Study of Modeling Approach for Fluid Catalytic Cracking Riser Reactor Using Pseudo Component Reaction Kinetics

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Abstract: Fluid catalytic cracking modeling and simulation are based upon different kinetic modeling .The kinetic models are classified on the basis of chemical entities. The entities are   "lumps" based on boiling point , chemical type and structured oriented lumping . Boiling point based lump models are easy to simulate because they have less complexity and required least amount of data, where as chemical type and structured based modeling require detail analysis of feed and data to calibrate the kinetic parameters. Pseducomponents based modeling approach for the kinetic parameter estimation, eliminates the need for determining a large number of rate constant required in conventional lumped models. Kinetic model play a important role in effective simulation of fluid catalytic cracking Most of the experimental works are limited to micro activity test (MAT) reactor. Due to poorly defined reaction mechanism, scale up from laboratory result to industrial scale is not possible. Major drawback lies in the single-event reaction mechanism being used for modeling/analysis of FCC kinetics. By using a new concept of pseudo-kinetic reaction mechanism better predictability of yield can be obtained if proper hydrodynamic model is used.

Key Words: *Fluid Catalytic Cracking, Kinetic Model, Kinetic parameters, pseducomponents.*

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1. INTRODUCTION

The selection of kinetic scheme is important in modeling of FCC. FCC feedstock's contain thousands of chemical species with a wide distribution of boiling temperatures[1-3]. The cracking of gasoline range hydrocarbons include a quite wide distribution of molecular weights, from C_1 to C_{20}. The multi component mixtures make the kinetic of FCC complex. To overcome this complexity alternative approach has been used considering lumped kinetic schemes. The kinetics modeling of catalytic cracking has based on using a lumping strategy: chemical species with similar behaviors are grouped together forming a smaller number of "pseudo" species. The "lumps" are boiling point lump or yield lump, which the refiner collects from the main fractionators following the FCC unit[4-6].

In general, there are two basic techniques in lumping the catalytic cracking of Vaccum Gas oil (VGO). The first method is to lump molecules in different distillation cuts "pseudo-species" and to consider chemical reactions between these lumps[7]. These lumps are usually the feedstock and the final cracking products, like gasoline, Light Cycle oil (LCO), light gases, and coke. The second approach is to lump different products based on main chemical families such as paraffins, olefins, naphthenes, and aromatics. With this approach important reaction data such as the reaction type (cracking, hydrogen transfer, or condensation) and stoichiometry can be included[8-9].

In the first three lump kinetic model proposed by Weekman(1968),the charge stock & products divided into three components namely, the original feedstock, the gasoline, and the remaining C4 's (dry gas & Coke).Yen and Woei (1988) and Lee et al (1989) developed a four lump kinetic model by dividing the light gas plus coke lump into two different lumps C_1-C_4 gas and coke. The yield of C_1-C_4 gas increases with increasing reaction temperature at the expense of the yield of gasoline and coke. In the advanced models of FCC riser model, three lump or four lump kinetic schemes are being generally used to avoid the mathematical complexities and load of computation that will be there if more number of lumps are considered.

More detailed kinetic schemes were presented by various researchers. Corella and Frances(1991) developed a 5-lump models ,in which the gas-oil lump was divided into its heavy and light fractions. Dupin et al (2006) simplified the 5-lump model of Corella and Frances for the specific case of the catalytic cracking of aromatic gas oil, by reducing the reactions involved in the lumping scheme. Another 5-lump model was developed by Larocca et al (1990) in which the 3-lump model of Weekman was modified by splitting the gas oil lump into aromatic, paraffinic and naphthenic lumps. Ancheyta et al (1999)followed a different approach in their 5-lump models development, in which they considered the gas oil as one lump, but divided the gas lump into two lumps liquefied product gas and dry gas. Takatuska et al used a six lumps

model including the heavy feedstock (vacuum reside), the vacuum gas oil (VGO) and the heavy cyclic oil (HCO), the light cyclic oil (LCO), the gasoline, the light gases, and the coke. Hagelberg et al (2002) expanded the 5-lump model of Anchetya –Jurez et al (1999) to an 8-lump model by dividing the gasoline fractions into paraffins, olefins, naphthenes and aromatics. A new reaction kinetic model was developed by Jacob et al by dividing the feed and products into a 10- lump reaction schemes including paraffins, napthenes, aromatic rings and aromatic substituent groups in light & heavy fuel oil fractions. The light lump refers in the boiling range between 221 & 343 ^{o}C, whereas heavy lump refers boiling point above 343 ^{o}C.[10] The new model considered the feed properties in addition to the boiling range. The advantage of this lumped model is that the composition of lumps can be measured with various experimental techniques. The rate constant which arises from the use of model are less sensitive to changes in feed and process conditions. With increase in number of lump, the requirement of cracking constant increases rapidly. These lumps are to be characterized as an indicator of the feedstock composition.

Pitault at al., proposed a model where lumps were classified by chemical family (e.g. paraffins, olefins, naphthenes, and aromatics) and molecular weight or boiling range. This approach was applied to the light gases, gasoline, LCO and feedstock cuts. It has to be emphasized that this model has the flexibility of being able to include important reactions like coking and hydrogen transfer.

Many researchers have developed complex reaction schemes based on basic chemical principles that involves thousands of chemical species. These can be classified into mechanistic models and pathway models. Mechanistic model track the chemical intermediates, such as ions and free radicals ,that occur in the catalytic FCC process. Froment and co-workers proposed single event models involving a detailed description of VGO catalytic cracking. This model considered, between other factors a mechanism including carbenium ions. However, the second generation of FCC models had many drawbacks given the extensive computational calculations due to large size and reaction complexity. A relatively new method ,called structure-oriented lumping(SOL),pathway based model ,for describing the composition ,reactions and properties of complex hydrocarbon mixtures has been developed by Quann and Jaffe(1992). The model tracks different compositional and structural attributes of a molecules(number of aromatic rings, number of nitrogen substitutes, sulfur substituent's, etc.) in a vector format[10].

2. Various Modeling Approaches
2.1 The Three Lump Model

The three lump model consists of one a feedstock lump (gas oil, VGO or any other heavy feed) and two product lumps: a) gasoline b) coke + light gases. The gasoline lump contains the fraction between C_5 up to the hydrocarbons with a 220°C boiling temperature. The coke + light gases lump contains in addition to coke, C_4 and lighter than C_4 hydrocarbons. This model can be represented as follows:
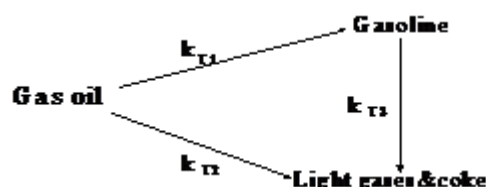

Fig:1 The Three lump model.

The reaction order assigned to the three lumps based on the crack abilities of different lump pseudospecies. The feedstock (VGO or gas oil) contains a mixture of several thousands compounds of widely different properties, the cracking of gas oil is of second order reaction considered[11]. However, since gasoline contains a restricted range of molecular weight hydrocarbons (C_5 to C_{12}), it was argued that a first order should be given to the gasoline cracking (Weekman and Nace; 1970).

Based on these assumptions the following equations can be considered:

a-) gas oil cracking can be represented as;

$$-r_{go}=k_{T0}\,\varphi_1\,C_{go}{}^2 \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\text{(i)}$$

b-) gasoline formation can be modeled as;

$$r_g=k_{T1}\,\varphi_1\,C_{go}{}^2 - k_{T3}\,\varphi_2\,C_g \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\text{(ii)}$$

c-) light gases and coke can be represented as;

$$r_C=k_{T2}\,\varphi_1\,C_{go}{}^2 + k_{T3}\,\varphi_2\,C_g \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\text{(iii)}$$

k_{T1}, k_{T2}, k_{T0}, k_{T3} represent the gasoline formation rate constant, the coke and gases formation rate constant, the overall VGO cracking rate constant, and the gasoline overcracking rate constant respectively (Nace et al., 1971). $\varphi =$ Catalyst decay function

2.2 The Four Lump Model:

In 1987, Yen et al. introduced the four lump model splitting the light gases + coke lump in two separate lumps: a) coke and b) light gases. These authors used a second

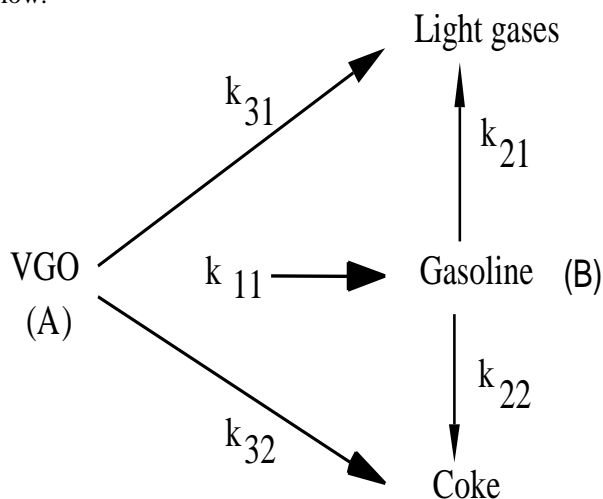order reaction for VGO cracking. A four lump model given below:

Fig:2. Four Lump model

where the rates of gasoline formation and gasoline consumption were described as,

a-) gas oil consumption rate

$$-r_{go} = k_{11}\varphi C_{go}^{2} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (iv)$$

b-) gasoline formation rate

$$r_{g} = k_{11}\varphi C_{go}^{2} - \varphi(k_{21} + k_{22})C_{g} \dots\dots\dots\dots\dots\dots\dots\dots (v)$$

c-) light gases formation rate

$$r_{lg} = k_{31}\varphi C_{go}^{2} + k_{21}\varphi C_{g} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (vi)$$

d-) coke formation rate

$$r_{c} = k_{32}\varphi C_{go}^{2} + k_{22}\varphi C_{g} \dots\dots\dots\dots\dots\dots\dots\dots\dots (vii)$$

k=rate constant , φ=decay of catalyst activity   The overall cracking rate is affected by the catalyst activity[12-13], its effect can be incorporated by considering the deactivation model of the Weekman. In this respect, Weekman (1968) employed to describe catalyst deactivation, the following two simple relations;

a)- exponential decay law

$$\varphi = \exp(-\alpha t)$$

…………………………………………………………………………………………..(viii)

b)- power decay law

$$\varphi = t^{-n}$$

…………………………………………………………………………………………(ix)

where t represents catalyst time-on-stream, α(catalyst decay coefficient) and n are rate constants of the catalyst decay

function. α the catalyst decay coefficients related to the riser temperature is given by Arrhenius equation: $\alpha = \alpha_0 \exp(-E/RT)$, E(Activation Energy), R(Gas Constant), T(Temperature).

2.3 Five Lump Model

Juarez et al., (1997) extended the four lump model to five lumps. These authors further divided the gases lump into two different lumps: a) dry gas, b) liquefied petroleum gas (LPG). Note that LPG can be formed either directly from gas oil or as a secondary product from gasoline overcracking . On the other hand, dry gas (H_2, C_1, C_2) can be formed either directly from gas oil cracking or as a secondary product from gasoline and LPG cracking.[14-16]. The five lump model can be schematically represented as:
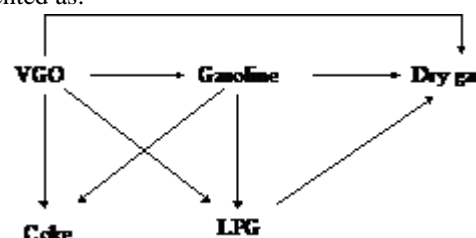

Fig:3 The five lump model

Table:1 Kinetic Parameters Reported From Literature:(k_{T0}, k_{T1}, k_{T2}, k_{T3} represent the overall VGO cracking rate constant, the gasoline formation rate constant, the gas and coke formation rate constant and the gasoline overcracking rate constant respectively (Corma et al., 1984)).

	Four Lump Model (Corma et al) $k(h^{-1})*10^{-5}$, at 480 _°C)
k_{T0},overall VGO cracking rate constant	2.91
k_{T1},the gasoline formation rate constant	2.44
k_{T2},the gas and coke formation rate constant	0.47
k_{T3},the gasoline over cracking rate constant	16.21

A new reaction kinetic model was developed by Jacob et al by dividing the feed and products into a 10- lump reaction schemes including paraffins, napthenes, aromatic rings and aromatic substituent groups in light & heavy fuel oil fractions. The new model considered the feed properties in addition to the boiling range. With increase in number of lump , the requirement of cracking constant increases rapidly. These lumps are to be characterized as an indicator of the feedstock composition.[10, 17-18]

648

Table: 2 Components of 10 lump kinetic model proposed by Jacob et al

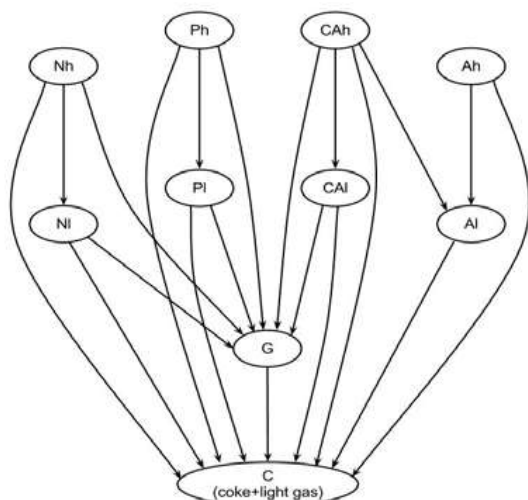| Initial Components in Feed	Cracked Product	
Heavy paraffinic (Ph)	Light Paraffinic (Pl)	Light Aromatic(Al)
Heavy naphthenic (Nh)	Light Naphthenic(Nl)	Gasoline(G)
Heavy Aromatic substituent's (Cah)	Light Aromatic substituent's (Cal)	Coke & Light gases (C)
Heavy Aromatic (Ah)		

Fig:4 10 lump kinetic model proposed by Jacob et al.

2.4 Pseudo Component Based Kinetic Approach:

Raj Kumar Gupta et al (2007)[7] developed a kinetic model for the fluid catalytic riser. The model incorporated a more realistic kinetic scheme for the cracking reactions based on Pseudo components, and a new correlation to evaluate Arrhenius type reaction rate constants.

Number of pseudo component considered in that work was 50 (N=50)(*Gupta.et.al)* . Each of these lumps was "characterized on the basis of average boiling point and specific gravity, and treated as hypothetical pure component with all physical properties known".

Coke as undesired product has been considered as separate lump in that modeling. Pseudo component based approach have been considered ,according to that 1 mole of pseudo component gives 1 mole each of two other smaller pseudo components and some amount of undesired product coke.

When there is cracking reaction then one mole of pseudo component breaks down to form pseudo component of lower molecular weights. Suppose, one mole of ith pseudo component PCi crack down , then it will produce one mole of PCm and PCn (or PCn and PCm) pseudocomponents with some coke formation as byproduct as shown below according to pseudoreaction mechanism:
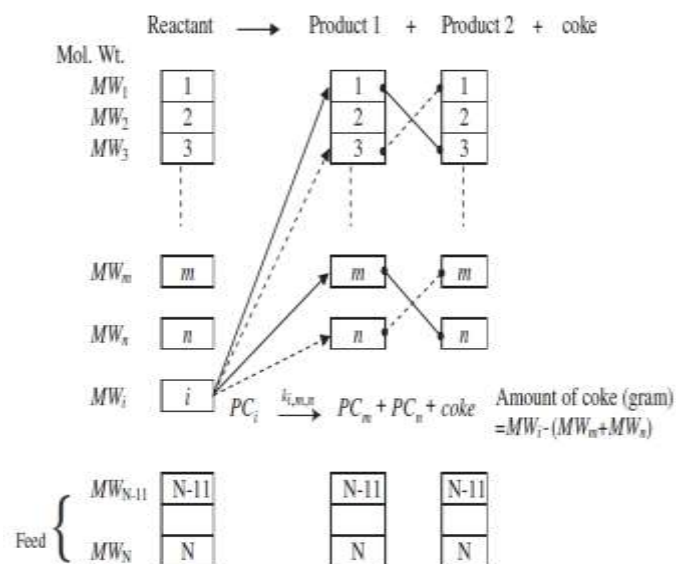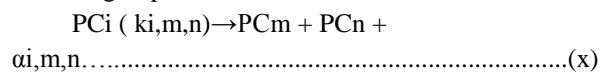
$$PCi (ki,m,n) \rightarrow PCm + PCn + \alpha i,m,n \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(x)$$

Fig.5 Schematic diagram showing reaction process (Gupta et al,2007)

Where i, m, and n are pseudocomponents' numbers, $\alpha i,m,n$, is the amount of coke formed (kg). There are several thousand possibilities for the reaction to occur in which one particular molecule of PCi can crack . Only those reaction are considered feasible for which the value of **αi,m,n,** calculated according to equation (x) is equal to zero or positive and eliminating all those reactions for which it is negative.

$$\alpha i,m,n = MWi - (MWm +MWn) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(xi)$$

Equation (xi) consider only those equation in which each compound of molecular weight Mwi gives two moleculer weights MWm and MWn along with coke. Considering all possible reaction value of m varies from 1 to i , as no product can be heavier than reactant. Value of n ranges from 1 to m , as the products PCm and PCn are interchangeable. Arrhenius equation is usually used in many cases to calculate reaction rate constant in which there is k0 (frequency factor) and ΔE (activation energy). These values are known through empirical relation given in some literature.Model equation which has been reported in *Gupta et.al* has considered different parameters k_0, E_0, ν , $\tau2$, μ and $\tau1$ and need to be estimated form experimental data.

649

$$k_{i,m,n} = \left[k_0 MW_i^{\mu} \right] e^{-\tau_1(MW_m - MW_n)^2} e^{-\frac{E_0 MW_i^{\nu}}{RT}} \left[\frac{e^{-\alpha_{i,m,n}/\tau_2} - e^{-MW_i}}{1 - e^{-MW_i}} \right]$$

………………………………………………...........(xii)

Which in its final form is reported below after some modification in the equation (xii) , because two parameters μ (frequency factor in term of molecular weight of pseudocomponent) and τ1 (cock forming tendency of pseudocomponents) does not pose much difference to rate constant. So model equation depend only on four parameters k_0, E_0, ν and τ2. ν correlated activation energy of individual pseudocomponents in term of its molecular weight and τ2 correlates the coke forming tendency of the feed .The modified form of equation is given below:

$$k_{i,m,n} = k_0 \, e^{-\frac{E_0 MW_i^{\nu}}{RT}} \left[\frac{e^{-\alpha_{i,m,n}/\tau_2} - e^{-MW_i}}{1 - e^{-MW_i}} \right]$$

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………………………………………………...(xiii)

Four tuning parameters (k_0, E_0, ν and τ2) from the paper of *Gupta et. al.* can be tuned to reduce minimum deviation between MAT experimental results and the predicted results which comes from model .

In the kinetic scheme cracking reactions rate are of first order considered as reported in many literature .Pseudo component is divided according to boiling point range which differs from next or previous pseudo component by little value in boiling point. As one heavier pseudo component breaks to two smaller pseudo components so it agree well for first order cracking rate.

3. Conclusions

Based upon different kinetic model, the yield lump models have the lowest complexity and require the least amount of data. The main disadvantage of this approach is that kinetic rate parameters depend on feedstock properties `and is not very useful to predict yield to coke, fuels. Chemical lumps require knowledge of the chemical type of the lump, namely, the paraffin, naphthene, and aromatic contents of each boiling point range. Pathway and mechanistic models require the detailed analysis of the feed data to develop molecular representation. The main advantage of this approach is that, kinetic parameters are not dependent on feedstock properties. Kinetic modeling of the riser reactor is based either on the lumping scheme or on the 'single events approach. The kinetic constants evaluated using the lumping scheme are empirical in nature and are too much feed and plant specific. Modeling using single event kinetics is more accurate and effective. Modeling approach and correlation based on pseducomponents for the

kinetic parameter estimation, eliminates the need for determining a large number of rate constant required in conventional lumped models.

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650

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