Kinetic Modeling and simulation of Hydrocracking Process

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Introduction

In Petroleum refining industry, Hydrocracking process is one of the most widely used processes for upgrading heavy feedstocks produced in upstream processing units due to its flexibility in terms of operating conditions and wider product spectrum. Kinetic modeling of this process is of paramount importance for simulation, optimization of operating variables and catalyst design .In this work , rate equations are derived using LHHW model based on fundamental mechanism proposed by Froment et al and those are coupled with continuity equations and plugged in to simplified pseudo homogeneous 1-D model by keeping the actual mechanism of the reaction intact. Therefore the concentration, temperature and pressure profiles obtained are quite consistent and in qualitative agreement with the actual industrial profiles.

Kinetic Modeling

Hydrocracking catalysts are dual function and contain a well dispersed metal in pores of acidic support material. The relative strength of two functions determines the nature and distribution of products. When a strong hydrogenation function such as Pt used, high hydroisomerisation and hydrocracking selectivities are obtained. At low temp. and high pressures hydroisomerisation yield is a unique function of total conversion and molar distribution of cracked products is symmetrical. This phenomena is termed as “ ideal cracking” , whereas at high temp. and lower pressures isomerisation is no longer unique function of total conversion and effect of operating variables reversed, which is termed as “non ideal cracking”.

Kinetic models of hydrocracking process can be categorized as : Lumped semi empirical models developed mainly by Mobil oil (Jaffe et al) and fundamental kinetic models by Froment et al. In early seventies, Mobil made first effort and developed a simple model containing three pseudo components : Gasoline, Gas oil and light gases, which was later refined in to 10 lumps defined on basis of physical properties like boiling point range. The limitation of these lump models is rate parameters vary with the type of feed and configuration of reactor. So extensive experimentation is required for each component if feed is a complex mixture of hydrocarbons. Therefore rate parameters increase rapidly with no. of lumps. Hence, requirement of a fundamental kinetic model arose, which can reflect actual mechanism keeping no. of rate parameters tractable.

Fundamental kinetic model

Froment and coworkers developed first such model in 1981 based on experimental evidence and well known carbenium ion chemistry principles. Hydrocracking has been described as a consecutive steps of hydroisomerisation and hydrocracking on acid sites.

The overall Hydrocracking reaction for a single n-alkane into two iso alkanes can be represented as :

$$\text{n-A} + H_2 \rightarrow \text{i-A}_1 + \text{i-A}_2$$

It is well understood that Hydrocracking proceeds through physisorption in zeolite pores then dehydrogenation on the metal sites of the bifunctional catalysts followed by protonation on acid sites. The carbenium ions thus formed then undergo isomerisation and β-Scission followed by deprotonation and hydrogenation.

The detailed seven step mechanism can be written as:

$$A(g)+S \Leftrightarrow AS \qquad \text{...Adsorption}$$
$$AS \Leftrightarrow BS+H_2(g) \qquad \text{...Dehydrogenation}$$
$$BS+H^+ \Leftrightarrow R^+S \qquad \text{...Protonation}$$
$$R^+S \Leftrightarrow iR^+S \qquad \text{...Isomerisation (RDS)}$$
$$iR^+S \Leftrightarrow CS+H^+ \qquad \text{...Deprotonation}$$
$$CS+H_2 \Leftrightarrow iAS \qquad \text{...Hydrogenation}$$
$$iAS \Leftrightarrow iA(g)+S \qquad \text{...Desorption}$$

Where, A & iA represents alkane and iso-alkane respectively. Whereas, B & C are alkenes and R^+ & iR^+ represents carbenium ions. Vacant site is denoted by S.

Kinetic studies with n-Octane shows that conversion of n-octane decreases with increase in total pressure and/or decrease in temp. and is almost independent of partial pressure of n-octane. This observation implies that H/C must reach equilibrium concentration in zeolite pores gives nearly zero order dependence with respect to H/C conc. in the rate expression. Weitkamp earlier showed that Hydrocracking proceeds by formation of carbenium ions on acidic sites on zeolites from the protonation of olefins produced by strong hydrogenation/dehydrogenation selective metal sites.

Experimentally, It has been proved that isomerisation step is quite slower than other De(hydrogenation) and (De)protonation steps and they can essentially be assumed into equilibrium. This assumption is also confirmed by the fact that the overall rate is independent of partial pressure as only this assumption leads to final rate expressions which shows this kind of behavior consistent with experimental data. Activation energy for all reactions are same since product distribution as a function of total conversion is unique .In other words it is independent of temperature.

To arrive at a kinetic model two relations are required :

1.An expression for physical adsorption isotherm relating concentration within the zeolite pores to the partial pressure in gas phase

2. Expression for overall reaction rate in terms of H/C concentration in zeolite pores.

It is well established fact that langmuir isotherm combined with Hougen-Watson catalytic kinetics is most consistent with the surface chemistry compared with Freundlich and BET isotherms and successfully applied to numerous industrial catalytic processes. Therefore in this paper, final rate equations are derived using LHHW model and surface isomerisation reaction on acid sites as rate determining step :

$$r = \frac{k_1 c_t K_{DH} C_{AS}}{P_{H_2} + \left(1 + \frac{1}{K_i}\right)\frac{K_{iA}'}{K_{HA}} C_{iAS} + \sum_j \frac{K_j'}{K_{Hj}} C_{jS}}$$

Where,

k_1 = forward rate coefficient of isomerisation step

c_t = total concentration of active sites

K_{HA} = Hydrogenation equillibrium constant

K_{iA}' = chemisorption equilibrium constant of deprotonation

C_{jS} = concentration of physically adsorbed species j

Langmuir Isotherm :

$$C_{AS} = \frac{c_{Sat} K_{LA} P_A}{1 + K_{LA} P_A + \sum_i K_{Li} P_i}$$

c_{Sat} = saturation concentration of A in zeolite pores

P_i = partial pressure of i

K_{Li} = Langmuir constant of species i

Combining both equations

$$r = \frac{k_1 C_t^{'} K_{DH} K_L C_{Sat} P_A}{\left[P_{H_2} (1 + K_L P_A + \sum_i K_{Li} P_i) + (1 + \frac{1}{K_i}) \frac{K_{iA}^{"}}{K_{HA}} P_i + \sum_j \frac{K_j^{"}}{K_{Hj}} P_j \right]}$$

When $C_t >>> C_{R^+}$ we can write above experession for reversible reaction for isomerisation of A into lump B in simplified form of lumped (overall) parameters

$$r = \frac{k(P_A - \frac{P_B}{K})}{P_{H_2} (1 + K_{LA} P_A + K_{LB} P_B)}$$

where, A subscript denotes Alkane and B denotes its branched isomer lump.

Overall Mechanism

Overall reaction scheme can be derived from certain experimental evidence.

1. At low conversions, until concentration of Multibranched isomers **(MTB)** is not high enough, cracking does not takes place
2. Concentration of Monobranched **(MB)** paraffins initially increases and then decreases
3. Concentration of MTB paraffins monotonously increases
4. Isomers within the same family are in equilibrium distribution that means we can lump all isomers within same family

These facts prove that nA-MB-MTB isomerisation are consecutive reactions and Cracked products produced from MTB isomers leads to following mechanism:

$$nA \xleftrightarrow{r_1} MB \xleftrightarrow{r_2} MTB \xrightarrow{r_3} CR$$

$$r_1 = \frac{A_1 e^{-\frac{E}{RT}} (P_A - \frac{P_{MB}}{K_1})}{P_{H_2}[1+K_L(P_A + P_{MB} + P_{MTB})]}$$

$$r_2 = \frac{A_2 e^{-\frac{E}{RT}} (P_{MB} - \frac{P_{MTB}}{K_2})}{P_{H_2}[1+K_L(P_A + P_{MB} + P_{MTB})]}$$

$$r_3 = \frac{A_3 e^{-\frac{E}{RT}} (P_{MTB})}{P_{H_2}[1+K_L(P_A + P_{MB} + P_{MTB})]}$$

Simulation of Hydrocracking Process

Industrial Hydrocracking process is carried out in fixed bed catalytic reactors at 200-400 ^{o}C and 80-150 atm. Catalysts used are either amorphous alumina / silica or zeolites with metal component either of Ni/Pt/Pd/W/Mo. The above derived model now can be combined with material, energy and momentum balance to simulate process. Commercial units are either three phase (H_2 in gas phase and H/C in liquid phase) or two phase (both H_2 and H/C in gas phase) reactors. In this work, I am simulating later one as kinetic data is easily available and also it is easy to deal with continuity equations.

Continuity equations

$$u\frac{dP_A}{dz} = (-r_1)\rho_b RT$$

$$u\frac{dP_{MB}}{dz} = (r_1 - r_2)\rho_b RT$$

$$u\frac{dP_{MTB}}{dz} = (r_2 - r_3)\rho_b RT$$

$$u\frac{dP_H}{dz} = (r_2 - r_3)\rho_b RT$$

$$\frac{dT}{dw} = \frac{(\frac{4U}{\rho bD})(T_r - T) + \sum_i [(-r_i)(-\Delta H_i(T))]}{F_{Ao}(\sum_i \Theta_i Cp_i + X\Delta C_p)} \quad ; \; w = A_c(1-\varphi)z$$

$$\frac{dP}{dz} = -\frac{(1-\varphi)G}{\rho(\frac{P}{Po})(\frac{To}{T})D_p\varphi^3}\left[\frac{150(1-\varphi)\mu}{D_p} + 1.75G\right] \quad ; G = \frac{\Sigma F_{io}M_i}{A_c}$$

Where,

r_i = rate of reaction i in overall mechanism

ρ_b = Bulk density of catalyst

D_p = Equivalent Diameter of catalyst particle

φ = Void Fraction

A_c = C/S area of catalyst bed

ΔH_i = Heat of reaction i

Cp_i = Heat capacity of component (lump) i

F_{Ao} = Initial molar flow rate of n - alkane feed

Θ_i = ratio of initial molar flowrate of i to alkane feed

μ = Viscosity of gas

U = overall heat transfer coefficient

T_r = Reference temperature

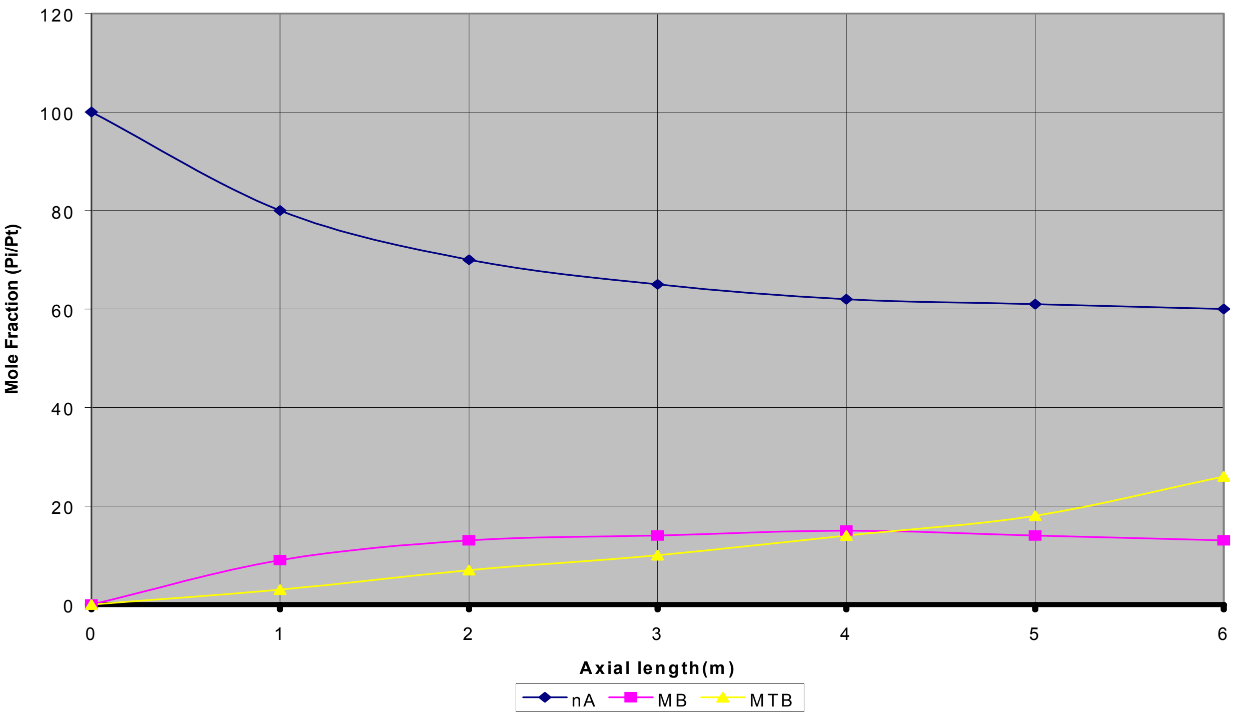
P_o, T_o, F_{io} = Reactor inlet conditions

Assumptions

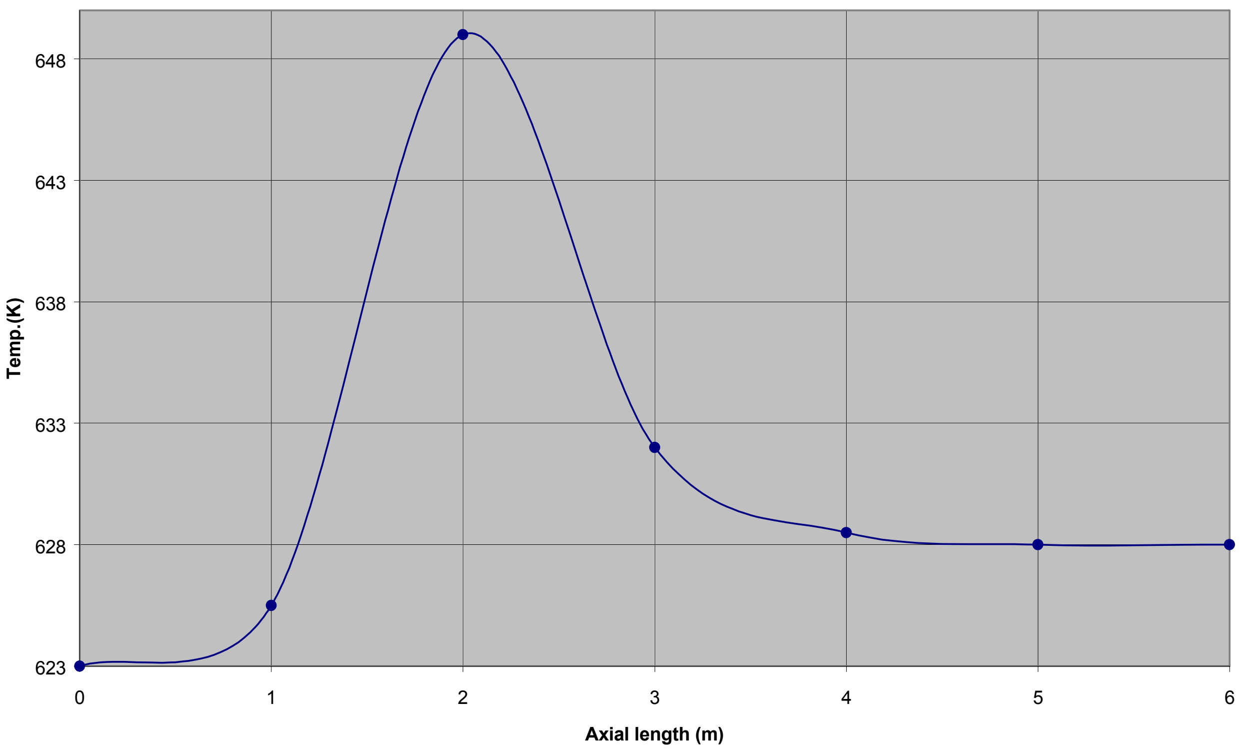
1. At first attempt, for the sake of simplicity, 1-D pseudo homogeneous model is chosen. In future work, Heterogeneous model can be used to get better simulation results.
2. Flow behavior of gas through catalyst bed (pressure drop calculations) is modeled by ergun equation which is the most reasonable flow model through packed beds. Radial variations and axial mixing is neglected.
3. All isomers within the same family are taken as a lump which is very valid assumption for the reasons described earlier.
4. Void fraction and bulk density of catalyst (in turn superficial velocity) is assumed constant throughout the bed.
5. Activation energies of isomerisation and cracking are taken equal which is very much valid as product distribution as a function of total conversion is independent of temp.
6. The equilibrium constants of reactions are calculated from thermodynamic data.

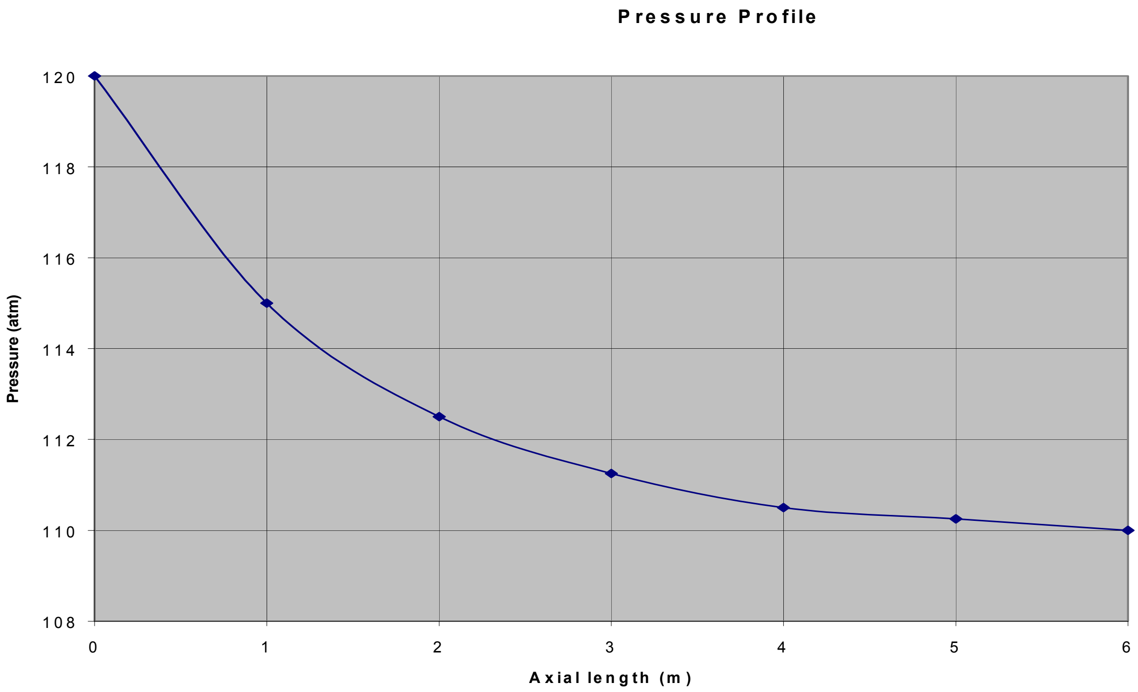
The catalyst here used is Pt / Ultra Stable Y zeolite having $\phi = 0.5$ and $\rho_{b} = 1200$ kg/m^3 . Figure shows Concentration profiles feed, branched isomers and hydrogen along the length of reactor. As can be seen MB concentration first increases and then decreases while MTB concentration monotonously increases which is consistent with consecutive step mechanism at low conversions . Adequate heat transfer area should be provided to keep ΔT less than limiting temp. rise of 35 K to avoid hot spot formation and production of unwanted lighter components due to secondary cracking (In our results which is 26 K well below 35K). We have got appx. 10 atm pressure drop which is quite near to observed 12-16 atm in industrial units.

Concentration Profiles



Axial Temepratrure Profile





Conclusion

A Fundamental kinetic model in terms of four lumps has been developed based on experimental data and well known principles of carbenium ion chemistry by Froment et al. Based on this mechanism and LHHW model , Rate equations are derived by assuming Isomerisation step on acid sites as a rate determining step (RDS). Equilibrium constants are calculated from thermodynamic data and activation energies and frequency factors are taken from literature. Derived kinetic model substituted in to 1-D pseudo homogeneous model to simulate process. Simulated results are quite consistent with actual profiles.