# Ultra deep Hydrotreatment of Iraqi Vacuum Gas Oil Using Modified Catalyst

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## ABSTRACT

A set of hydro treating experiments are carried out on vacuum gas oil in a trickle bed reactor to study the hydrodesulfurization and hydrodenitrogenation based on two model compounds, carbazole (non-basic nitrogen compound) and acridine (basic nitrogen compound) which are added at (0-200ppm) to the tested oil, and dibenzotiophene is used as a sulfur model compound at (3000ppm) over commercial $CoMo/Al_2O_3$ and prepared $PtMo/Al_2O_3$. The impregnation method is used to prepare (0.5% Pt) $PtMo/Al_2O_3$.The basic sites are found to be very little, the two catalysts exhibit good metal support interaction.

In absence of nitrogen compounds over the tested catalysts in trickle bed reactor at temperatures (523 to 573 K), LHSV (1 to 3 $hr^{-1}$), and a pressure range of 16 to 20 bar, the results show an increase in conversion from (0.2214 to 0.6748), (0.2920 to 0.7341) for (CoMo) and (PtMo) respectively with the increase of temperature, a little positive effect on conversions when pressure increases, and a significant decrease in conversion (0.6748 to 0.3284), (0.7341 to 0.3734) for (CoMo) and (PtMo) respectively when LHSV increases. The results showed a first order kinetic of DBT hydrodesulphurization. The activation energies are (75.399) and (67.983) kJ/mol for HDS of DBT over CoMo and PtMo respectively.

**Keywords: Hydrotreatment, vacuum gas oil, catalyst**

## INTRODUCTION

Hydrotreating is a part of complex refining processes to remove undesirable impurities (sulfur, nitrogen, oxygen, metal, aromatic constituents) and lower the molecular weight of heavy petroleum feed stock in presence of hydrogen and a suitable catalyst (Hossain, 2000). Petroleum fractions generally treated are hydrogen plant treat gas, naphthas (straight run, cracked, etc), kerosene, jet fuel, heating oils, distillate fuels, catalytic cracking feed, lube oils, waxes, tar sands products, etc. The two major objectives of hydroprocessing are to meet product purity specifications (usually pollution) and to remove impurities that act as poisons for other refining processes (octane reforming, hydrocracking) (Remesat, 2007).

The purpose of any hydrotreating catalyst is to increase the rate by which the overall hydrotreating reactions of interest approach complete conversion. The commonality that exists between all types of hydrotreating catalysts is that they are high surface area pellets consisting of an active component and one or more promoters. These materials exist in the form of nanometer-sized particles that are dispersed on the surface of a catalyst support (Sigurdson, 2009).

The commercial HDS catalysts, Co-Mo/γ-$Al_2O_3$ and Ni-Mo/γ-$Al_2O_3$ are most common. The Co-Mo based catalyst is highly selective for HDS whereas Ni-Mo based catalyst is more selective for HDN and hydrogenation. As a result, Ni-Mo based catalysts result in higher hydrogen consumption than Co-Mo based catalysts for the same extent of HDS with identical feed (Vishwakarma, 2007).

The most common promoter/active component combinations used for bimetallic hydrotreating catalysts used are NiMo, CoMo, NiW sulfide catalysts. This includes the reactor operating conditions, the feedstock impurities in relation to one another, and the priority of each hydrotreating reaction (i.e. HDS, HDN, HDA, etc.) (Sigurdson,2009). The main objectives of this research is to prepare a catalyst (PtMo/alumina) to make ultra deep hydrotreatment for the sulfur compounds in the range of (0-200) ppm for the basic compounds and 3000 ppm for the dibenzothiphenes which are not treated in the hydrocrackers and may cause serious problems in refinery stream lines and may poison their catalysts and compare its performance with the commercial catalyst (CoMo/alumina) by studying the HDS of DBT in VGO at different conditions.

## EXPERIMENTAL WORK
### Materials and Chemicals

The feedstock uses in this study is non-hydrotreated VGO which is obtained from North Refineries Company**.** DBT is used as model sulfur compound while acridine and carbazole are used as model nitrogen compounds (basic and nonbasic). Hydrogen gas used for HDS of DBT while nitrogen used for purge oxygen from the system before any run. The catalyst ((0.5%) $PtMo/Al_2O_3$) is prepared and characterized as discussed previously by Saba A. and Walled (2010).

**Experimental procedure**

The experiments are performed in a trickle bed reactor consists of a 316 stainless steel tubular reactor, 77cm long, and internal diameter of 1.6 cm. Fig. (1) show experimental trickle bed reactor .In all experiments, a DBT concentration of 3000 ppm is constant. The number of runs in this study is calculated as : 1-The number of runs for HDS of DBT without nitrogen compound for two catalysts: 2*3*3*3 = 54 runs , 2-The number of runs for HDS of DBT with nitrogen (basic and nonbasic) compound for two catalysts: 2*3*3*3*2*2 = 216 runs. The total number of runs =54+216=270 runs

**Laboratory tests**

**High Performance Liquid Chromatography (HPLC)**

DBT content in feedstock and product are determined using a computerize H.P.L.C DIONEX (UV (JYNKOTYK)/VIS160S) .A C18 reverse phase column (Philips, 5 µm x 0.4 cm). The mobile phase flow rate is 1 ml / min. DBT can be calculated by comparing the HPLC recorded area with calibration curves of DBT.

**RESULTS AND DISCUSSION**

The experiments of HDS are carried out at pressure range of (16-20) bar, temperature range of (250-300°C) and LHSV of (1, 2, 3 $hr^{-1}$) over two catalysts (CoMo and PtMo) without inhibition of nitrogen compounds according to the matrix of experiments illustrated in Table (1). Figs (2) and (3) show the conversion of (DBT) as a function of temperature at constant pressure and LHSV for the commercial (CoMo) and homemade (PtMo) catalysts. Generally, it can be concluded that the conversion of DBT increases with the increase of temperature. The commercial catalyst at (20 bars &1 LHSV) exhibits an increase in conversion of DBT from (0.2214 to 0.6748) with the increase of temperature from 523 to 573 K whereas for the homemade catalyst at the same conditions conversion increases from (0.2920 to 0.7341). These findings agree with Tanaka (1996), Farag (1999), Steiner (2002), and Rodrigues (2008). These results can be explained due to some parameters such as reaction enthalpy (ΔH), entropy (ΔS) and Gibbs free energy (ΔG), are related to temperature directly by the following equation:

$$\Delta G = \Delta H - T\Delta S \quad \text{...........................} \quad (1)$$

ΔH depends on the type of reaction whether it is exothermic or endothermic, HDS reactions are exothermic reactions, therefore any change in temperature will affect ΔH of that reaction. When temperature rises, the collisions of molecules increase so (ΔS) of molecules will rise.

Erying`s equation (Farag, 2007) relates these thermodynamic parameters with reaction rate constant:

$$ln(k_R) = ln\left[\frac{k_B}{h}\right] + ln(T) - \frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad \text{....} \quad (2)$$

Where: $k_R$ is the reaction rate constant of DBT at temperature T, $k_B$ is the Boltzmann constant ($1.381\times10^{-23} JK^{-1}$), h is Plank constant ($6.626\times10^{-34} Js$), R is the general gas constant, ΔH is reaction enthalpy , ΔS is reaction entropy. These results agree with that of Farag (2007). The tested feed (VGO) or model solvent having different characteristics due to its type like diffusivity of gas hydrogen in solvent and adsorption parameter of DBT in a solvent on the surface of catalyst. The increase of temperature contributes in an increase of magnitudes of adsorption parameter of DBT in solvent. This result agrees to Kabe (1991). The oil feed contains sulfur percentage of (0.1-2.5%) range and sulfur compounds approaches to 90 types in some of oil cuts, these percentage differs due to crude oil origin. The oil feed also contains other component such as nitrogen compounds, aromatics and saturated hydrocarbons which varies from type to another. The increase of temperature contributes in an increase in conversion of DBT for each type of crude oil and petroleum cuts. These results agree to Andari (1996) and Sanchez (2001). Figs (4) and (5) show the conversion of DBT as a function of LHSV at constant pressure and temperature for the tested catalysts. Generally it is obvious that the conversion of DBT decreases with the increase in LHSV at constant pressure and temperature. In the case of commercial catalyst at (20 bars &573 K) the conversion of DBT decreases from (0.6748 to 0.3284) with the increase in LHSV from (1 to 3 $hr^{-1}$) whereas for the homemade catalyst at the same conditions the conversion decreases form (0.7341 to 0.3734) with same increase of LHSV. These results agree with Farag (1999), Steiner (2002), and Farag (2007). These results can be explained due to the following factors:

**1-Residence time:** The increase in LHSV will decrease the contact time between reactants (VGO and $H_2$) and catalyst particles, thereby the reaction time and conversion decreases. These results agree to those of Andari (1996), and Schmitz (2004).

**2-VGO flow rate:** The variation of the VGO volumetric flow rate affect catalyst wetting, radial and axial dispersion (back mixing), and liquid hold up. So, the increase in VGO flow rate decreases DBT conversion because of a deviation from plug flow to non-ideal flow these results agree to those of Tsamatsoulis (1998). Figs (6) and (7) show a comparison between the present study and other researchers. Fig. (6) shows a compartment between commercial catalysts (CoMo) in the present study and other commercial catalysts (CoMo) which were used by other researchers whereas Fig. (7) shows the compartment between the homemade catalyst

(PtMo) in the present study and other prepared catalysts (PtMo) which are used by other researchers. The results indicate that the operating conditions temperature, pressure, and LHSV play imperative role in HDS of sulfur compounds. The type and characteristics of catalyst play important role in HDS of sulfur compounds. The type of solvent which is a carrier of sulfur compound affects the conversion of sulfur compounds in HDS. The homemade catalyst seems to be more active than the commercial catalyst; this indication can be enriched by applying all steps of catalyst preparation in commercial scale. These results agree to Farag (2007), Rodrigues (2008).

## CONCLUSIONS

1- HDS of DBT present in VGO is highly dependent on temperature and liquid hourly space velocity variation for both catalyst (CoMo and PtMo) at 3000 ppm concentration of DBT under pressure range of 16 to 20 bar, temperature range 523 to 573K, liquid hourly space velocity range 1to 3 hr $^{-1}$.

2- PtMo is the better catalyst for HDS of DBT than CoMo at all tested conditions and the optimum conditions for PtMo are 573K, 1LHSV and 20 bar, with a conversion of 0.7341% and the optimum conditions for CoMo are 573K, 1LHSV and 20 bar, the conversion at these conditions is 0.6748%.

3- The LHSV was effected inhibition of HDS. The conversion decreases with the increase in LHSV for both catalysts. DBT conversion decreases by basic compound more than non basic compound for the two tested catalysts. The decrease of conversion for (CoMo) was higher than (PtMo) for basic and non basic compounds. Thus the prepared catalyst could be simulated in a pilot plant of trickle bed reactor after hydrocrackers in refinery to ensure high elimination of sulfur compounds.

## ABBREVIATIONS

DBT: Dibenzothiophene
HDS: Hydrodesulphurization
VGO: Vacuum gas oil
LHSV: Liquid hourly space velocity

## REFERENCES

- Andari, M., K., Abu-Seedo, F., Stanislaus, A., Qabazard, H., M.,1996. "Kinetics of individual sulfur compounds in deep hydrodesulfurization of Kuwait diesel oil", *Fuel*, vol: 75, Issue: 14, 1664-1670.
- Farag, H., 2007 "A Comparative Assessment of The Effect of H2S on hydrodesulfurization of dibenzothiophene over nanosize MoS2- and CoMo-based Al$_2$O$_3$ catalysts", *Applied Catalysis A: General*, vol: 331, 51–59.
- Farag, H., Whitehurst, D., D., Sakanishi, K., Mochida, I., 1999. "Carbon versus alumina as a support for Co-Mo catalysts reactivity towards HDS of dibenzothiophenes and diesel fuel", *Catalysis Today*, vol: 50, 9-17.
- Hossain, M., M, 2000. "Experimental Investigation of Hydrogen Spillover on Co-Clay Hydrotreating Catalysts by Nobel Metals", *Master of Science thesis*, king fahd university of petroleum & minerals.
- Kabe, T., Ishihara, A., Tajima, H., 1992. "Hydrodesulfurization of Sulfur-Containing Polyaromatic Compounds in Light Oil", *Ind. Eng. Chem. Res.*, vol: 31, 1577.
- Remesat, D, 2007. "Improving Vacuum Gas Oil Hydrotreating Operation via a Lumped Parameter Dynamic Simulation Modeling Approach", *Doctor of philosophy thesis*, Unviersity of Calgary.
- Rodrı´guez, E., C., Lo´pez, A., J., Quesada, D., E.,2008. "Nickel and cobalt promoted tungsten and molybdenum sulfide mesoporous catalysts for hydrodesulfurization", *Fuel*, vol: 87, 1195–1206.
- Sanchez, G., M., Juarez, J., A., Zuniga, A., R., Torres, E., F.,2001. "Effect of Crude Oil Properties on the Hydrodesulfurization of Middle Distillates over NiMo and CoMo Catalysts", *Energy & Fuels,* vol: 15, 1213-1219.
- Sigurdson, S., K., 2009. "Hydrotreating of Light Gas Oil Using Carbon Nanotube Supported NiMoS Catalysts: Influence of Pore Diameters", *Master of Science thesis*, University of Saskatchewan.
- Steiner, P., Blekkan, E., A.,2002. "Catalytic hydrodesulfurization of a light gas oil over a NiMo catalyst: kinetics of selected sulfur components", *Fuel Processing Technology*, vol: 79, 1 – 12.
- Tanaka, H., Boulinguiez, M., Vrinat, M., 1996."Hydrodesulfurization of thiophene, dibenzothiophene and gas oil on various Co-Mo/TiO$_2$-Al$_2$O$_3$ catalysts", *Catalysis Today*, vol: 29, 209-213.
- Tsamatsoulis, D., Papayannakos, N.,1998. "Investigation of intrinsic hydrodesulphurization kinetics of a VGO in a trickle bed reactor with backmixing effects", *Chemical Engineering Science*, vol: 53, Issue: 19, 3449-3458.
- Vishwakarma, S., K.,2007. "Sonochemical and Impregnated Co-W/γ-Al$_2$O$_3$ Catalysts: Performances and Kinetic Studies on Hydrotreatment of Light Gas Oil", *Master of Science thesis*, University of Saskatchewan.

**Table (1) Experimental Variables for HDS of DBT with Nitrogen (basic and nonbasic) Compounds**

| Parameter | Value |
|---|---|
| Catalyst | Commercial Cat., homemade Cat. |
| Temperature | 523, 548, 573 K |
| pressure | 16, 18, 20 bar |
| Liquid hourly space velocity | 1, 2, 3 hr$^{-1}$ |
| Nitrogen compounds | Acridine, carbazole |
| Con. of nitrogen compounds | 100, 200 ppm |
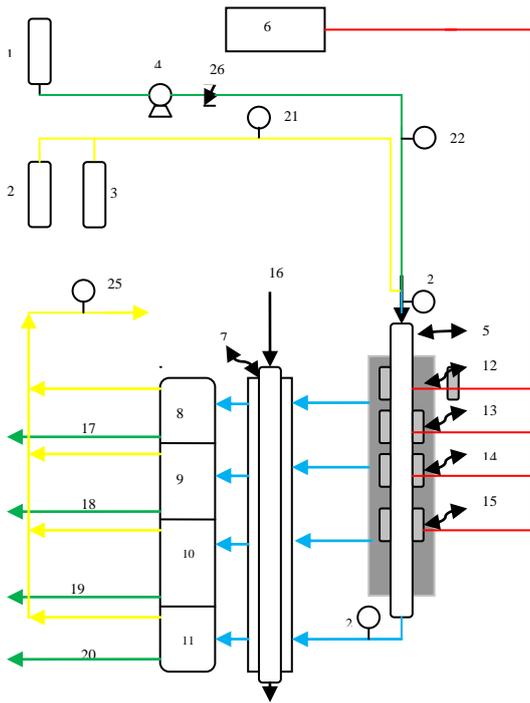


**Fig. (1): Experimental trickle bed reactor device**

| Serial number | Description | Specification |
|---|---|---|
| 1 | Feed tank | Box , 20 litter |
| 2 | hydrogen bottle | 150 bar |
| 3 | Nitrogen bottle | 50 bar |
| 4 | Pump | Dosapro Milton Roy / Italy, Max flow = 1.27 litter/hr , Max. pressure = 20 bar |
| 5 | Trickle bed reactor | Stainless steel 316 1.6 cm * 73 cm |
| 6 | Control box | Control box |
| 7 | Heat exchanger (Cooler ) | Shell and tube (Four tubes) Stainless steel |
| 8 , 9 , 10 , and 11 | Separator | Stainless steel |
| 12,13,14, and 15 | Reactor heating jacket | Electrical coils |
| 16 | Cooling water | 20 $^{o}$C |
| 17,18,19,and 20 | Sample points | - |
| 21 | Gas flow meter | Yamamoto 0-6 litter/min |
| 22 | Liquid flow meter | Colongo Monzese 0-3.2litter/hr |
| 23 | Pressure gauge | Neu-tec / Italy 0-35 bar |
| 24 | Pressure gauge | Neu-tec / Italy 0-35 bar |
| 25 | Off gas flow meter | Yamamoto 0-6 litter/min |
| 26 | Check valve | TORK , T-GH101 0-50 bar |
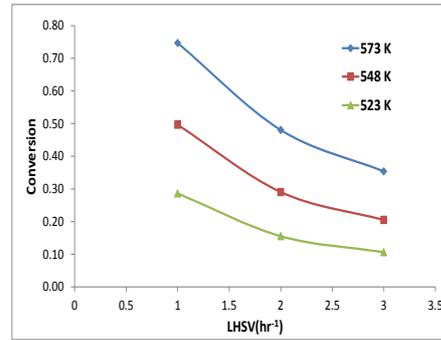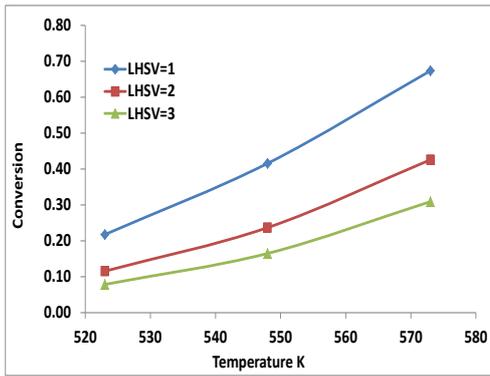
**Figure(2): Effect of temperature on conversion of DBT over catalyst CoMo/γ-Al₂O₃ at 20 bars**



**Figure(3): Effect of temperature on conversion of DBT over catalyst PtMo/γ-Al₂O₃ at 20 bars.**



**Figure (4): Effect of LHSV conversion of DBT over CoMo/γ-Al₂O₃ catalyst at 20 bars**

**Figure (5): Effect of LHSV conversion of DBT over PtMo/γ-Al₂O₃ catalyst at 20 bars**



**Figure (6): Compartment between present study (commercial catalyst CoMo, 20 bar&1LHSV) and other studies.**



**Figure (7): Compartment between present study (prepared catalyst PtMo, 20bar &1LHSV) and other studies.**