NO	Feed	20510A2	20430A	20510A3
P, MPa		6	6	6
T, °C		350	350	350
R, m <sup>3</sup> /m <sup>3</sup>		300	350	450
LHSV, 1/h		2.5	2.5	2.5
D, g/cm <sup>3</sup>	0.8924	0.8775	0.8674	0.8672
S, % [ppm]	0.39	443	[273]	234
Br, gBr/100 g	21.9	2.55	1.2	1.1
N <sub>T</sub> , ppm	749	300	117	104
N <sub>B</sub> , ppm	273	20	8	5
IBP, °C	205	166	139.5	135
10%	227	212	211	209
20%	239.5	228.5	227	227
30%	251.5	259	238	2360
40%	269.5	254	253.5	252
50%	283.5	271	268	267
60%	301.5	287	284.5	283.5
70%	317	305	303.5	304
80%	335	321	320.5	320.
90%	345	338	337.5	337
100%	>350	>350	>350	>350

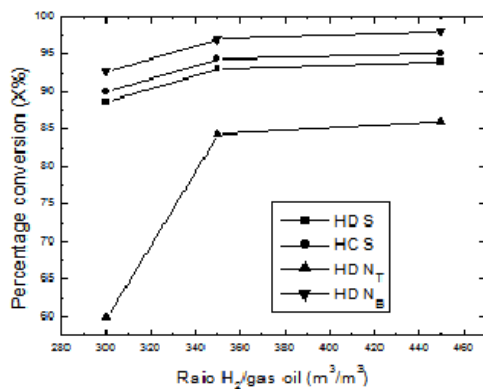


Figure 3.7: Effect of ratio of hydrogen / gas oil on percentage conversion for HDS, HCS and HDN

oil on product density, percentage conversion of sulfur, hydrocarbon saturation, and nitrogen content. According to the experimental data, increasing ratio of hydrogen /gas oil will decrease product density, IBP, sulfur, nitrogen, and unsaturated hydrocarbon. This is possible due to increase in hydrogen partial pressure by increas-

ing of ratio of hydrogen / gas oil as the results the rate of HDT will increases. Similar results of improvement of product properties as a function of increasing ratio of hydrogen /gas oil was reported by Varg et al. [8]

### Hydrotreating Kinetics

Total sulfur & nitrogen in power law equation was used to determine the overall reaction order for HDS, HDN, and hydrocarbon saturation. Kinetics Model The power law equation is

$$r = \frac{dC}{dt} = -K'_n (C)^n \quad (3.1)$$

The ideal plug flow model equation is

$$\frac{dC}{dz} = K''_n (1 - \varepsilon) \frac{(C)^n}{LHSV} = K'_n \eta \frac{(C)^n}{LHSV} \quad (3.2)$$

By using equation (3-2) and if the effectiveness factor is combined with the rate constant, we can integrate equation (3-1) giving the following:  
For n=1



$$\ln \frac{C_i}{C_o} = \frac{k_1}{LHSV} \quad (3.3)$$

$$\frac{1}{C_o} - \frac{1}{C_i} = \frac{k_2}{LHSV} \quad (3.4)$$

and for n=2

The integrated equation for the n<sup>th</sup> order reaction is

EA=activation energy,

Ta = mid-temperature for temperature range considered,

Ta= (573.2+603.2+623.2+623.2)/4=613.2 K

k<sub>o</sub> = Ae<sup>(-E/RT<sub>a</sub>)</sup>

r can be written as

$$(C_o)^{1-n} - (C_i)^{1-n} = (n-1) \frac{k_n}{LHSV} \quad (3.5)$$

The data in Table 3.3 were used to solve equation (3-5), by using statistical module non-linear estimation, then activation energies and frequency factor were calculated from Arrhenius equation, namely

$$k = Ae^{(-E_A/RT)} \quad (3.6)$$

or

$$\ln k = -\frac{E_A}{R} \left( \frac{1}{T} - \frac{1}{T_a} \right) + \ln k_o \quad (3.7)$$

Where

A=frequency factor or Arrhenius constant,

EA=activation energy,

Ta = mid-temperature for temperature range considered,

Ta= (573.2+603.2+623.2+623.2)/4=613.2 K

k<sub>o</sub> = Ae<sup>(-E/RT<sub>a</sub>)</sup>

EA/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. Table (3.5) shows the reaction order, rate constant and frequency factor for up flow HDS, HCS, and HDN reaction using catalyst A. The reaction order n for HDS is 1.44, for HCS is 1.37, for HDNT is 1.52, and for HDNB is 1.17. The activation energies using Arrhenius equation for HDS is 998.32 kJ. / kmol, for HCS is 264.61 kJ. /kmol, for HDNT is 613.42 and for HDNB is 360.84 kJ. / kmol. These results agree with those reported in literature [7,11]. 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, ratio of hydrogen /gas oil 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 outlet we expected that the order of hydrotreating reaction as follow saturate unsaturated hydrocarbon followed by hydrodesulfurization, since HDN reaction temperature >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 3.5:** Reaction order, rate constant, and activation energy and frequency factor of HDT reactions at up flow reactor with catalysts A

Factor	n	300 °C, k	330 °C, k	350 °C, k	380 °C, k	E <sub>A</sub> , kJ. / kmol	A
HDS	1.44	6.09967 h <sup>-0.44</sup>	11.53298, h <sup>-0.44</sup>	18.79948 h <sup>-0.44</sup>	36.02053 h <sup>-0.44</sup>	998.316093	18.53794 h <sup>-0.44</sup>
HCS	1.37	2.71582 h <sup>-0.37</sup>	3.79445 h <sup>-0.37</sup>	4.14461 h <sup>-0.48</sup>	4.35125 h <sup>-0.48</sup>	264.61390	3.91925 h <sup>-0.37</sup>
HDN <sub>T</sub>	1.52	10.76893 h <sup>-0.52</sup>	25.42707 h <sup>-0.52</sup>	30.08105 h <sup>-0.52</sup>	31.66488 h <sup>-0.52</sup>	613.42314	24.88643 h <sup>-0.52</sup>
HDN <sub>B</sub>	1.17	13.59979 h <sup>-0.17</sup>	15.93869 h <sup>-0.17</sup>	22.30382 h <sup>-0.17</sup>	24.78119 h <sup>-0.17</sup>	360.83714	20.20193 h <sup>-0.17</sup>

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