International Journal of Engineering Innovation & Research
Volume 4, Issue 1, ISSN: 2277 – 5668

# Stochometry Equation of Hydrotreating Process

**Afaf G. Abadi, Hiba ABadia, Elaf E.Hassan. U of K**
Email:afafghais2000@gmail.com
University of Khartoum, Chemical Eng. Dept

***Abstract:*** **In spite of the low sulfur content in Sudanese Crude, the global environmental challenge of low sulfur content (LSC) was not reached. In this contribution, CHEM CAD 6 used to simulate hydro treating fixed bed reactor in Khartoum refinery- Algilly - Sudan. The stochometric equation controlled the process had been determined and the sulfur and nitrogen content reduced to 14.9 and 11.2 respectively.**

***Keywords:*** **HDS, HDN, Stochometry Equation, CHEM CAD.**

## 1. INTRODUCTION HYDRO TREAT PROCESS

Gasoline, diesel fuel, and jet fuel all contain sulfur that is emitted in the form of sulfur oxides after combustion. Although motor vehicle emissions currently account for only about 3% of the total national sulfur oxide emissions, [(1).] Diesel fuel and gasoline demand continue to rise, with projections for further increases of 1 and 2 million barrels per day, respectively, from 2002 to 2020 (DOE, 2001, EIA Annual Energy Review) [(2)] . As of 2002, diesel fuel is being produced with 350 ppm sulfur [(3)]. Since 2004, Diesel required to meet the "80/20" rule, with production of 80% ultralow-sulfur diesel (ULSD) with 15 ppm maximum 7–10 ppm average and 20% 500-ppm highway diesel between , and a 100% requirement for ULSD after 2010 [(2).]

Hydro treating technology is designed to remove contaminants such as sulfur, nitrogen, olefins, metals and aromatics. Feed stocks used in the process range from naphtha to vacuum residue, and the products are used as environmentally acceptable clean fuels. Hydro treating is the process in which selected petroleum fractions react with hydrogen in the presence of monofunctional catalysts (metallic sulfides or oxides) to improve the safety corrosiveness and combustion performance of the oil product, by means of hydrogenolysis reactions. Desulfuration and denigration currently used to indicate the nature of the main heteroatom, the removal of which is sought, but in all cases all the heteroatom is affected [(4).]

### *1.1 Impact of sulfur, nitrogen and unsaturated contained in petroleum cuts and product:*

During the combustion of the products, the sulfur atoms react with the oxygen in air and transformed into sulfur oxides SO2 and SO3, causing acidic rains, corrosion, bad smell, and catalyst poisoning. Nitrogen in the hydrocarbons is bounded inside the chemical structure of the molecules, as sulfur, with color instability, foaming problems. Unsaturated compounds in the crude oil are aromatics, But the cracking processes like FCC, visbreaker and steam cracker generate a lot of olefins, diolefins and aromatic compounds, need to be saturated [(4)].

### *1.2 Hydro treating Reaction Steps:*

Chemical reactions occur during the hydrotreating process (depending on the impurities present) are:

1. Sulfur removal, also referred to as desulfurization or hydro-desulfurization (HDS) in which the organic sulfur compounds are converted to hydrogen sulfide
2. Nitrogen removal, also referred to as denitrogenation or hydro-denitrogenation(HDN) in which the organic nitrogen compounds are converted to ammonia
3. Oxygen removal, in which the organic oxygen compounds are converted to water.
4. Olefin saturation, in which organic compounds containing double bonds are converted to their saturated homologues.
5. Aromatic saturation also referred to as hydro-dearomatization, in which some of the aromatic compounds are converted to naphthenes[(5)] .

### *1.3 Hydro-desulfurization (HDS):*

Sulfur removal occurs via the conversion to H2S of the organic sulfur compounds present in the feedstock. Sulfur is found throughout the boiling range of petroleum fractions from naphtha to atmospheric residue range.

In an industrial hydrodesulfurization unit, such as in a refinery, the hydrodesulfurization reaction takes place in a fixed-bed reactor at elevated temperatures ranging from 300 to 400 °C and elevated pressures ranging from 30 to 130 atmospheres of absolute pressure, typically in the presence of a catalyst consisting of an alumina base impregnated with cobalt and molybdenum [(5)] .

### *1.4 Hydro-denitrogenation (HDN)*

Nitrogen is mostly found in the heaviest end of petroleum fractions in five and six membered aromatic ring structures. Both the molecular complexity and quantity of nitrogen containing molecules increases with increasing boiling range.

Nitrogen is more difficult to remove and consumes more hydrogen than sulfur removal because the reaction mechanism involves aromatic ring saturation prior to nitrogen removal. In desulfurization, the sulfur is less often associated with aromatic rings and when it is, the sulfur can be removed without ring saturation.

Crude oils with higher viscosities and higher densities usually contain higher amounts of more complex sulfur compounds. The aliphatic acyclic sulfides (thioethers) and cyclic sulfides (thiolanes) are easy to remove during a hydrodesulfurization process or by thermal treatment. On

the other hand, sulfur contained in aromatic rings, such as thiophene and its benzologs (e.g. benzothiophene, diben- zothiophene, benzonaphthothiophene) are more resistant to sulfur removal by hydrodesulfurization and thermal con- version [(6)].

Copyright © 2015 IJEIR, All right reserved

## 2. OBJECTIVES

Study objective is to upgrade Fulla crude oil to produce low sulfur,low nitrogen diesel in Khartoum Refinery Company (KRC)-Sudan. The study determined the stochimetric equation of the two reaction steps HDS and HDN, by CHEMCAD pachage.

## 3. METHODOLOGY

*Materials:*

The feed entering the fix bed reactor is 80% diesel and 20% naphtha (Hydrotreaterfeed) used to produce 110,455 kg of diesel /year, Table 1.

Table 1: Properties of KRC Fix bed ReactorFeedstock[7]

| Properties | Value |
|---|---|
| Density (20°C) ,g/cm$^3$ | 0.8181 |
| Viscosity (20°C), mm$^2$/s | 2.704 |
| TAN mg KOH/100 ml | 83.3 |
| S, ppm | 498 |
| N, ppm | 374 |

The feed stream added to hydrogen stream, passing through multi heating steps in three heat exchangers and furnace, and then entered the fixed bed reactor.

*CHEM CAD 6*

CHEMCAD 6 is a powerful and flexible chemical process simulation environment,built around three key values of innovation, integration, and open architectureWithin the industries, chemical engineers work CHEMCAD 6 used to address a variety of challenges:

1. Initial design of new processes
2. Optimization or de-bottlenecking of existing processes
3. Design and rating of process equipment such as vessels, columns, heat
4. Exchangers, piping, valves, and instrumentation
5. Pressure and flow balancing of complex piping networks
6. Reconciliation of plant data
7. Advanced process control (APC), including model predictive control (MPC)
8. Real-time optimization (RTO), and operator training systems (OTS)
9. Batch reaction rate regression from process or lab data

CHEMCAD is capable of delivering the results needed to stay competitive in an increasingly fast and fluid global market [8].

## 4. RESULTS

*Stochiometric Equation of Hydrotreating Reactions:*

From Figures 1,2, at pressure of 76 barand a temperature of 340 $^0$C, The conversion factor of desulfurization and denitrogenation reactions are 0.98 and 0.96 respectively.

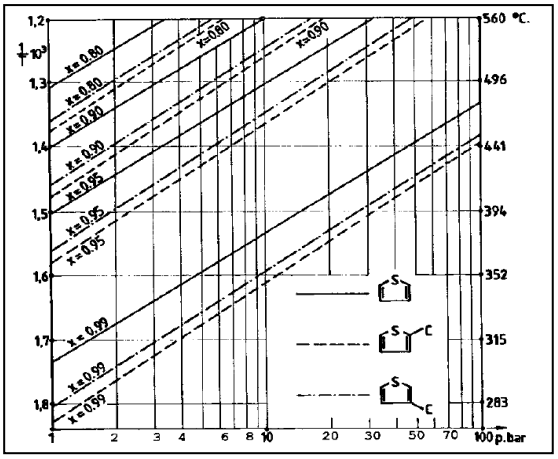

Fig.1. Hydrogenolysis Equilibrium Conversion for Thiophen, 2-Methyl-thiophen and 3-Methylthiophe

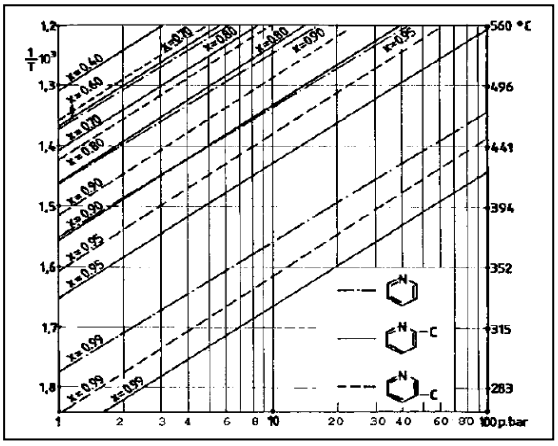

Fig.2.Hydrogenolysis Equilibrium Conversion for Nitrogen Compounds

The average conversion of hydrotreating reaction could be taken as an average of (x=0.97). The reaction conditions and HDS, HDN conversion factor applied to CHEM CAD 6 simulation and reactor section, so as to find the stochiometric equation:

The feed (C6+) reacted with hydrogen in fixed bed reactor,followed chemical reaction:

Feed + 1.5 $H_2$ ⟶ 0.34 Methane + 0.07 Ethane +0.024 Propane +0.024 I-Butane +0.008 N- Butane +0.022 I-Pentane +0.028 N-Putane +0.045 N-Hexane+ 0.028 $H_2O$ +0.05$H_2S$+0.006 $NH_3$ +Product $C_6$

Depended on the stochiomeric equation the sulfur content reduced to 14.9 ppm and the nitrogen content to 11.22 after hydrotreatig

## 6. CONCLUSION AND RECOMMENDATION

Upgrading of crude oil will increase the crude products quality and price. The Desulfurization and denitrogination of crude will remove the corrosive sulfur compounds and nitrogen gases from the crude products. The temperature and the pressure of the reactor will affect the upgrading process.

The researcherrecommend further work to estimate the effect of various temperature on the reaction kinetics.

Copyright © 2015 IJEIR, All right reserved

## ACKNOWLEDGMENT

The authors stated their pleasure to Khartoum Refinery Company staff members for their unlimited help and support.

## REFERENCES

[1] Lawrence K. Wang, Clint Williford, and Wei-Yin Chen, "Desulfurization and Emissions Control", from Handbook of Environmental Engineering, Volume 2: Advanced Air and Noise Pollution
[2] US DOE, "The Transition to Ultra-Low-Sulfur Diesel Fuel Effects on Process and Supply, Energy Information Administration, US Department of Energy, Washington, DC, 2001.
[3] J. T. Capps, "Refiner Outlook for Clean Fuels, Hart World Fuels Conference", 2001;
[4] Afaf G. A, HibaA.Badia.ElafE.Hassan "Upgrading of Fula Crude", university of Khartoum ,June,2009
[5] en.wikipedia.org/wiki/, "Hydro desulfurization", Wikipedia,Free encyclopedia, 10 January 2015, 9.30 Am.
[6] Gray MR, Ayasse AR, Chan EW, Veljkovic M (1995) Kinetics of hydrodesulfurization of thiophenic and sulfide sulfur in Athaba- sca bitumen. Energy Fuels 9:500–506.
[7] Khartoum Refinery Company, 2009.
[8] CHEM CAD

## AUTHOR'S PROFILE

**Afaf Ghais Abadi** I born in Aljazira State-Sudan ,1974. I'm the Head of Chemical Engineering Department, Faculty of Engineering, University of Khartoum-Sudan.
My PhD study is the desalting of heavy crude oil which I finished in 2008. My research interest is the utilization of waste materials .I had many publications in paper reuse and fly ash utilization, in addition to corrosion in crude oil equipment andupgrading of petroleum's cuts

Copyright © 2015 IJEIR, All right reserved