International Journal of Engineering and Advanced Technology (IJEAT)
ISSN: 2249-8958 (Online), Volume-8 Issue-2S, December 2018

Mathematical Model of Radial Flow Reactor for Naphtha Hydrodesulphurization

M. Shireesha, N. Rama, P. Kartheek Rao, J Sarada Prasad

Abstract - In the present study, a mathematical model is developed for centrifugal radial flow reactor for hydro desulphurization of naphtha with kinetics available in the literature. Also, an investigation into the effect of various process parameters like temperature, pressure, LHSV and H2/Naphtha ratio on the design of centrifugal radial flow reactor. Effect of the above process parameters on mal distribution has been evaluated using the mathematical model.

Keywords: Hydro Treatment, Desulfurization, Thiophene, Naphtha, Modeling.

I. INTRODUCTION

Naphtha hydrodesulphurization or more generally Hydro Treatment is done to reduce the poisonous heteroatom, e.g. S, N, Cl metals to limits, acceptable to reformer catalysts. Sulfur compounds are one of the most important hetero-atoms or impurities present in the petroleum fractions in organic form in varying amount. In addition to these, some hydrogen sulfide is also present and occasionally, traces of elemental sulfur can also be found. The types of sulfur compounds present in the petroleum fraction also change with boiling range. Organic Sulfides, disulfides, Mercaptans and Thiophenes are found in the lighter boiling fractions. Different derivatives of Thiophenes e.g. Benzo Thiophenes, Di-Benzo Thiophenes etc., are predominant in the heavier fractions.

Hydro treating reactions require the breaking of a C-S, C-N, or C-O bond or saturation of C=C bond. Reaction rates are much faster for Mercaptans and Disulfides than Thiophenes. Reaction rates for Phynile Mercaptans and Diethyl Sulfide are about 70 times and 15 times respectively that of Thiophene. The commonly found heteroatoms in Naphtha hydrotreater feed and their reactions are given in table 1

Table 1: Hydro Treating Reactions

Compound Desulfurization	BP (^{0}C)	Reactions
N-Butyl Mercaptan C_4H_9SH	98	$C_4H_2SH + H_2 \rightarrow C_4H_{10} + H_2S$
Diethyle Sulfide C_4H_9SH	92	$C_4H_2SH + 2H_2 \rightarrow 2C_4H_6 + H_2S$
Thiophene C_4H_2SH	84	$C_4H_4S + 4H_2 \rightarrow C_4H_{10} + H_2S$
N-Butyle Mercaptan C_4H_9SH	98	$C_4H_9SH + H_2 \rightarrow C_4H_{10} + H_2S$

All the above reactions are exothermic and generate heat. However, the heat effect for straight run naphtha feed is mild and temperature rise is 0-6^{0}C, whereas for cracked feed stock the rise in temperature is higher, 11-22^{0}C. The hydrogen flow rate for straight run feed is 50-100 Nm^3/m^3 of naphtha and for cracked Naphtha feed is 300- 1000Nm^3/m^3 of naphtha. The reaction order of HDS is considered to be one and activation energy is about 10 k cal/mol. The catalysts for naphtha hydro treating are Co-Mo or Ni-Mo or Co-Ni-Mo catalysts on alumina support. Co-Mo catalysts are used for straight run feed stocks and Ni-Mo catalysts are normally preferred for cracked feed stocks.7u=q

II. REACTOR DESIGN

Naphtha hydro desulfurization reactions are carried out in axial flow fixed bed reactor or Radial flow fixed bed reactor. In axial flow Naphtha and required amount of hydrogen (reactants) move through a catalytic bed axially and react. In radial flow configuration the reactants flow radially through the bed of catalyst. The catalyst is packed in between two Co-axial cylindrical perforated baskets. As the gas flow see an area of 2ΠrL, its velocity will be less compared to that of axial flow fixed bed reactor. Hence radial flow reactors offer less pressure drop. Also the gas contact time with catalyst will be more compared to that of axial flow reactor. Hence it has been decided to mathematically model a radial flow reactor with naphtha hydro-desulfurization kinetics already available in the literature and check the effect of various process parameters on the design of radial flow reactor. A Mathematical model has been developed using MATLAB. Runge-Kutta mathematical method has been used to solve first order differential equations.

Transport equations describing heat and mass transfer in centrifugal radial flow reactor with initial value boundary conditions (available in the literature) have been used in the design. The equations have been developed based on the following assumptions:

- Heat and mass transfer in radial direction can be described by Pseudo homogeneous model
- Channeling or shortcut effects do not occur.
- The first order reaction without volume change takes place.

Manuscript published on 30 December 2018.
***** Correspondence Author (s)
M. Shireesha, Department of Chemical Engineering, Anurag Group of Institutions, Hyderabad, Telangana, India
N. Rama, Department of Chemical Engineering, Anurag Group of Institutions, Hyderabad, Telangana, India
P. Kartheek Rao, Department of Chemical Engineering, Anurag Group of Institutions, Hyderabad, Telangana, India
Dr.J Sarada Prasad, Department of Chemical Engineering, BVRIT, Hyderabad, Telangana, India

- The physical properties of reacting gas (e.g. specific heat, density, etc.) are characterized by mean values.
- Absence of gradients of concentration and temperature within the catalyst particle.
- Absence of gradients in axial as well as angular direction.
- The reactor is considered to be run in the steady state.
- Thiophene reaction has been taken as model reaction

2.1 Design model

A mathematical model is developed for the design of Centrifugal Π configuration radial flow reactor with naphtha hydrodesulfurization reaction.

The catalyst volume is calculated by the following equation.

$$\text{Catalyst volume (V)} = \frac{\text{m}^3\text{/h of feed at 15°C}}{\text{LHSV}} \qquad (1)$$

$$\text{Catalyst volume (V)} = \pi/4\ (R22 - R12)\ L \qquad (2)$$

Where R_1 = Central pipe radius, m, R_2 = Outer basket radius, m, L = Bed length, m.

During the design of radial flow reactor R_1 is fixed at 0.1 m and length L = 1m

R_2 is calculated using the following equation

$$R_2 = \sqrt{\left\{\frac{V}{\pi L} + R_1{}^2\right\}} \qquad (3)$$

Sulfur in the form of Thiophene reacts with H_2 supplied as per the reaction

$$C_4H_4S + 4H_2 \rightarrow C_4H_{10} + H_2S \qquad (4)$$

The conversion (mole %) is calculated by the following equation

$$\text{Conversion (mole\%)} = \frac{\text{Thiophene in} - \text{Thiophene out}}{\text{Thiophene in}} \qquad (5)$$

Thiophene in (moles/s) = (kg/s)of Naphtha * wt fraction of Thiophene/Mol wt of Thiophene *(5a)*

Thiophene out (moles/s) = moles/s of H_2S *(5b)*

The required amount of H_2 is calculated by H_2/Naphtha ratio

Naphtha flow rate at 150C (m^3/h) = Naphtha Feed rate (kg/s)/Density of Naphtha at 150C *(6)*

The reaction rate of desulfurization is of first order with respect to H_2S and defined as

$$-r_{H2S} = k * (\text{Partial Pressure of } H_2S)^n \qquad (9)$$

k is calculated as $k = k_0 * e^{\left(-\frac{E}{R}\right)*\left(\frac{1}{T}\right)}$ *(10)*

k_0, frequency factor and (-E/R) are calculated from the Arrhenius plot for hydro desulfurization in light petroleum distillates.

Partial Pressure of H_2S = P * Mole fraction of H_2S *(11)*

$$\text{Mole fraction of } H_2S = \frac{\text{moles of H2S}}{\text{moles of naphtha} + \text{moles of } H_2} \qquad (12)$$

Moles of Naphtha = Feed rate of Naphtha (kg/s)/$MW_{Naphtha}$ *(13)*

Moles of H_2 = H_2 flow (Nm^3/s)*H_2 density at 150C and 1 bar pressure (kg/Nm^3) /H_2 Mol wt *(14)*

H_2 density (kg/Nm^3) = P * H_2 $MW_{Thiophene}$/R *T *(15)*

Where, Naphtha Mol wt = 215; H2 Mol wt =2.008; Thiophene Mol wt = 93

R = 0.0823 T=Temperature, K; P = Pressure, bar

2.2 Mass Balance equations

The mass and energy balance equations as given in the publication[4] have been used in the design of radial flow reactor. The mathematical model for mass balances is as given below

$$\frac{dF_{H2S}}{dr} = (-rH2S * 2\,\pi\, r\, L) \qquad (16)$$

Where F_{H2S} is molar flow rate of H_2S (moles/s), r is radius (m), L is length of the bed (m)

Initial boundary conditions: At r = R_1 → F_{H2S}=F_0 (assumed as per recycle composition)

2.3 Heat Balance equations

The mathematical model for heat balances is as given below

$$\frac{dT}{dr} = \frac{-rH2S * \Delta H}{F * C_p} * 2\,\pi\, r\, L \qquad (17)$$

Where ΔH= heat of reaction in J/mol, C_p = heat capacity in J/kg.K

F = moles of naphtha/s = kg/s of naphtha/Mol wt of naphtha *(18)*

At r = R_1; T= T_0

2.4 Pressure drop equation:

The mathematical model for pressure drop is as given below

$$\Delta p = \frac{f\, s\, \sigma\, Q^2}{2\, g\, 4\, L^2\, \pi^2 \epsilon^3}\left(\frac{1}{R_1} - \frac{1}{R_2}\right) \qquad (19)$$

Where f is friction factor which is calculated as

$$f = 0.023\ Re^{-0.25} \qquad (20)$$

Where Re is Reynolds number is calculated as

$$Re = \frac{D*G}{\mu} \qquad (21)$$

Where D, G are calculated by the following equations

$$D = 2(R_2 - R_1);\quad G = \frac{\text{Total flow} * \text{Avg Mol wt}}{2\pi r L} \qquad (23)$$

Total flow (mol/s) = Naphtha mole flow + H_2 mol flow *(24)*

Avg Mol wt = Average molecular weight of feed = Mole fraction of Naphtha * $MW_{Naphtha}$ + Mole fraction of H_2 * MW_{H2} *(25)*

Published By:
Blue Eyes Intelligence Engineering
and Sciences Publication (BEIESP)

International Journal of Engineering and Advanced Technology (IJEAT)
ISSN: 2249-8958 (Online), Volume-8 Issue-2S, December 2018

III. RESULTS AND DISCUSSION

The model has been tested by keeping three process parameters constant and varying one process parameter for a capacity of 300000TPA of vis-breaker naphtha. The central pipe radius has been fixed at 0.1 m. The bed length has been varied (=1, 1.5, 2, 2.5 and 3m). In all cases the conversion has been fixed at 99 mole% and allowable pressure drop less than 0.05 bar. The gas distribution in radial flow reactor has been quantified using a mal distribution factor (Mf) which is defined as the ratio of pressure drop at the bottom to pressure drop at the top.

3.1 Effect of Temperature

While studying the effect of Temperature in the range of (625K, 630K and 635K), other process parameters have been maintained at LHSV (1.0 hr-1), H_2/Naphtha (50Nm^3/m^3) and Pressure (20 bar). The sulfur concentration has been considered as 1.23 wt%. It has been noticed from Fig.3.1and Fig 3.2, that temperature has no effect on outer radius and it varied only with bed length. The mal distribution factor in all the cases is more than one which signifies the presence of mal distribution

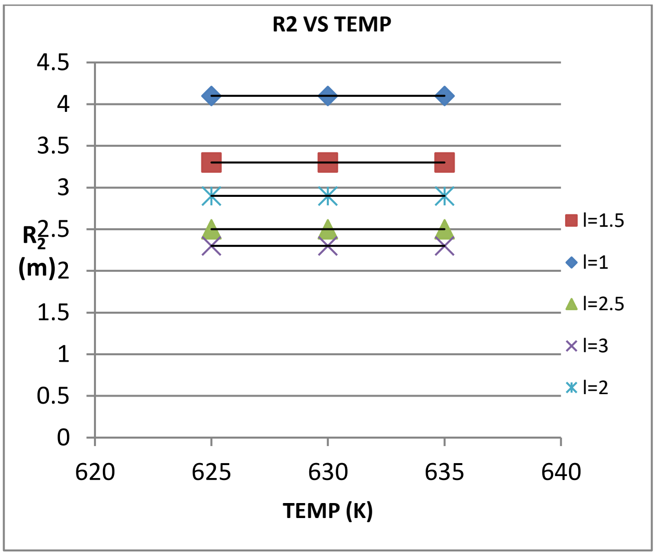

Fig 3.1Variation of outer radius (R2) with Temperature at different bed lengths

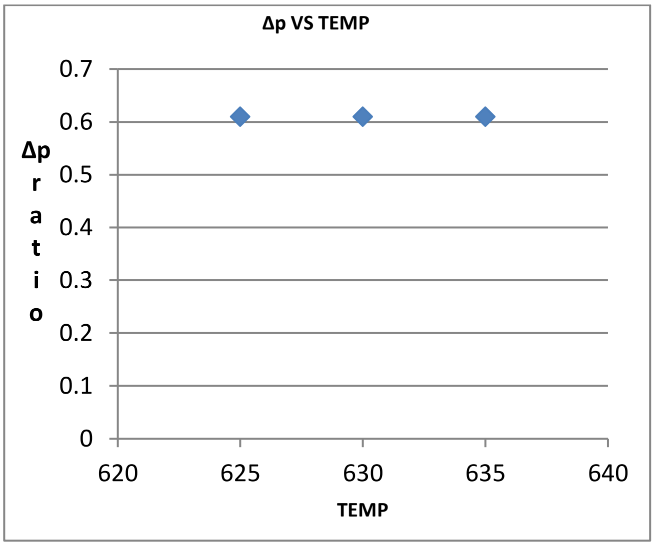

Fig .3.2 Mal distribution factor (Mf) Vs. Temperature

3.2 Effect of LHSV

While studying the effect of LHSV in the range of (1, 3 and 5 hr-1), other process parameters have been maintained at temperature (625 K), H2/Naphtha (50Nm3/m3) and Pressure (20 bar). The sulfur concentration has been considered as 1.23 wt%. It may be noticed from Fig.3.3 that with increase in LHSV the outer radius decreases at all bed lengths. This may be explained with the quantity of catalyst. As LHSV increases, the catalyst quantity decreases which in turn affect the outer radius. However the mal distribution factor is more than one at all bed lengths (Fig 3.4).

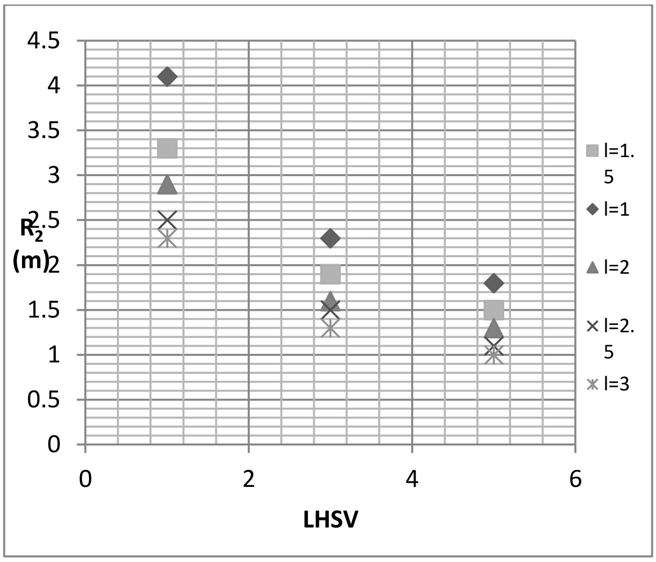

Fig 3.3Variation of outer radius (R2) with LHSV at different bed lengths

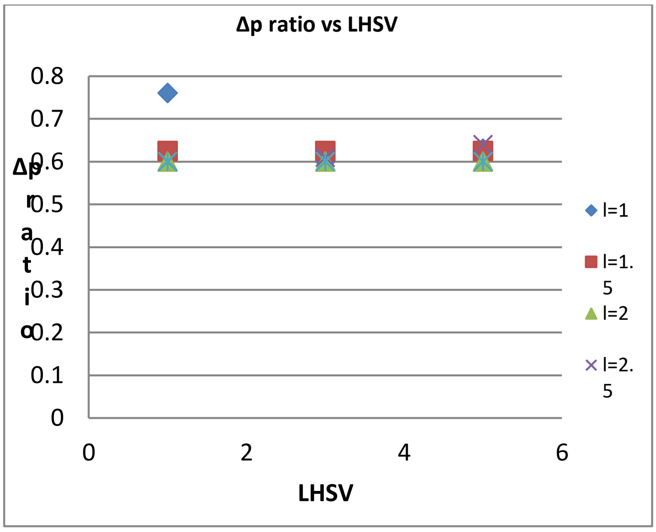

Fig 3.4 Mal distribution factor (Mf) Vs. LHSV at different bed lengths

Published By:
Blue Eyes Intelligence Engineering
and Sciences Publication (BEIESP)

3.3 Effect of pressure

While studying the effect of pressure in the range of (15, 20, 25 bar), other process parameters have been maintained at temperature (625 K), H_2/Naphtha (50Nm^3/m^3) and LHSV (1.0 hr^{-1}). The sulfur concentration has been considered as 1.23 wt%. It has been noticed from Fig.3.5 and Fig 3.6, that pressure has no effect on outer radius and it varied only with bed length. The mal distribution factor in all the cases is more than one which signifies the presence of mal distribution.

7u=

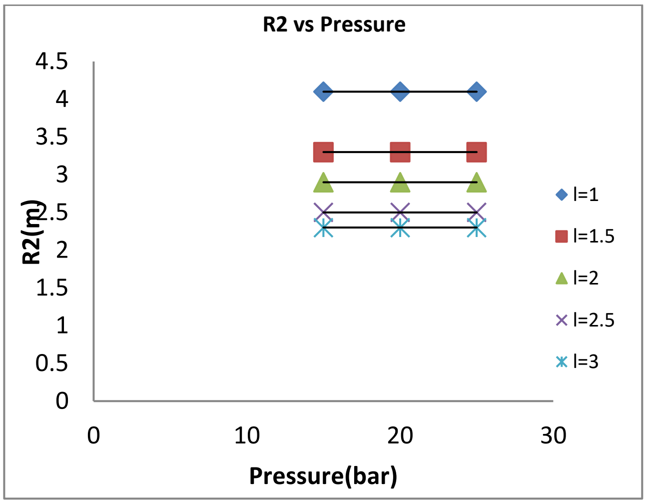

Fig 3.5 Variation of outer radius (R2) with Pressure at different bed lengths

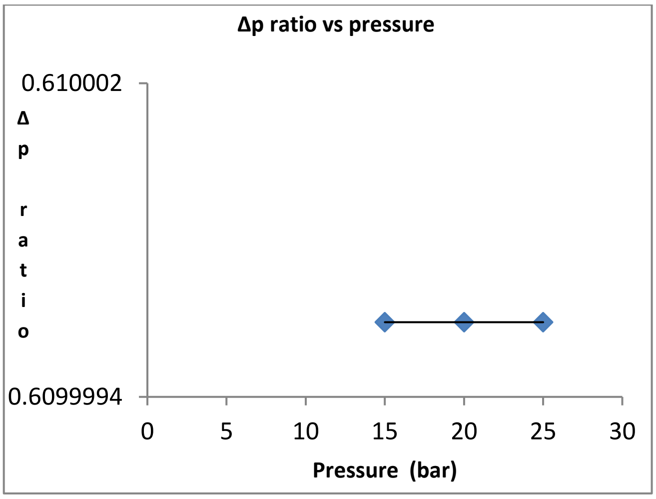

Fig 3.6 Mal distribution factor (Mf) Vs. Pressure at different bed lengths

3.4 Effect of H2/Naphtha ratio

While studying the effect of H2/naphtha ratio (50, 75,100 Nm^3/m^3), other process parameters have been maintained at temperature (625 K), pressure (20 bar) and LHSV (1.0 hr^{-1}). The sulfur concentration has been considered as 1.23 wt%. It has been noticed from Fig.3.7 and Fig 3.8, that H_2/Naphtha ratio has no effect on outer radius and it varied only with bed length. The mal distribution factor in all the cases is more than one which signifies the presence of mal distribution.

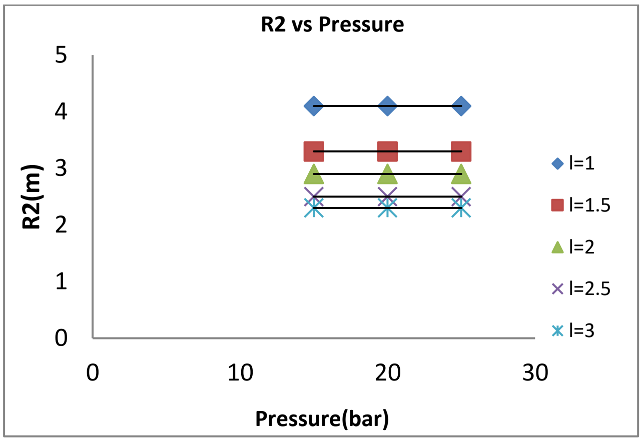

Fig 3.7 Variation of outer radius (R2) with Pressure at different bed lengths

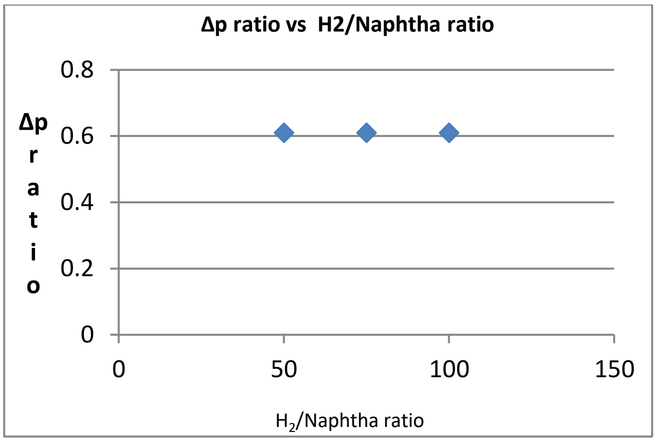

Fig 3.8 Mal distribution factor (Mf) Vs. Pressure at different bed lengths

3.5 Performance of Process parameters

The performance of radial flow reactor has been evaluated at the following parameters after studying their effect.

Temperature: 625 K; Pressure: 20 bar; LHSV: 1.0 hr^{-1}; H_2/Naphtha ratio: 50 Nm^3/m^3; S concentration: 1.23 wt%

At an outer radius of 3.5m at a bed length , conversion reaches to 100% (Fig 3.9) and temperature across the bed is around 630K (Fig 3.10)

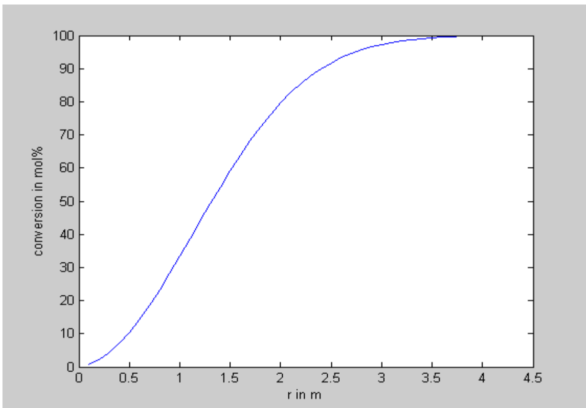

Fig 3.9 Conversion vs. Outer radius (R2)

Published By:
Blue Eyes Intelligence Engineering
and Sciences Publication (BEIESP)

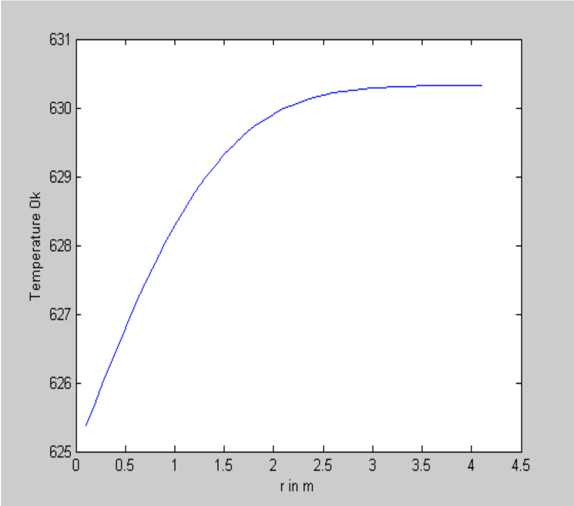

Fig 3.10 Temperature vs. Outer radius (R2)

It may be noticed from the velocity profile (Fig 3.11) that the mal distribution linearly increases along the radius.

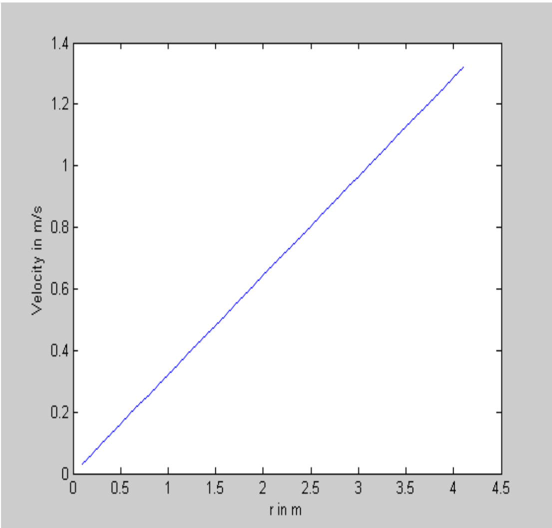

Fig 3.11 Velocity vs. Outer radius (R2)

IV. CONCLUSIONS

Radial flow reactors are used in catalytic reforming, isomerisation and hydro desulphurization processes. Compared to axial flow reactor, radial flow reactor offers less pressure drop, low fluid velocity, better fluid contact with catalyst. Radial flow reactors can be used at low LHSV values and can accommodate large amount of the catalyst at less pressure drop.

A mathematical model for centrifugal radial flow reactor for hydro desulphurization of naphtha was developed with kinetics available in the literature. The effect of the various process parameters on the outer radius at different bed lengths has been investigated.

It has been observed that pressure, temperature and H2/Naphtha ratios have marginal effect on outer radius and depends mainly on bed lengths. With increase in LHSV the outer radius decreases at all bed lengths. The mal distribution factor in all the cases is above one. It may be concluded that other geometric parameters such as open areas of outer basket and that of central pipe need to be looked for correcting mal distribution in radial flow reactors.

FUTURE WORK

Process parameters such as LHSV, Pressure, Temperature, H2/naphtha ratio has no effect on mal distribution. A flow dynamic model need to be developed and a study is required to investigate the geometrical parameters such as central pipe open area, outer basket open area, annular gap.

REFERENCES

1. Anshu Nanoti, Soumen Dasgupta, Vasudha Agnihotri, Pushpa Gupta, A zeolite based vapor phase adsorptive desulfurization process for naphtha based on Microporous and Mesoporous Materials 146 (2011) 158–165.
2. I.V. Babich, J.A. Moulijn, Novel processes for deep desulfurization of oil refinery streams based on Fuel 82 (2003) 607–631.
3. Jamal A. Anabtawi, Khurshid Alam, Mohammed A. Ali, Syed A. Ali, Performance evaluation of HDS catalysts by distribution of sulfur compounds in naphtha. Fuel Vol. 74 No. 9, pp. 1254-1260, 1995
4. Francisco Hernández-Beltrán, Juan Carlos Moreno-Mayorga, Roberto Quintana-Solórzano, Jaime Sánchez-Valente, Sulfur reduction in cracked naphtha by a commercial additive: effect of feed and catalyst properties. Applied Catalysis B: Environmental 34 (2001) 137–148.
5. Hui-feng Xue, Xiao-yun Zhang, Man-cang Liu, Zhi-de Hu, Simultaneous determination of major characteristic parameters of naphtha by capillary gas chromatography. Fuel Processing Technology 87 (2006) 303 – 308.
6. Changlong Yin, Genquan Zhu, Daohong Xia, A study of the distribution of sulfur compounds ingasoline fraction produced in ChinaPart 2. The distribution of sulfur compounds in full-range FCC and RFCC naphthas. Fuel Processing Technology 79 (2002) 135–140.
7. Georgina C. Laredo, José L. Cano, Carla R. López, Ricardo Saint Martin, Alternate use of heavy hydrotreatment and visbreaker naphthas by incorporation into diesel. Fuel Processing Technology 88 (2007) 897–903.
8. David J. Perez-Martinez, Pierre Eloy, Eric M. Gaigneaux, Sonia A. Giraldo, Aristobulo Centeno, Study of the selectivity in FCC naphtha hydrotreating by modifying the acid–base balance of CoMo-Al2O3 catalysts. Applied Catalysis A: General 390 (2010) 59–70.
9. R. Prins, M. Egorova, A. Ro¨thlisberger, Y. Zhao, N. Sivasankar, P. Kukula, Mechanisms of hydrodesulfurization and hydrodenitrogenation. Catalysis Today 111 (2006) 84–93.
10. Robert J. Angelici,An over view of modeling studies in HDS HDN. Polyhedron Vol. 16, No. 18, pp. 3073-3088, 1997.
11. P. Raje, Shuh-Jeng Liaw, Ram Srinivasan, Burtron H. Davis, Second row transition metal sulfides for the hydrotreatment of coal-derived naphtha I. Catalyst preparation, characterization and comparison of rate of simultaneous removal of total sulfur, nitrogen and oxygen. Applied Catalysis A: General 150 (1997) 297-318
12. Estrada-Villagrana, G.B. Quiroz-Sosa, M.L. Jim´enez-Alarc´on, Comparison between a conventional process and reactive distillation for naphtha hydrodesulfurization Chemical Engineering and Processing 45 (2006) 1036–1040.
13. C. Laredo, José L. Cano, Carla R. López, Ricardo Saint Martin, Alternate use of heavy hydrotreatment and visbreaker naphthas by incorporation into diesel Fuel Processing Technology 88 (2007) 897–903
14. Ali, SA; Siddiqui, MAB; Zaidi, SMJ Factors Influencing The Performance Of Naphtha Hydrodesulfurization Catalysts, PETROCHEMICAL INDUSTRIES 1995; pp: 225-234; Vol: 100.
15. Zuze Mu, Jinfu Wang, Tiefeng Wang, Yong Jin, Optimum design of radial flow moving-bed reactors based on a mathematical hydrodynamic model, Chemical Engineering and Processing 42 (2003) 409_/417. .
16. G. C. A. SCHUIT and B. C. GATES, Chemistry and Engineering of Catalytic Hydrodesulfurization. AlChE Journal (Vol. 19, No. 3) May, 1973 Page 417.
17. Calo,J.M., ‘Cell model studies of radial flow fixed bed reactors ‘ACS.Symp.ser ,65,550(1978).
18. Chang and J.M.Calo, radial flow reactors –how are they different. ACS.Symp.ser, 168,305(1981).

Published By:
Blue Eyes Intelligence Engineering
and Sciences Publication (BEIESP)

19. Chang and J.M.Calo, design criterion for radial flow fixed bed reactors. AICHE V 29,N6 ,(1983).
20. Dilman V.V., Sergeev S.P, and Genkin V.S. teor .osn.khim.Tekhol, 5(4) PP 564-571, (1971).
21. Dilman V.V., Sergeev S.P, and Genkin V.S. teor .osn.khim.Tekhol, 10 PP 626-629, (1976).
22. Dudukovic,M.P., and H.S.Lamba, Analysis of the radial flow fixed bed reactors 80th AICHE National meeting, Paper 576(1975).
23. Genkin,V.S., V.V. Diman and S.P. Sergeev, The distribution of a gas stream over the height of a catalyst bed in a radial contact apparatus. Int. Chem. Eng, 13(24),(1973).
24. Heggs, P.J, Ellis, D.I and Ismail M.S, The modeling of fluid flow distribution in annular packed beds, Gas Sep Purify 8, 25, (1994).
25. Heggs, P.J, Ellis, D.I and Ismail M.S, Prediction of flow distribution and pressure changes in multilayered annular packed beds. Gas Sep. Purify 243 (1995).
26. Lobanov, E.L and Yu. A. Skipin, Increasing the operating efficiency of radial reactors in reforming.Khimiya Teknologiya Topliv Masel, N6, PP 9_11, June (1986).
27. Macdonald, I.F, El-Sayed, M.S. MOW and Dullen , F. A. L. Flow through porous media – The Ergun equation revisited. Ind. Eng. Chem. Fundam, 18,199(1979).
28. Perry,R.H and Green, D. Chemical engg. Handbook 6th Edn. McGraw Hill, (1984).
29. Rase H.F, Fixed bed reactors design and diagnostics: Gas phase reactions, Butterworths, London, (1990).
30. Xuqi Song, Zhanwen Wang, Yong Jin and Mesishn Gong, Investigations on hydrodynamics of radial flow moving bed reactors .Chem .Eng. Technl, 16, pp 383-388(1993).

Published By:
Blue Eyes Intelligence Engineering
and Sciences Publication (BEIESP)