STEADY STATE MODELING AND SIMULATION OF HYDROCRACKING REACTOR

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Abstract

Hydrocracking has great importance in present day refining due to strict environmental and norms of quality of fuel. In recent years the demand for middle distillate and gasoline has increased tremendously while that of heavy gas has decreased. In the present work we have modeled and then applied five lump scheme to hydrocracker reactor. The first order kinetics was assumed for the conversion in the model developed and Pseudo components were used to simulate the model. The system is modeled as an isothermal tubular reactor with an axial dispersion, where the hydrogen flows upward concurrently with the oil while the solid catalyst particles stay inside the reactor in an expanded bed regime. MATLAB 7 was used to solve the model for a five lump scheme for different values of liquid superficial velocity, reactor length and temperature.

Keywords: Five lump; reactor; simulation; hydrocracking.

1. Introduction

Catalytic cracking is the conversion of large molecular weight hydrocarbons to smaller molecular weight hydrocarbons in presence of catalyst. Two types of catalytic cracking units are used in petroleum refinery. These are Fluid catalytic cracking (FCC) and Hydrocracking. In comparison between fluid catalytic cracking & hydrocracking units, products from FCC contain large quantity of sulphur. Coke deposition occurs on the catalyst surface in FCC unit. However hydrocracking deals with hydrogenation, coke does not deposit on catalyst. Hydro-cracking is two stage catalytic process. Two types of reactions occur in hydrocracking. These are cracking and hydrogenation reactions. Mohanty et. *al.* [7] described the kinetics and reactor modeling of hydrocracker. Generally two type of modeling are used for hydrocracking (Reactor Modeling and kinetic modeling). Kinetic modeling is used to predict kinetic aspects and mechanism of the reaction and Reactor modeling is used to measure the product distribution in a hydrocracker. Govindhakannan et. *al.* [4] described the kinetic modeling methodologies. The kinetic modeling methodologies can be classified in two categories (lumped modeling and mechanistic modeling). In the lumped modeling, actual reaction network is divided into few equivalent independent classes from the lumped species. These lumps can vary by changing the types of compounds, which are present in feedstocks and products. Mechanistic modeling is used for actual chemistry of cracking. Klein et. *al*. [10] discussed about mechanistic modeling

The reactor considered in this work is an isothermal tubular reactor with excess hydrogen in (gas phase) flowing concurrently upward with heavy oil (liquid phase) while the catalyst (solid phase) remains inside the reactor in an expanded bed regime (confined bed). The hydro-cracking reactions can be mainly thermal Mosby et al. [8] or catalytic Krishna and Saxena et al [11] depending on the catalyst being used and the operating conditions. In thermal hydro-cracking the catalyst is used for other reactions, such as hydrodemetallation and removal of other heteroatoms. The description of the concentration profiles in this process may be useful for future work in the field of design, optimization and control of hydroprocessing reactors.

2. Mathematical modeling of hydrocracking reactor

Fixed bed trickle flow reactor is used in the hydrocracking of heavy gas oil. The reactor model is based on following assumptions:-
a) Operation is at steady state.

b) Flow pattern in the trickle flow reactor is plug flow type.
c) Heat losses are negligible and commercial reactors operate under isothermal conditions.
d) Rates of reaction are independent of hydrogen as it is present in excess.
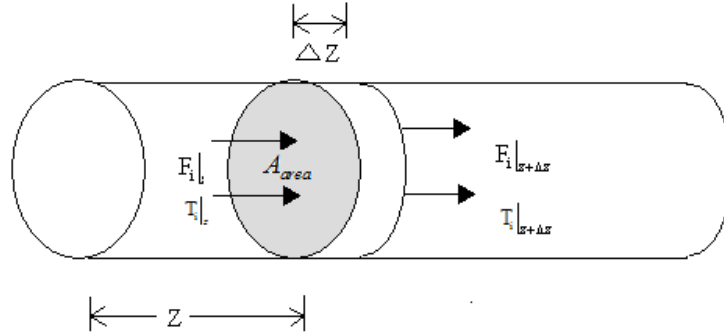e) Concentration varies only with variation of axial distance.

Fig. 1 Schematic diagram of reactor

Mass balance

IN (at particular z location) – OUT (at z+Δz) + NET GENERATION (REACTION) = ACCUMULATION

$$\text{Area} * F_{I,Z} - \text{Area} * F_{I,\, z+\Delta z} + \Sigma\, r_{f}* p * \text{Area} * \Delta z - \Sigma\, r_{d} * \text{Area} * \Delta z = 0 \quad I = 1 \text{ to } 5 \qquad (1)$$

Dividing by **Area** $* \Delta z$ and taking limit $\Delta z \sim 0$;

$$(\partial F_I / \partial Z) + P * (r_f - r_b) = 0 \qquad (2)$$

$$F_{I,Z} = - \varepsilon * D_{I,J} * (\partial C_I / \partial Z) + y_I * (W_{I,Z} + W_{I,J}) \qquad (3)$$

$$U * C_I = y_I * (W_{I,Z} + W_{I,J}) \qquad (4)$$

As the reaction kinetics is assumed to be first order,

$$r_{f,I} = K_{f,I} * C_I \qquad (5)$$

$$r_{d,I} = K_{d,I} * C_I \qquad (6)$$

By overall balance, we get

$$\varepsilon * D_I * (\partial^2 C_I / \partial^2 Z) - U * (\partial C_I / \partial Z) + \Sigma\, P * \varepsilon * (K_{f,J} * C_J - K_{d,I} * C_I) \qquad (7)$$

3. Model validation

3.1 Kinetic network

General five lump kinetic scheme was applied to validate the reactor model. Heavy oil was taken as feed to this reactor model containing products in small quantities. Feed is converting in to gases, naphtha, middle distillates and vacuum oil.
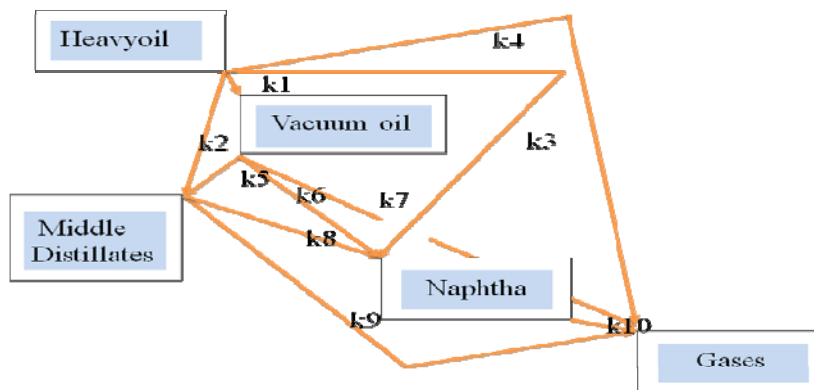

Fig. 2 Five lump kinetic scheme

In the feed the mass fraction of heavy is 0.9 was other species was taken as 0.025.The values of kinetic constants at different temperatures of operating range ie, 370°C to 430°C was taken from Sanchez et al [9].

Table 1 Kinetic constant at different temperatures [9]

Rate constant	Temperature, ($^{\circ}$C)							Ea (kcal/ mol)
	370	380	390	400	410	420	430	
k1	0.02485	0.045248	0.080914	0.142215	0.245865	0.418394	0.701303	50
k2	0.00671	0.011438	0.019188	0.031696	0.051594	0.082812	0.131141	44.5
k3	0.006073	0.0096	0.014966	0.023026	0.034984	0.052513	0.077919	38.2
k4	0.031956	0.044486	0.061314	0.083706	0.113239	0.15186	0.201962	27.6
k5	0.01411	0.022817	0.036367	0.057166	0.088678	0.135827	0.205538	40.1
k6	0.002192	0.003436	0.005313	0.00811	0.012227	0.018218	0.026837	37.5
k7	0	0	0	0	0	0	0	0
k8	0.001461	0.002798	0.005253	0.009681	0.017524	0.031183	0.054586	54.2
k9	0	0	0	0	0	0	0	0
k10	0	0	0	0	0	0	0	0

3.2 Dimensionless variables

The mathematical equation for the reacting species given by equation 7 was transformed into the following equation by introducing various dimensionless variables.

$$(\partial^2 \varphi_I / \partial^2 x) * \frac{1}{P} - U*(\partial \varphi_{,I} / \partial x) + \sum P * (\varepsilon * L/U)*(Kf_{,J} * (C_{J,0}/ C_{I,0}) * \varphi_J - K_{d,I} * \varphi_I) = 0 \quad (8)$$

The following boundary conditions were assumed;

$\varphi = 1$ $\forall$ I,J   at x = 0   (9)
And $(\partial \varphi_{,I} / \partial x) = 0$; at x=1; which means neglecting variations at exit   (10)
where:
P = Peclet number; φ_I(dimensionless concentration) = $C_I / C_{I,0}$, x (dimensionless distance) = Z/L.

4. Mathematical solution

The equation 8 was applied to all five species namely heavy gas oil, vacuum gas oil, middle distillate, naptha and gases resulting in 5 simultaneous ordinary differential equation of order 2. The equations were reduced to first order differential equations by taking first derivate as a new variable. It resulted to 10 simultaneous ordinary differential equation of order 1. The equations were simulated in MATLAB 7 for different values of length of reactor, temperature and space velocity using Range-Kutta 4th order solution method.

5. Results

The model equations for solved for different values of temperature which is indicated by figure 1 to 4 at superficial velocity of 0.864 m/hr. It can be clearly seen that heavy oil conversion increases by increase in temperature while that of middle distillate increases sharply with increase in temperature.
The length of the reactor was also varied between 1.8 m to 2.4 m to check the concentration profile of various species. Residence time increases by increasing the length of reactor , so conversion of heavy gas oil increased which is clearly indicated by figure 5 to 7 The model equation were also solved for different values of superficial velocities ranging between 0.576 m/hr to 0.864 m/hr .
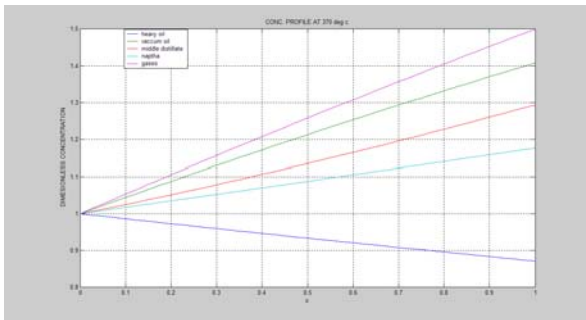
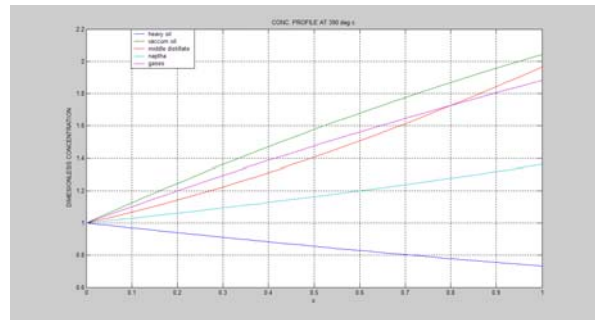Fig.1 Concentration profile at 370°C for different reacting species

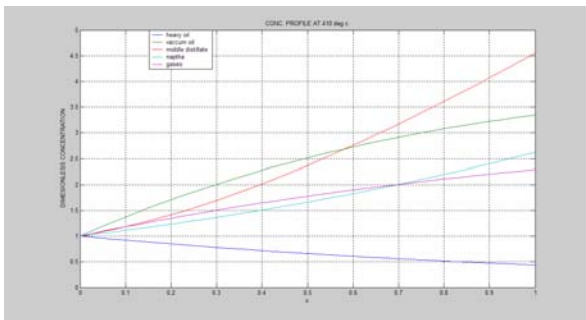Fig. 2 Concentration profile at 390^{0}C for different reacting species

Fig. 3 Concentration profile at 390°C for different reacting species
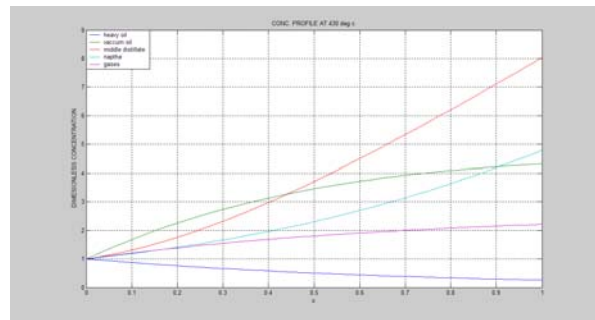

Fig. 4 Concentration profile at 430^{0}C for different reacting species
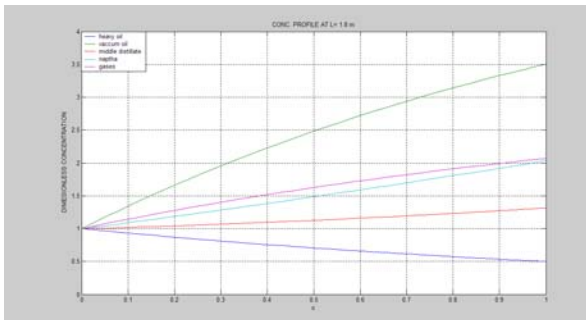

Fig. 5 Concentration profile at L=1.8 m & U=0.864m/hr for different reacting species
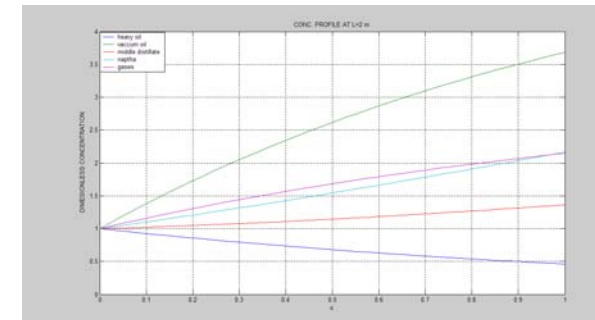

Fig. 6 Concentration profile at L=2 m & U=0.864m/hr for different reacting species
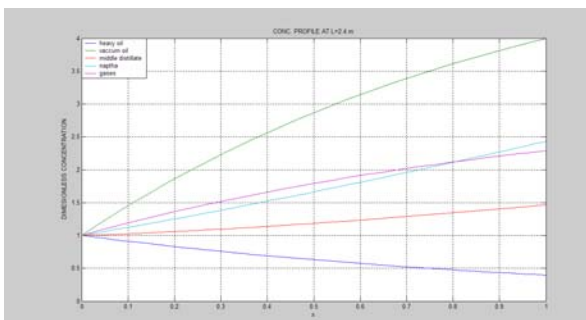

Fig. 7 Concentration profile at L=2.4 m & U=0.864m/hr for different reacting species
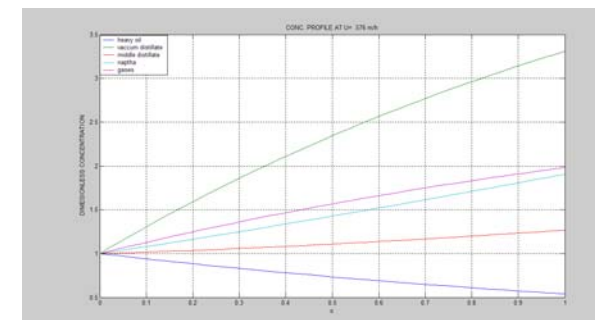

Fig. 8 Concentration profile at L=2 m & U=0.576 m/hr for different reacting species

Conversion of heavy gas oil to various products was higher at lower a superficial velocity which is shown by figure 8 to 10. There was predominant increase in concentration of vacuum distillate.
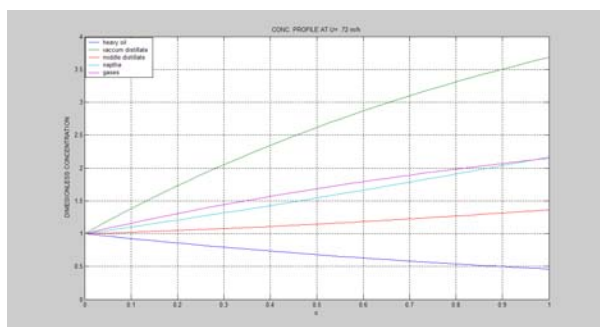
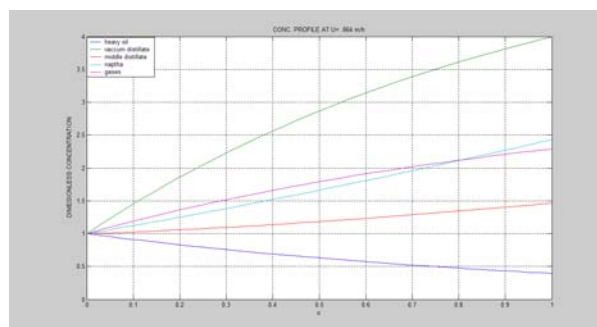Fig. 9 Concentration profile at L=2 m & U=0.72 m/hr for different reacting species

Fig. 10 Concentration profile at L=2 m & U=0.864m/hr for different reacting species

6. Conclusion

In the hydrocracking unit, simulation of the model is extremely difficult. By using lumped scheme technique, model can be simulated easily. Lumping shows very typical reaction pathways. The results can be used in future work in optimizing hydrocracking reactor. This work can be extended to unsteady state analysis of reactor. This model was solved by assuming that reactor was isothermal, so this work can be extended to thermal analysis.

Notations:

C_I concentration of lump I , mol/m^3
$C_{I,0}$ initial concentration of lump I , mol/m^3
C_J concentration of lump I , mol/m^3
$C_{J,0}$ initial concentration of lump I , mol/m^3
D axial dispersion coefficient, m^2/hr
k_1 First-order rate constant for the hydrocracking of heavy oil to vacuum oil (hr^{-1})
k_2 First-order rate constant for the hydrocracking of heavy oil to middle distillates (h^{-1})
k_3 First-order rate constant for the hydrocracking of heavy oil to naphtha (hr^{-1})
k_4 First-order rate constant for the hydrocracking of heavy oil to gases (hr^{-1})
k_5 First-order rate constant for the hydrocracking of vacuum oil to middle distillates (hr^{-1})
k_6 First-order rate constant for the hydrocracking of vacuum oil to naphtha (hr^{-1})
k_7 First-order rate constant for the hydrocracking of vacuum oil to gases (hr^{-1})
k_8 First-order rate constant for the hydrocracking of middle distillates to naphtha (hr^{-1})
k_9 First-order rate constant for the hydrocracking of middle distillates to gases (hr^{-1})
k_{10} First-order rate constant for the hydrocracking of naphtha to gases (hr^{-1})
K_f constant of reaction for formation, 1/hr
K_d constant of reaction for dissociation, 1/hr
P   Peclet number
L   length of reactor, m
U   superficial velocity, m/hr
ρ bulk density, (g/cm^3)
ε liquid hold up
z   axial distance, m

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