

Simulation of FCC Riser Reactor Based on Ten Lump Model

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Abstract

The ten lump strategy and reaction schemes are based on the concentration of the various stocks i.e., paraffins, naphthenes, aromatic and aromatic substituent groups (paraffinic and naphthenic groups attached to aromatic rings). The developed model has been studied using C++ programming language using Runge-Kutta Fehlberg mathematical method. At a space time of 4.5 s, the gasoline yield is predicted to be 72 mass % and 67 mass % for naphthenic and paraffinic feedstock respectively. Type of feed determines the yield of gasoline and coke. A highly naphthenic charge stock has given the greatest yield of gasoline among naphthenic, paraffinic and aromatic charge stock. In addition to this, effect of space time and temperature on the yield of coke and gasoline and conversion of gas oil has been presented. Also, the effect of catalyst to oil ratio is also taken in studies.

Key Words: Fluid catalytic cracking, Riser reactor, Ten-lump model.

I. INTRODUCTION

Fluid catalytic cracking process is one of the most important units for the conversion of gas oil and certain atmospheric residues to higher octane gasoline and light gases. The unit consists of two reactors, the riser reactor, where almost all the endothermic cracking reactions and coke deposition on the catalyst occur, and the regenerator reactor, where air is used to burn off coke. The regeneration process, in addition to reactivating the catalyst pellets, provides the heat required by the endothermic cracking reactions. The development of new, highly active cracking catalysts and the introduction of the additives which greatly enhance the productivity and the selectivity of the catalyst, allow the cracking reactions to be completed in the riser. The particle separator vessel acts as a disengaging chamber to separate the catalyst from the gaseous products by stripping steam.[1]

Commercial FCC feedstock usually contains thousands of chemical species with a wide distribution of boiling temperatures. Even the cracking of gasoline range hydrocarbons can include a quite wide distribution of molecular weights, from C₁ to C₂₀.

In general, there are two basic techniques in lumping the catalytic cracking of gas oil. The first strategy is to lump molecules according to their molecular weight and to consider chemical reactions between these lumps. These lumps are usually the feedstock and the final cracking products, like gasoline, light gases, and coke. The second strategy is to lump different products based on main chemical families such as paraffins, olefins, naphthenes, and aromatics. A three lump model [2] have been developed for the cracking reactions taking place in the riser reactor.

The three lump model consists of one a feedstock lump (gas oil, Volatile Gas Oil (VGO) or any other heavy feed) and two product lumps: a) gasoline b) coke and light gases. The gasoline lump contains the fraction between C₅ up to the hydrocarbons with boiling temperature around 220°C. The coke and light gases lump contains in addition to coke, C₄ and lighter than C₄ hydrocarbons.

Next, the coke was separated out of the light gas, considering it as two separate lumps C₁-C₄ gas and coke, thus developed the first four lump model[3,4] for FCC.

The four lump model was extended to five lumps [5]. The 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 over cracking. On the other hand, dry gas (H₂, C₁, C₂) can be formed either directly from gas oil cracking or as a secondary product from gasoline and LPG cracking.

A ten lump model[6] has been presented. The ten lumps are interconnected by twenty separate rate constants, which describe the overall reaction network. The lumping strategy and reaction schemes are based on the concentration of the various stocks i.e., paraffins, naphthenes, aromatic and aromatic substituent groups (paraffinic and naphthenic groups attached to aromatic rings). The kinetic model also incorporates the effect of nitrogen poisoning, aromatic ring adsorption, and time dependant catalyst decay..

The experimental units were described by the continuity equation for an isothermal vapor phase,

plug flow reactor with negligible inter particle diffusion and a time decaying catalyst[6]:

$$\left(\frac{\partial y_i}{\partial x}\right)_z + v_v \left(\frac{\partial y_i}{\partial x}\right) = r_i$$

In development of the model a uniform reactor cross section and void fraction was assumed. A catalyst decay term was also taken to account for the rapid deactivation of the catalyst, which occurs during the catalytic cracking of gas oil. Other features included were adsorption term for nitrogen poisoning, activation energies, molar expansion and oil partial pressure.

The adsorption of heavy, inert aromatic rings on the catalyst surface influences the availability of active sites and consequently the rate of reaction thus,

$$r_i = -\left(\frac{1}{k \cdot A_h}\right) \times \emptyset(t_c) \times a \times y_i$$

II. PROCESS DESCRIPTION

The FCC unit consists of two reactors, (1) The riser reactor, where almost all the endothermic cracking reactions take place and also coke deposition on the catalyst occur, (2) The regenerator reactor, where air is used to burn off the coke. The regeneration process, in addition to reactivating the catalyst pellets, provides the heat required by the endothermic cracking reactions.

Figure 1 shows a typical FCC process [7] that consists of two major operating parts, the reactor riser and the regenerator. The cracking of the hydrocarbon feed takes place in the riser, while the regenerator does the work of reactivating the catalyst by burning the coke deposited on the catalyst in the riser reactor. The feed is then preheated to a temperature of 450-600 K in a furnace or in a pump-around from the main-fractionator.

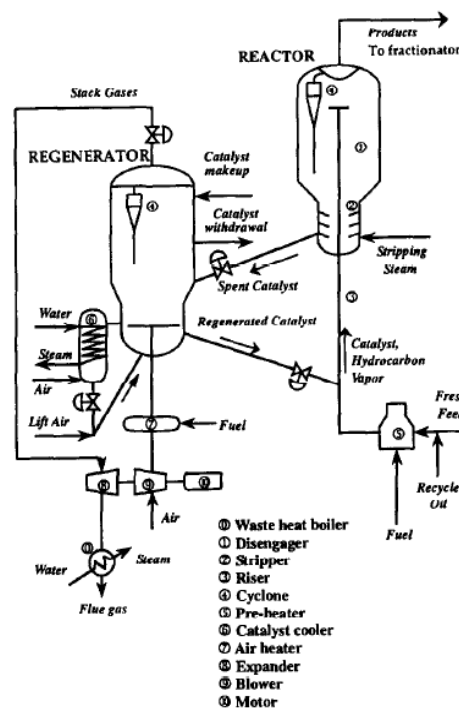


Figure 1: Schematic diagram of fluid catalytic cracking unit

The hydrocarbon vapors undergo endothermic catalytic cracking reactions as they move up through the riser reactor. Lighter hydrocarbons are produced as main cracking products along with by-product coke which deposits on the catalyst surface and this also lowers the catalyst activity.

III. TEN-LUMP MODEL:

The lumping and reaction schemes of ten lump model[6] are based on the concentrations of paraffins, naphthenes, aromatic rings and aromatic substituent groups (paraffinic and naphthenic groups attached to aromatic rings) in both heavy and light fraction of the charge stock.

The kinetic model for ten lump is shown in Fig. 2. Ten lumps are necessary to understand the cracking of volatile gas oils and recycle the charge stocks. This lumping scheme successfully treats gasoline (G-lump, C₅ – 222°C), C-lump (C₁ to C₄ + coke, H₂S, H₂) and light fuel oil (222 – 342°C) yields as a result of cracking of gas oil. The total conversion (mass %) is the sum of G-lump and C-lump. Detailed compositions changes resulting in the LFO (light fuel

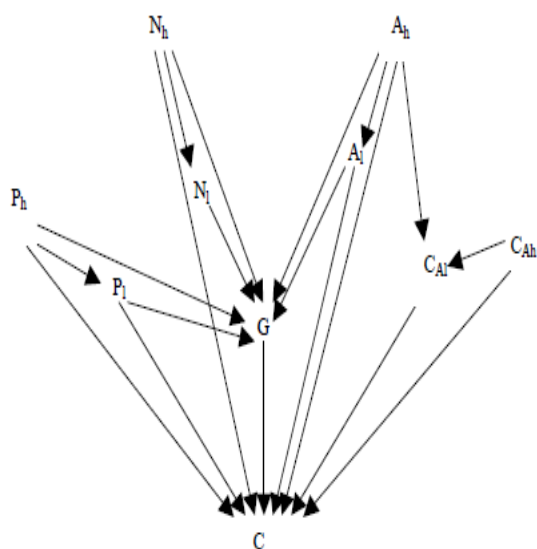


Figure 2: Ten-Lump Kinetic Model

- P_h mass % paraffinic molecules, 222-342°C
- N_h mass % naphthenic molecules, 222-342°C
- A_h mass % carbon atoms among aromatic rings, 222-342°C
- C_h mass % aromatic substituent groups, 222-342°C
- P_h mass % paraffinic molecules, 342°C +
- N_h mass % naphthenic molecules, 342°C +
- A_h mass % carbon atoms among aromatic rings, 342°C +
- C_h mass % aromatic substituent groups, 342°C +
- G G-lump ($C_5 - 222^\circ C$)
- C C-lump (C_1 to C_4 + coke)
- $C_1 + P_1 + N_1 + A_1 = LFO$ (222 – 342°C)
- $C_h + P_h + N_h + A_h = HFO$ (342°C+)

oil) and HFO (heavy fuel oil) are obtained by following the conversions of paraffinic, naphthenic, aromatic rings and substituent groups of gas oil cracking proceeds.

The kinetic scheme as shown in Fig. 2, is that a paraffinic molecule in HFO will crack to form paraffinic molecules in LFO and molecules in G-lump and C-lump. Paraffinic molecules in LFO can crack only to G-lump and C-lump. Likewise a naphthenic molecule in HFO will form naphthenic molecules in LFO and molecules in G-lump and C-lump. This suggests that there is no interaction between the paraffinic, naphthenic and aromatic groups.

The side chain and naphthenic rings attached to aromatic rings react similarly except for a single interaction step which allows $C_h \leftrightarrow A_l$. This is the only reaction step in the model and designated by the rate constant k_3 in the matrix of rate constant. The aromatic rings LFO (A_l) do not form gasoline but

result in the formation of the C-lump and primarily manifested as the coke contribution to the C lump.

Bare aromatic rings cannot form gasoline as the rings are very stable. However, an aromatic ring with a substituent group can undergo a cracking reaction such that this group can react to give the G-lump and C-lump. In this case the associated aromatic ring could then drop into the gasoline fraction (due to the resultant lowering of the boiling point). In the kinetic model, the entire group is included in the rate constant of the substituent group. The rate constant for $A_l \leftrightarrow G$ is considered as zero. This treatment therefore recognizes that aromatic rings by themselves cannot form gasoline if the substituent attached to ring is removed. No distinction is made between P, N and the molecules in the gasoline fraction; consequently, all the gasoline molecules are lumped together with a single cracking rate.

- Gas flow in the reactor is in ideal plug flow
- Axial dispersion in the reactor is considered to be negligible
- All Gas oil cracking reaction is first order reaction
- Both gas oil and gasoline have identical activity decay function ϕ
- Heavy aromatics do not produce gasoline
- Coke intent in feed is very low
- The riser wall is adiabatic
- Feed viscosity and heat capacities of all components are constant
- Adsorption and dispersion inside the catalysts particles are negligible
- Pressure changes throughout the riser-height are due to static head of catalyst in the riser
- The reactor cross section and void fraction are uniform throughout the length of the reactor

Based on the above assumptions and the depiction of the ten-lump model diagram, the overall reactions can be expressed in equation below [6]:

$$\frac{dy_i}{dt_v} = \frac{1}{(k \cdot A_h)} \times \phi(t_v) \times a \times y_i$$

Where,

a is the matrix of rate constants, given in fig 3.

y_i Concentration of the i^{th} lump, mass %

t_v Gas Oil space time, s

k Heavy aromatic rings adsorption coefficient (mass % A_h)⁻¹

$$a = \begin{matrix} \cdot & P_h & N_h & S_h & A_h & P_l & N_l & S_l & A_l & G \\ P_h & -k_0 - k_5 - k_8 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ N_h & 0 & -k_1 - k_6 - k_9 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ S_h & 0 & 0 & -k_2 - k_3 - k_7 - k_{10} & 0 & 0 & 0 & 0 & 0 & 0 \\ A_h & 0 & 0 & 0 & -k_4 - k_{11} & 0 & 0 & 0 & 0 & 0 \\ P_l & k_0 & 0 & 0 & 0 & -k_{12} - k_{15} & 0 & 0 & 0 & 0 \\ N_l & 0 & k_1 & 0 & 0 & 0 & -k_{13} - k_{16} & 0 & 0 & 0 \\ S_l & 0 & 0 & k_2 & 0 & 0 & 0 & -k_{14} - k_{17} & 0 & 0 \\ A_l & 0 & 0 & k_3 & k_4 & 0 & 0 & 0 & -k_{18} & 0 \\ G & k_5 & k_6 & k_7 & 0 & k_{12} & k_{13} & k_{14} & 0 & -k_{19} \\ C & k_8 & k_9 & k_{10} & k_{11} & k_{15} & k_{16} & k_{17} & k_{18} & k_{19} \end{matrix}$$

Figure 3 Matrix for Ten Lump Model

$$\emptyset(t_c) = \exp(-\alpha * t/c)$$

t_c = Catalyst residence time, s

α = Catalyst deactivation constant

$$\alpha = k_0 \exp(-E/(R*T))$$

k_0 = pre exponential factor, (1/s)

A catalyst decay term is needed to account for the rapid deactivation of the catalyst, which occurs during the catalytic cracking of gas oils. The rate of disappearance of a chemical species I in a single reaction is assumed to be proportional to the concentration of species i. the adsorption of heavy, inert aromatic rings on the catalyst surface influences the availability of the active sites and the reaction rates; therefore it is included in the reaction term. In addition, the evaluation of the temperature changes in the riser cracker[7] can be accounted using the following differential enthalpy balance:

$$\frac{dT}{dt_v} = -F_{if}/(F_{rgc}C_{p,c} + F_{if}C_{p,fv}) \sum_{i=1}^9 \frac{dy_i}{dt_v} \Delta H_{ri}$$

In case where the initial temperature at the riser reactor is not available, there the inlet temperature is calculated by using the following equation:

$$T(t_v = 0) = (F_{rgc}C_{p,c}T_{rgc} + F_{if}C_{p,fl}T_{feed} - \Delta H_{evp} F_{if}) / (F_{rgc}C_{p,c} + F_{if}C_{p,fv})$$

Basic nitrogen compounds are known to poison acidic cracking catalyst. The effect of nitrogen poisoning has being incorporated into the model by the addition of a catalyst deactivation term related to the nitrogen adsorption and the use of scalar quantity on the gasoline formation rate constants.

Nitrogen deactivation[6] is accounted for by a deactivation constant $f(N)$ given by

$$f(N) = \frac{1}{1 + \frac{N * K_n}{gm - catalyst}} = \frac{1}{1 + k/100 \frac{wt \% N_{inc} charge}{cat} \theta}$$

Where N= mass of basic nitrogen in gram to which the catalyst has been exposed at catalyst residence time t_c . At high catalyst/oil ratios, there are small quantities of basic nitrogen per cracking site, and the deactivation is insignificant. θ is the normalized catalyst residence time. $f(N)$ is a scalar multiplier on the rate constant matrix.

The model at steady state is solved by the Runge-Kutta-Fehlberg method by using the kinetic parameters are given in the Table 3 and 4

IV. RESULTS AND DISCUSSIONS

Compositional Effect: Simulation results for plot of gasoline yield vs. space time for three different charge stocks, is given in Fig. 4a

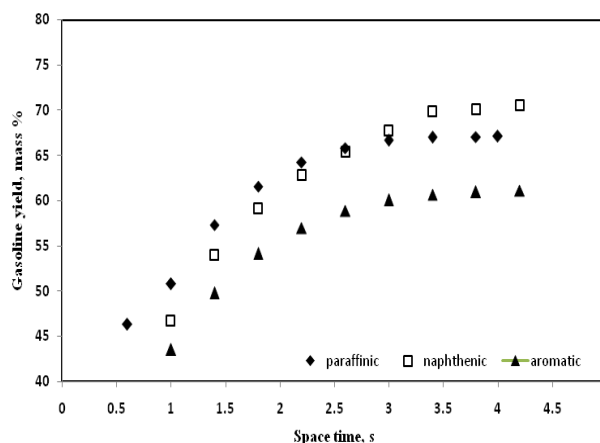


Figure 4a: Effect of composition on Gasoline yield

Composition of various feed stocks is presented in the Table 6. A highly naphthenic charge stock has given the greatest yield of gasoline, which is followed by paraffinic and naphthenic stock. At a space time of 4.5 s, the gasoline yield is 72, 67 and 59 mass % for naphthenic, paraffinic and aromatic feed stock

respectively. The side chain on aromatic ring crack quite readily, but aromatic rings are very stable and are extremely resistant to cracking reactions. P1, N1 and PA331 charge stocks are taken in present simulation which is given in Table 6.

The production of C-lump for different feed stocks is shown in Fig.4b. The figure shows that paraffin charge stock produces lesser amount of C-lump. The C-lump yield is 16.5 % at a space time of 4.2 s. while for the same space time the C-lump yield is 18% and 20.1% for the naphthenic and aromatic feed stocks respectively. Thus, the aromatic feed gives stock maximum yield of C-lump compared to other feed stocks.

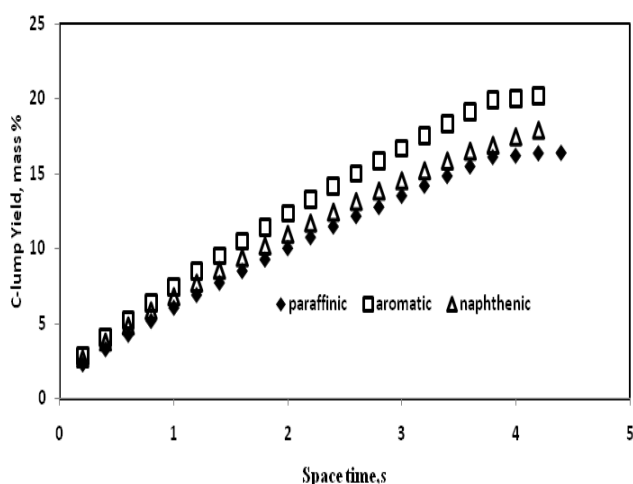


Figure 4b: Effect of composition on C-Lump yield

With model parameters (composition, C/O, temperature, space time) the trends in the HFO (Heavy Fuel Oil) and LFO (Light Fuel Oil) compositions are traced as conversion proceeds[6]. Detailed analyses of the LFO and HFO are shown in the Fig. 5a and 5b respectively for paraffinic charge stock

In Fig. 5a it may be seen that light paraffins first increases with the increases as the conversion and then decreases as it cracks to G-lump and C-lump. Naphthenes and light aromatic substituent group first shows a rise and then falls as conversion increases. It can be seen in Fig. 5a that aromatic rings increases continuously as the conversion of gas oil increases. The model follows the decrease of the kinetic lumps in HFO as shown in Fig. 5b.

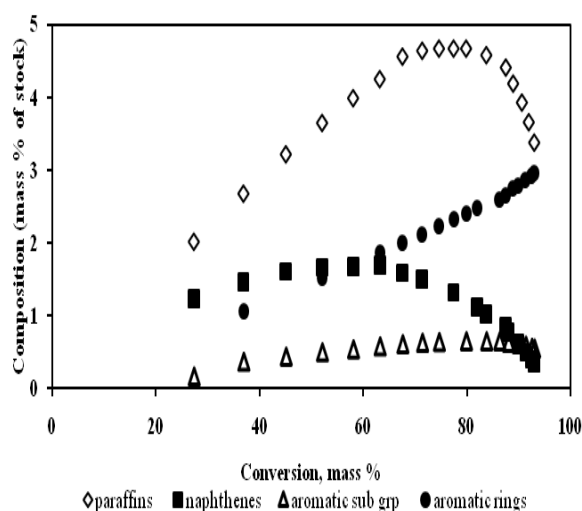


Figure 5a: Variation of LFO as the conversion proceeds

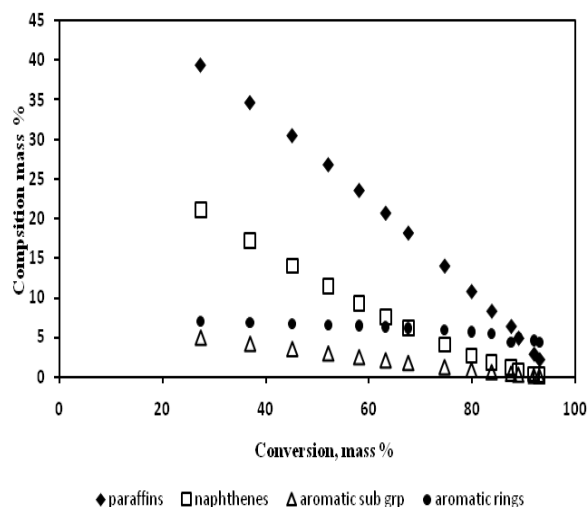


Figure 5b: Variation of HFO as the conversion proceeds

Effect of space time and temperature: The effect of space time on yield of G-lump at a temperature of 755.5 K, for paraffinic, feedstock is shown in Fig. 6a. The increase in space time increases the gasoline yield. At a higher temperature that is at 821.5 K, same trend is observed as shown in Fig. 6b. Therefore, it is always recommended running the FCC riser reactor at a lower space velocity, because this provides more space time for processing. In a space time of 2 s (kg of feed/kg of catalyst/s) most of HFO decomposes. 70 mass % of G-Lump is obtained at 4.5 s space time and 755.5 K with C-Lump yield of 18 %, while 62 mass % G-lump and C-Lump yield of 18 % at 821.5 K.

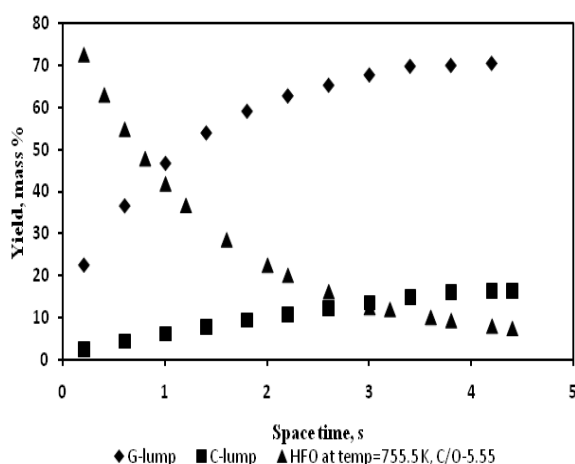


Figure 6a: Effect of space time on Yield at 755.5 K

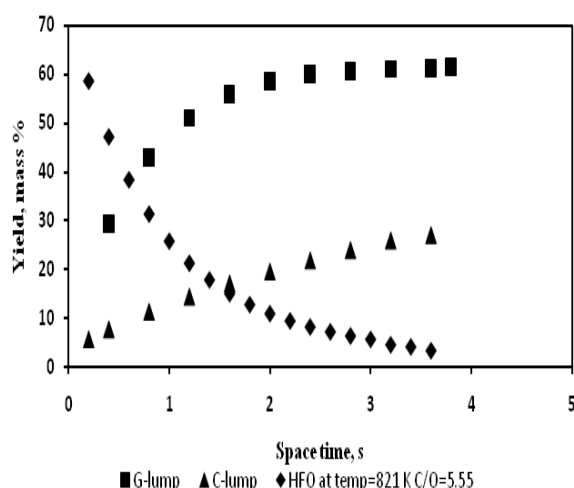


Figure 6b: Effect of space time on Yield at 821 K

At 821.5 K, the riser reactor converts a greater amount of gas oil. The total conversion is 70 % of the charge stock at 821.5K and 61 % at 755.5K at a space time of 4 s. Higher temperature does not favor gasoline production. In addition, as temperature increases, the C-lump yield also increases.

Effect of catalyst to oil ratio: C/O ratio is an important factor as it is related to the number of active sites available for gas oil cracking. C/O ratio is a primary variable, controlled by changing the catalyst circulation rate. The study is conducted by varying the C/O ratio between 4-10. Increase in C/O ratio increases the conversion as well as the reactor temperature. As shown in Fig. 7, when the C/O ratio is 5.5 the gasoline yield is 70.59 %. However as the C/O ratio is increased the gasoline yield increases.

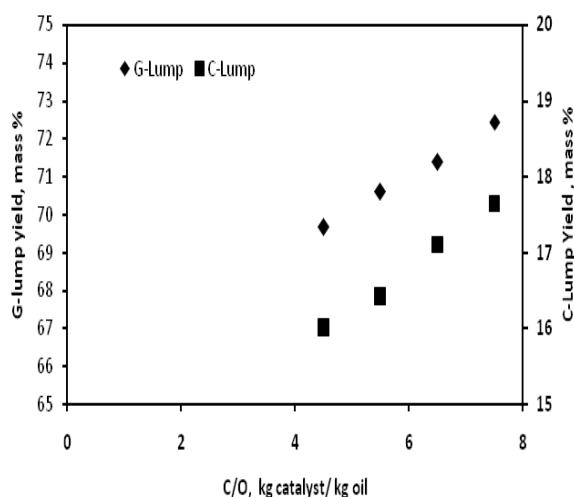


Figure 7: Effect of C/O ratio on yield of various product

Conclusions

The differential equations formed by the catalytic cracking reactions have been simulated. The model presented in the literature is solved at steady state condition using the Runge-Kutta-Fehlberg method for a set of ordinary differential equations. The code language used is C++ language. The simulation results are found to be in the right trend.

A highly naphthenic charge stock gives the greatest yield of gasolines compared to paraffinic charge stock and naphthenic. The increase in temperature leads to the rise in conversion of gas oil. However there is also an increase in yield of coke.

An increase in space time causes gas oil conversion to increase as the contact between gas oil and catalyst is more.

The increase in catalyst to oil ratio increases the gas oil conversion as well as the coke yield. This is because of the increase in catalyst sites, on which the cracking take place.

TABLE 1. Feed Properties and Conditions

Feed Properties and Conditions	
API	24.70
K _{UGP}	12.19
Inlet feed temperature	609K
Feed	Gas Oil
Specific Heat	3.430 kJ/kg/K

TABLE 2. Process Conditions of the Riser-Reactor

Riser-Reactor	
Gas oil flow rate	55.56 kg/s
Regenerated catalyst flow	308.5 kg/s
Catalyst to oil ratio	5.55
Riser Temperature	595K-755K
Gas oil residence time	2-10s
Pressure	2.6-2.8 kg/cm ²
Stripping steam	0.718kg/s
Make-up catalyst flow	0.417 kg/s
Nozzles	4
Inclination of nozzles	90 ⁰

Regenerator		
Regenerated catalyst temperature	945 K	
Flue gas temperature	978 K	
Regenerator temperature	1000-1200 K	
Pressure	3.10 kg/cm ²	
Entrained catalyst flow rate	0.023 kg/s	

TABLE 3. Process Conditions of the Regenerator

TABLE 4. Ten-lump kinetic data [8]

Reaction Rate Constant	Value of rate constant, s ⁻¹ at 811K	Activation Energy, kJ/kmol	Pre exponential Factor, s ⁻¹	Heat of Reaction, kJ/kg of reaction
k ₀	0.196	57615.89	1007.6	58.15
k ₁	0.196	57615.89	1007.6	58.15
k ₂	0.196	57615.89	1007.6	58.15
k ₃	0.489	57615.89	2513.0	58.15
k ₄	0.049	57615.89	251.9	58.15
k ₅	0.611	21854.3	15.619	151.19
k ₆	0.939	21854.3	27.225	151.19
k ₇	0.685	57615.89	3521.0	151.19
k ₈	0.099	69536.42	2981.0	523.35
k ₉	0.149	69536.42	4487.7	523.35
k ₁₀	0.198	69536.42	5963.0	523.35
k ₁₁	0.149	69536.42	4487.7	523.35
k ₁₂	0.282	21854.3	7.209	93.04
k ₁₃	0.752	21854.3	19.22	93.04
k ₁₄	0.196	57615.89	1007.6	93.04
k ₁₅	0.099	69536.42	2981.7	465.2
k ₁₆	0.099	69536.42	2981.7	465.2
k ₁₇	0.050	69536.42	1505.0	465.2
k ₁₈	0.010	69536.42	301.0	465.2
k ₁₉	0.048	39735.1	17.401	372.16

TABLE 5. Physical Properties of the Gas, Catalyst and Air[10]

Hydrocarbons	
Density	8.40 kg/m ³
Specific Heat (gas)	3.430 kJ/kg/K
Vaporization Temperature	698 K
Heat of Vaporization	156 kJ/kg
Specific heat(liquid)	2.670 kJ/kg/K
Catalyst	
Density	1500 kg/m ³
d _p (Particle Size)	75 μm
Specific heat	1.15 kJ/kg/k
Air	
Density	0.97 kg/m ³
Specific Heat	1.121 kJ/kg/K

TABLE 6. Molecular Composition of the feed stock [9]

Charge Stock	Mass Spectroscopy			n-d-m method		
	Paraffins, wt%	Naphtenes, wt%	Aromatics, wt%	C _P , wt%	C _N , wt%	C _A , wt%
P1	51.9	33.7	14.4	66.5	24.7	8.8
P2	40.9	36.7	22.6	69.9	22.8	7.4
P3	46.4	35.1	18.5	66.7	25.0	8.2
N1	11.3	68.8	19.9	40.1	53.8	6.1
N2	8.6	59.4	32.4	48.4	40.7	10.9
N3	9.8	64.0	26.3	43.5	47.5	9.1
PN33	27.8	49.9	22.5	54.3	35.9	9.7
PA31	33.8	26.1	40.1	56.1	25.9	18.0
PA32	32.1	31.9	36.0	56.7	25.4	17.9
PA33	31.3	30.4	38.3	57.9	26.1	15.9
PA331	17.7	26.2	56.1	47.9	29.5	22.6
PA34	34.9	28.6	36.5	59.6	23.6	16.8
PA37	30.2	23.7	46.1	58.8	6.1	35.1
PA38	32.5	26.5	41.0	64.4	18.1	17.5
AA45	11.0	14.2	78.4	53.0	15.7	31.3

Nomenclature

A_r	Cross sectional area of the riser, m^2
C/O rate	Cycling catalyst rate/feedstock mass flow rate
CCR	Rate of cycling catalyst kg/sec
$C_{p,c}$	Catalyst heat capacity, $kJ/(kg.K)$
$C_{p,fl}$	Liquid oil feed heat capacity, $kJ/(kg.K)$
$C_{p,fv}$	Liquid oil feed heat capacity, $kJ/(kg.K)$
E	Activation energy, $kJ/kmol$
F_{rgc}	Regenerated catalyst flow rate, kg/s
F_{sc}	Spent catalyst flow rate, kg/s
F_{if}	Oil feed flow rate, kg/s
G_F	feed stock mass flow rate kg/s
H	Catalyst hold up, kg
h_c	Specific enthalpy of catalyst, kJ/kg
h_h	Specific enthalpy of hydrocarbon, kJ/kg
ΔH_{evp}	Heat of oil feed evaporation, kJ/kg
H_{lri}	Heat loss from riser, kJ/kg
$k_{i,j}$	Rate constant for the species j involved in the formation of I species, s^{-1}
q_{react}	Heat of reaction per unit volume, $kJ/(m^3.s)$
R	Gas constant. $8.314 \text{ kJ}/(\text{kmol. K})$
S	Slip factor, dimensionless
S_v	Space velocity, $kg \text{ feed}/(kg \text{ catalyst}.s)$
T	Temperature, K
t_c	Catalyst residence time, s
t_v	Gas oil space time, s
v_c	Catalyst velocity in bed, m/s
V_R	Volume of riser, m^3
v_v	Gas velocity in bed, m/s
x	dimensionless length of the reactor
y_i	Mass fraction of i^{th} lump in feed stock
Z_0	Length of the riser, m

Greek letters

α	Catalyst deactivation constant
ϵ	Void fraction
\emptyset	Catalyst activity decay function
θ	Dimensionless time
ρ	Density of gas oil feed kg/m^3
ρ_c	Catalyst density, kg of catalyst / m^3 of bed

Subscripts

c	catalyst
i	hydrocarbons

rgc	Regenerated catalyst
ris	Riser
vap	Vapor

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