

Cobalt-Molybdenum-Aluminium Oxide Catalyst Weight for Hydro-De-Sulphurization in Packed Tubular Catalytic Reactor

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Abstract— The hydro-de-sulphurization of petroleum products light distillates is a catalyst-hydrodynamics flow-driven refining process in any of the heterogeneous reactors. This research focused on applying packed-bed catalytic reactor integral design model analogous to plug flow reactor model developed from first principles of balance; incorporating catalyst weight in the reactor. The model was integrated numerically to predict catalyst weight required for HDS actions at 100 percent catalyst efficiency. The prediction result of catalyst weight in the packed-bed catalytic reactor at conversion of 85 percent was determined as 3.1785kg. The rate of catalyst cobalt-molybdenum-aluminum oxide ($C_o-M_oAl_2O_3$) decay for the research obeyed a first order reaction rate law as a function of time with a progressive conversion of distillates to sulphur-free products to serve as environmentally friendly downstream feeds.

Keywords— Packed tubular catalytic reactor, hydro-de-sulphurization, catalyst-decay, Petroleum products, integral-plug-flow-model, integration.

I. INTRODUCTION

The paper delves into the determination of weight of catalyst in reactors for hydro-de-sulphurization actions on distillates. Heterogeneous reactors are reactors which essentially carry out two to three-phase reaction processes. They are widely used in the in petroleum refining, petrochemical plant, chemical and process industries, pollution treatment and biochemical industries. In the refinery plant operations, the reactors are used in the refining of petroleum products of light and heavy distillates. Crude oil containing organic sulphur compounds, including thiols, thiophenes, organic sulhides and disulphides, and benzothiophenes, dibenzothiophene many others are usually also present in hydrocarbon products. These sulfur compounds will be removed because of deleterious effects of [corrosion tendencies, blocking of heat exchangers and condensers, poison catalysts lead] leading to heavy financial burden to the private sectors. Hydro-de-sulphurization is a chemical process used to remove these identified pollutants in crude oil, natural gas, and from refined petroleum products such as gasoline or petrol, jet fuels of [ATK] aviation turbine kerosene, diesel fuel, and fuel oils (residue and low pour fuel oil) (Petrochemical & Refinery reminiscences, 2019).

(Farrauto & Bartholomew, 1998) posited that it creates products such as ultra-low-sulfur products, is to help reduce the sulfur dioxide (SO_2) emissions that result from using those

fuels in automotive vehicles, aircraft, railroad locomotives, ships, gas or oil burning power plants, residential and industrial furnaces, and other forms of fuel combustion. It results in the cleavage of the C-X chemical bond, where C is a carbon atom and X is a sulfur (S), nitrogen (N) or oxygen (O) atom.

The net result of a Hydrogenolysis reaction is the formation of C-H and H-X chemical bonds. Thus, hydro-de-sulfurization is a Hydro-genolysis reaction (Gary & Handwerk, 1984); (George, 1984). The industrial hydrodesulphurization processes include facilities for the capture and removal of the resulting hydrogen sulfide (H_2S) gas. In petroleum refineries, the hydrogen sulfide gas is then subsequently converted into by-product elemental sulphur or sulphuric acid (H_2SO_4).

In fact, the vast majority of the 64,000,000 metric tons of sulfur produced worldwide in 2005 was by-product sulfur from refineries and other hydrocarbon processing plants. An HDS unit in the petroleum refining industry is also often referred to as a hydrotreater (Gary & Handwerk, 1984).

For a fluid-solid heterogeneous reactors (Coulson & Richardson, 2006); (Octave Levenspiel, 1999); (Fogler, 2006) posited that the rate of reaction of a substance A (feed) is expressed as

$$(-r_i) = g \text{ molecule of species A reacted/s-g catalyst} \quad (1)$$

The mass of solid is used because the amount of the catalyst is what is important to the rate of reaction; the reactor volume that contains the catalyst is of secondary significance schematically shown below:

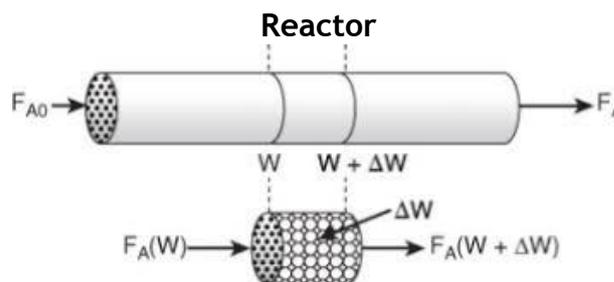


Figure 1. Elemental volume of packed tubular catalytic reactor

The focus of this paper therefore is to quantify the catalyst weight in the catalytic reactor using the integral plug flow

reactor design model by applying the constraints as clearly stated: $X = 0$, at $W/v_o = 0$, $t = V/v_o = 0$, and $P = 0$ (i.e absence of pressure drop), eventually to obtain weight of catalyst required for HDS in the tubular reactor.

II. MATERIALS AND METHODS

2.1 Materials

Research data:

Weight of cobalt-molybdenum-aluminum oxide catalyst C_oM_o/Al_2O_3

Vapour-phase feed contact catalyst at $370^{\circ}C$ Reactor pressure 20 atoms

Hydrogen: Hydrocarbon ratio 1:1

Reactor containing 25 tons of a co- M_o/Al_2O_3 catalyst ($\rho_b = 1.05 K_g L^{-1}$)

Rate law expression for thiophene HDS is given as (Scatter field and Roberts, 1968);

$$r_{HDS} = K P_T P_H / [1 + K_T P_T + K_{H_2S} P_{H_2S}]^2 \quad (2)$$

2.2 Methods

To quantify the catalyst weight in the packed tubular catalytic reactor using the integral plug flow reactor equation applying the limits of $X = 0$, at $W/v_o = 0$, $t = v/v_o = 0$, $X = 0$, i.e absence of pressure drop, to obtain weight of catalyst in the reactor. Present the profiles of model results and the catalyst weight estimated from the integral plug flow reactor. Environmentally, friendly fuels are achieved.

2.2.1 Applying Integral Plug Flow Reactor Model - IPFRM Theoretical concepts

The types of reactors suitable for the removal process are packed-bed catalytic reactor, tubular catalytic reactor, fluid-catalytic reactor, slurry reactor.

The design model incorporates catalyst weight W necessary to effect reaction process to complete conversion.

Hence, catalyst weight [Mass in Kg] required for HDS process must be determined for a conversion process at 85 percent.

This is by applying the reactor configuration/geometry on the integral balance model from first principles of balance on reactor design in the absence of pressure drop effects $\Delta P = 0$;

Packed Bed Catalytic Reactor

The derivation of the differential and integral forms of the design equations for packed bed reactors is analogous to those for a PFR.

$$F_{AO} \frac{d\alpha}{dW} = (-r'_A) \quad (3)$$

The differential form of the design equation (i.e. eqn. (3)) must be used when analyzing reactors that have a pressure drop effects along the length of the reactor. In the absence of pressure drop i.e., $\Delta P = 0$, we can integrate (3) with limits $\alpha = 0$ at $W=0$ to obtain

$$W = F_{AO} \int_0^{\alpha} \frac{d\alpha}{(-r'_A)} \quad (4)$$

Equation (4) can be used to determine the catalyst weight W necessary to achieve a conversion α when the total pressure

remains constant; and by extension the catalyst weight required for HDS.

Applying design equations for flow reactors

Equation (4) can be multiplied by the density of catalyst ρ_{cat} .

$$\rho_{cat} W = F_{AO} \rho_{cat} \int_0^{\alpha} \frac{d\alpha}{(-r'_A)} = \int_0^{\alpha} \frac{1}{k[C_{AO}(1-\alpha_A)]} d\alpha \quad (5)$$

$$\rho_{cat} W = \vartheta C_{AO} \rho_{cat} \int_0^{\alpha} \frac{1}{k[C_{AO}(1-\alpha_A)]} d\alpha \quad (6)$$

$-r'_A$ define w.r.t catalyst weight, ρ_{cat} .

F_{AO} Feed rate to the reactor

α_A Fractional conversion of feed final

$$(-r'_A) = k_1 C_A = k[C_{AO}(1-\alpha_A)] \quad (7)$$

From the integral reactor model we have,

$$W = \vartheta P_{AO} \rho_{cat} \int_0^{\alpha} \frac{1}{k[C_{AO}(1-\alpha_A)]} d\alpha \quad (8)$$

Where: $k[C_{AO}(1-\alpha_A)] = r'_{HDS} = \frac{k P_T P_{H_2}}{[1 + k_T P_T + k_{H_2S} P_{H_2S}]^2}$ (9)

Weight of catalyst can be obtained by integrating the model below

$$W = \vartheta P_{AO} \rho_{cat} \int_0^{\alpha} \frac{1}{(-r'_{HDS})} d\alpha \quad (10)$$

$$W_{cat} = F_{AO} \rho_{cat} \int_0^{\alpha} \frac{1}{(-r'_{HDS})} d\alpha \quad (11)$$

$-r'_{HDS}$ determine separately by plotting $\frac{1}{(-r'_{HDS})}$ against conversion α_A

Equation (2) is applied for catalyst weight determination in the packed tubular catalytic reactors for hydrodesulphurization process. Fundamentally, $PTCR$ is a tubular reactor filled with catalyst particles. The derivations of differential and integral forms of the performance design models are analogous to plug flow reactor is in affirmation in this research.

III. RESULTS AND DISCUSSION

The results of the design equations developed for the hydrodesulphurization of petroleum distillate is presented.

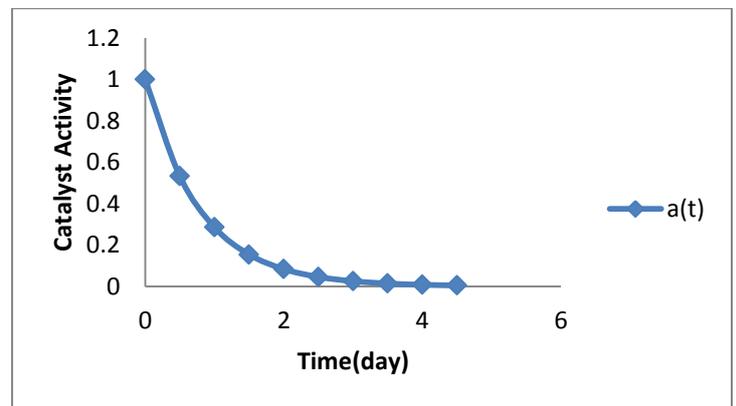


Figure 2. Plot of catalyst activity with time

Figure 2 depicts the profile of catalyst activity, $a(t)$ as a function of time. As shown, the activity of the catalyst is inversely exponentially related to the time since at time, $t = 0$, the catalyst activity there is deactivation of catalyst activity reduces exponentially to almost zero(0) as time increases to maximum.

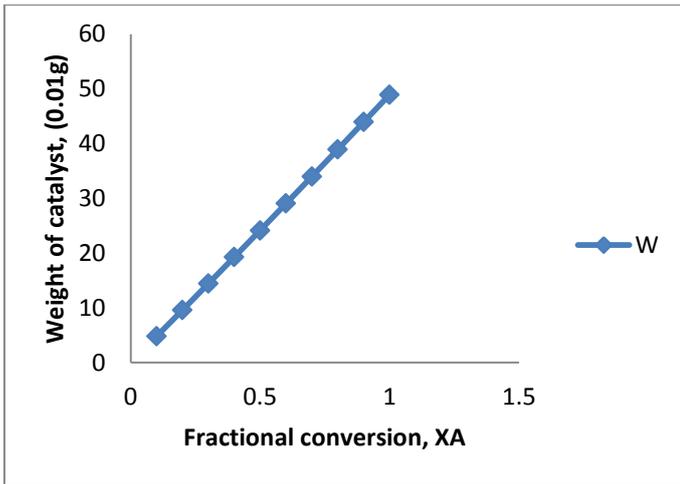


Figure 3. Plot of catalyst weight, W versus fractional conversion, α_A

Figure 3 shows the plot of weight of catalyst with fractional conversion. The variation is linearly related. As fractional conversion increases, the weight of catalyst also increases. Hence, the weight of catalyst is a function of fractional conversion.

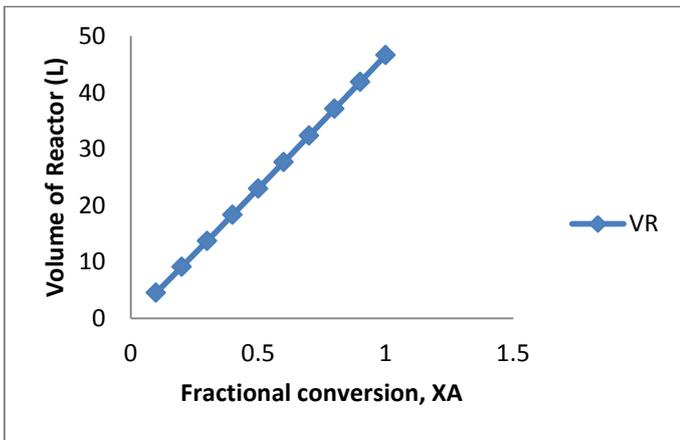


Figure 4. Plot of volume of reactor, V_R against fractional conversion, α_A

Figure 4 depicts the profile of the volume of the reactor with fractional conversion. The volume of the reactor is proportionally and linearly related to fractional conversion. As fractional conversion increases, the volume increases too. As $X_A=1$, $V_R=46.61$ Litres.

Figure 5 shows the variation of the rate of reaction with fractional conversion. From the plot, it is seen as the driving force for the hydrodesulphurization is the rate of reaction. Hence, the rate of reaction is related to fractional conversion and decreases as fractional conversion increased.

Figure 6 shows the variation of Length of reactor with fractional conversion. From the plot, it is seen that as the length of reactor increases, the fractional conversion also increases showing production of hydrodesulphurization. As seen in Figure 6, the length of reactor increases as the fractional conversion and at $\alpha_A = 1, L_R = 7.5m$

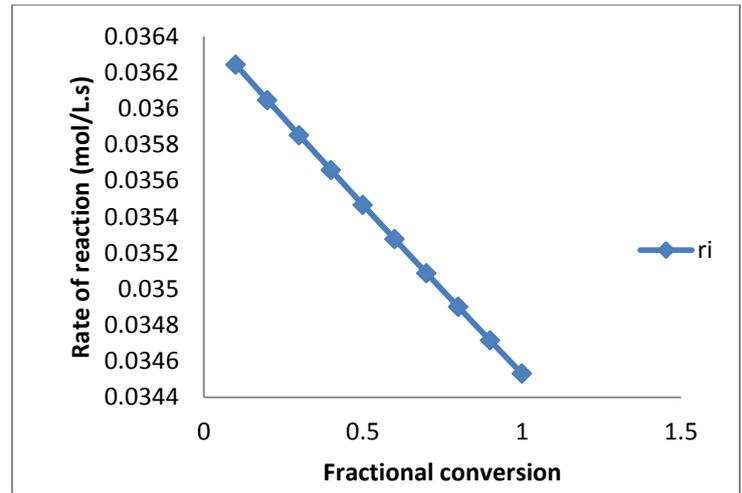


Figure 5. Plot of Rate of reaction, $(-r_A)$ versus fractional conversion, α_A

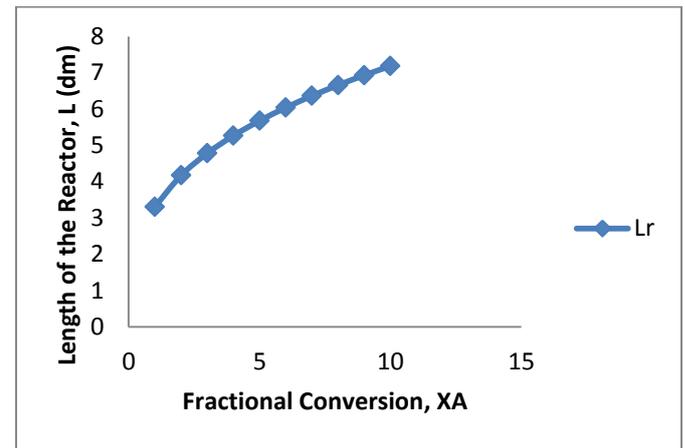


Figure 6. Plot of length of reactor L_R against fractional conversion, α_A

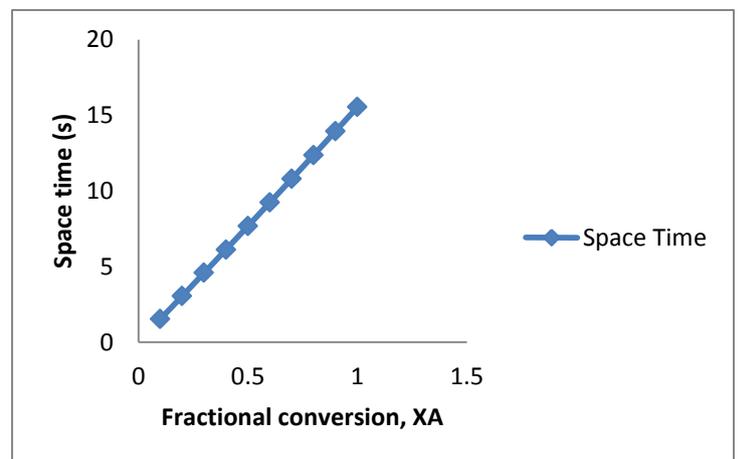


Figure 7. Plot of space time, τ versus fractional conversion, α_A

Figure 7 shows the variation of space time of reactor with fractional conversion. From the plot, it is seen that as the space time increases with the fractional conversion. Space time gives the time it takes a reactor to convert feed material to product. Figure 7 depicts the increment with fractional conversion.

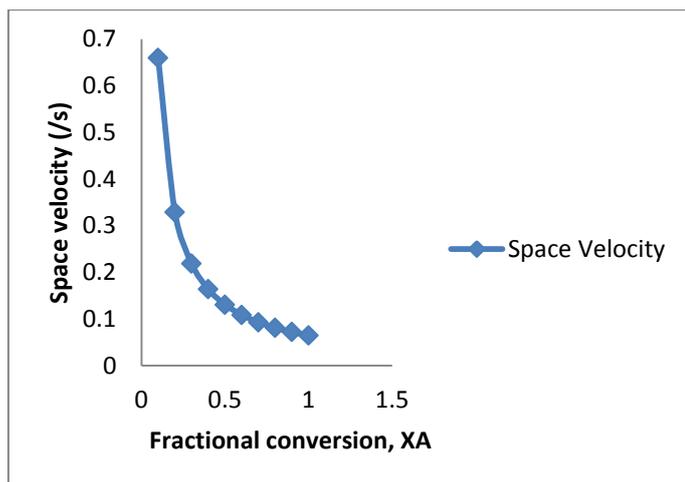


Figure 8. Plot of space velocity, S_v against fractional conversion, X_A

Figure 8 shows the variation of space velocity of reactor with fractional conversion. From the plot, it is seen that the space velocity decreases with an increase in fractional conversion.

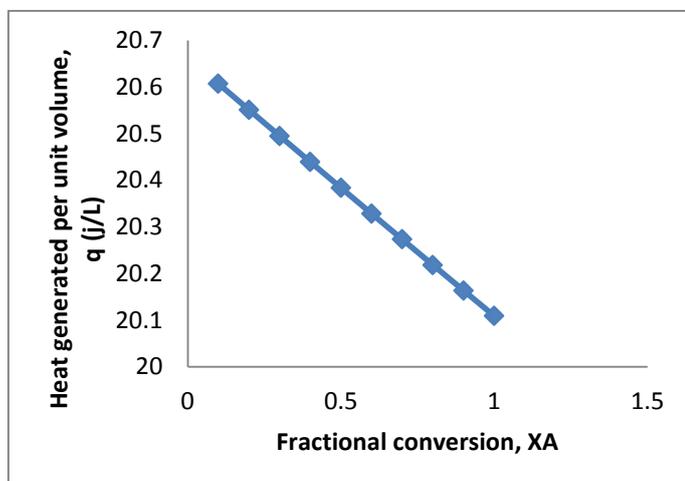


Figure 9. Plot of quantity of heat generated per unit volume versus fractional conversion

As shown in Figure 9, the rate of heat generated per unit volume decreases as fractional conversion increases. This implies that the smaller the value for q at higher conversion gives the best performance of the reactor.

IV. CONCLUSION

This work entails the determination of catalyst weight for Hydro-desulfurization (HDS) of petroleum distillates. Hydrodesulfurization is a process that is widely used to remove sulfur (S) from natural gas and from refined petroleum products, such as gasoline or petrol, jet fuel, kerosene, diesel fuel, and fuel oils.

The purpose of removing the sulfur, and creating products such as ultra-low-sulfur diesel, is to reduce the sulfur dioxide (SO_2) emissions that result from the use of these fuels. The equation used to determine the weight of catalyst and other

relevant performance equations were derived by the application of the principle of conservation of mass.

The equations were solved using MATLAB software and the result for 90% degree of conversion are: weight of catalyst 3.1785kg [$3.078m^3$], length of reactor 12m, space time 0.03s, space velocity 35.5 and total heat load 432Kw.

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