Optimization of Fluid Catalytic Cracker for Refining of Syncrude Oil for Production of High Quality Gasoline

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Abstract
Fluidized catalytic cracking is major refining process for production of high quality gasoline from syncrude gas oil-SGO and it is being increasingly utilized in world-wide industries in order to meet increasing demand of high quality gasoline. Solution to cope with the exceeding demand of high quality gasoline lies in running well optimized fluidized catalytic cracking units. Since in a unit or industry cannot be made to run on its peak optimized form in the practical world, the best approach is to look for highly optimized solutions for such real operating units. This research article aims to optimize them first using some highly compact software which scientist and researchers have developed through series of evolutionary steps. The simulation of fluidized catalytic cracking unit can be efficiently done on MATLAB and ASPEN HYSYS can give us solutions to meet increasing yield of high quality gasoline. The behavior of real time fluidized catalytic cracking units can also be modeled by software. This will provide us with optimized value of critical parameters through simulations for the entire efficiency of the unit. Simulation relies on convergence of reactor section of fluidized catalytic cracking unit which is heart of process. Simulation of reactor section was useful in predicting low residence time and catalyst activity. Riser has been simulated using modeling techniques for modeling the reaction kinetics. The simulation is performed for equations of LUMP MODEL. The results of simulations on these soft wares agree with real world fluidized catalytic cracking. These simulations and modeling were aimed at compact understanding of the dynamic behavior of the fluidized catalytic cracking unit. This dynamic behavior understanding of fluidized catalytic cracking is very important in designing aspects and running the unit in its peak efficiency.

Keywords: Fluid catalytic cracker unit, High quality diesel, Simulation, Lamp model, Euler method, Peak efficiency.

1. Introduction
In the field of oil refining sector, production of clean oil by means of Fischer Tropsch synthesis technology gaining more attention and viable way of liquid fuel production. The whole process broadly speaking comprises of FT synthesis and refining of FT syncrude oil. Both the fuel production process and the combustion of the final products generate less amounts of GHG as compared to conventional fossil fuels. The refinery offers process units in which the FT syncrude can be co-processed with crude oil, as well as utility systems for hydrogen and steam. Moreover, integration with the refinery has the benefit of a long tradition and knowledge of producing transportation fuels. An additional challenge facing the refining industry is how to deal with the bottom of the barrel under more stringent environmental constraints. The residue fraction of crude oil contains high concentrations of metals and asphaltenes, and cannot be upgraded easily. These methods are capable of separating non-distillable residua, but they also are tedious and produce only small amounts of sample. the thermal cracking gives the straight run gasoline by simply breaking the carbon to carbon bond the need was realize around 1920s that more high octane number and branched gasoline can be produced by using a suitable and economical viable catalyst like consisting of aluminum and silica which give the highly branched and high octane number gasoline owing to different branched structure carbocation’s mechanism. This process was then termed as catalytic cracking. Catalyst are mostly used are in form of beds the bed may be fluidized from their first came the process of fluidized catalytic cracking.

Riser is heart of whole fluidized catalytic cracking unit. Riser is part of reactor section of fluidized catalytic cracking unit where catalytic cracking reaction takes place. When hot regenerated catalyst enter form the regenerator. The feed is also introduced into the riser. Steam is also provided for the atomization in feed injection system. Due to high temperature of catalyst particle the feed vaporizes. Due to vaporization the feed get converted form liquid to vapor state. Volume expansion and pressure gradient occur in the riser. Due to this the gaseous feed flow through the catalyst particle in upward direction due to gradient of pressure. As result of these gas particles gives drag to catalyst particles. Particles also start to rise
depending upon their weight. A point will come when gaseous velocities are so high that they balance the weight of particles. This state is known as fluidization regime. Cracking progresses in the fluidization regime. As feed moves upward it is cracked into the products. In the present case feed is vacuum gas oil. These reactions are endothermic due to which temperature along the length of riser decreases.

1.1. Riser model development
For riser simulation on MATLAB a model must be created as we have already mentioned. The model making process in the riser was very complex due to hydraulics, fluid dynamics and chemical reaction kinetics. Riser is a tubular portion in fluidized catalytic cracking unit. Main phenomena happening in the riser that will help in riser modeling are as follow
a) Chemical reaction kinetics
b) Fluid dynamics
c) Transport phenomena
These three aspect most import being the first one will be used to develop model for riser of fluidized catalytic cracking.

1.2. Plug flow assumption
The reactant and product flow regimes in the riser is modeled as plug flow assumptions. Plug flow is that reactor regime in which fluid moves in form of plugs. And along the length of riser there is variation in composition. That is there are axial variations. Fluid composition is changing. However radial variations are not present. Along each cross section the composition with respect to spatial and time domains is constant. Plug flow assumption is very useful in modeling the riser since there is no back mixing. Back mixing is condition where the reactor products catalyst etc is moved to rector influent. There they mix with reactant. This implies that a lot of catalyst is needed if back mixing has to occur. More over residence time will also increase. And also back mixing leads to condition of mixed flow reactor. And in mixed flow reactor there is always a less conversion as compared to plug flow. And in our case we are requiring higher conversion. Back mixing with bring catalyst with the reactant and product to influent. Due to this catalyst contact with products the secondary reaction will start to occur. These secondary reactions are undesirable in the catalytic cracking because undesired products are produced due to further cracking of previously formed products.
In our case of fluidized catalytic cracking the feed is vacuum gas oil and its cracked products gasoline, coke and lights gases. This reaction mixture fluid is assumed to move in form of plugs in the riser. Then to each plug the principle of chemical reaction kinetic is applied. And integral- differential equations have been set.

\[(\text{Moles/concentration/weight fraction in}) = (\text{moles/concentration/weight fraction out}) + (\text{consumption/production}) + (\text{accumulation})\]

In this case we will consider accumulation to be zero. Now look at this equation of material balance shall be applied to plug flow case of riser couple with the reaction kinetics. Then model will be developed for the riser. Riser cracking therefore occurs in plug flow regime which purpose is to maximize desirable reactions and minimize the undesirable reaction due to lack of back mixing. Also residence time is less which also minimizes the undesirable reaction. The main part played in the material balance of plug flow applied to catalytic cracking is consumption/production term. For obtaining this term whole of model rests on development of chemical reaction kinetics.

1.3. Chemical reaction kinetics
Chemical reaction kinetics is also called as reaction kinetics. It is study of progress of chemical reaction and their rates. Rate of reaction tells us how fast reaction is proceeding. Reaction rate are based on volume basis, weight basis etc. Rate of reaction also tells about quantity (number of moles) consumed or produced with respect to time. Order which is power to which concentration of reaction is raised is very important aspect in modeling any chemical reaction. It is always experimental. Molecularity tells how much molecules are involved in particular reaction. Moreover CRE modeling also require what type of reactor flow regime you have assumed. For example plug flow or mixed flow reactor flow regimes.

2. Model development on basis of chemical reaction kinetics
While studying fluidized catalytic cracking of heavy hydrocarbons like vacuum gas oil, it was assumed that cracking or breakdown of such heavy hydrocarbon occurs in lumps.

2.1 Lump models
Basically there are two techniques in lumping. The first lumping strategy is to consider reaction and product species into different lumps according to hydrocarbons family they belong. Like most of chemical species involved in SGO cracking are paraffin, olefins, aromatics and napthenes. Such chemical species involve reaction like beta scission, proton transfer reactions and condensation and carbonium ion reactions. To account for each of such reaction will become very difficult. So it will be very
difficult to account of reaction kinetics for thousands of reaction happening for thousands of products and reactants. This approach is called as structure oriented lumping. On the other hand physical properties help us lot in predicting reaction kinetic of such reactions. A model has been developed which accounts for the lumps that are categorized on the basis of their physical properties. These physical properties are boiling point and molecular weight. Lumps classified on such basis are called as pseudo components. Because lumps are not consisted of single compound rather group of compounds having not the sharp boiling point. In fact range of boiling point exist in which such compound falls. Such compound is called as lump or pseudo components. This is called lump model. On basis of lump model SGO, gasoline coke and light gases have been modeled as separate lumps. SGO is lump consisting of C30 and onward. Gasoline is lump containing C6 to C11. Light gases C3 to C6. And coke is considered as separated lump and then reaction have been defined. This lump is called as four lump models. In fact as many as 50 lump models can be created. This depends upon further lumping. But four lump models is parent lump model which shows tendency of each reaction in fig. 1.

Cracking of syncrude gas oil is taking place through three reactions vacuum gas oil is represented by 1.
- Cracking of syncrude gas oil into gasoline
- Cracking of syncrude gas oil into light gases
- Cracking of syncrude gas oil into coke
- Cracking of gasoline is taking place through two reactions.
- Cracking of gasoline into light gases
- Cracking o gasoline into coke.
- Following are assumptions in cracking reaction of lump model.
- Gas flow in reactor is in ideal plug flow
- Axial dispersion is neglected
- The cracking of gasoline is modeled as first order reaction
- Syncrude gas oil cracking is considered to be second order.
- Catalyst activity is function of time
- Catalyst activity is incorporated into each reaction.
- No coke is produced form light gases due to no aromatics
- Coke content in feed is negligible

2.2. Mathematical model
From this lump reaction we have to model this reaction in mathematical form. From our chemical reaction kinetics knowledge we know that equation relating rate of reaction, concentration (mole fraction/wt. fraction) and order is as follow

\[
\text{Rate of reaction} = r
\]
\[
\text{Concentration} = c = \frac{\text{number of moles}}{\text{volume of mixture}} = \frac{n}{v}
\]
\[
\text{Weight fraction} = y
\]
\[
\text{Density of mixture} = \rho
\]
Then
\[
r = K \cdot C
\]
where \( K \) is rate constant
\[
r = (1/v) \frac{d(n)/dt}{\partial y}
\]
Eliminating \( r \) from both equations
\[
(1/v) \frac{d(n)/dt}{\partial y} = k \cdot c
\]
\[
\text{Volume} = \text{mass/density} = M/\rho
\]
Number of moles = \( n = \text{mass/molar weight} = m/M \)
Wight fraction = \( m/M \)
Putting relation of \( v, ni \) and \( c \) in the above equation eq1
Equation transforms to
\[
\frac{dy}{dt} = ky
\]
‘\( y \)’ is wt. fraction and we have deduce it for first order. For nth order this equation is
\[
\frac{dy}{dt} = k^n(y^n)
\]
‘\( n \)’ is order
Since catalyst is also involved in our reaction. In fact rate of reaction is directly proportional to catalyst activity. More the catalyst fresh and active more it would contribute to rater of change of weight fraction of particular lump.
\[
\frac{dy}{dt} = \frac{k}{\rho} \Phi \cdot y^n
\]
Converting proportionality into equality
\[
\frac{dy}{dt} = k^n(\Phi \cdot y^n)
\]
This equation is applied to all lumps
Where \( \Phi \) is the catalyst activity
For gas oil lump using above equation we note that it is being consumed so negative sign tells this fact.
\[
R1 = \frac{dy1}{dt} = \text{disappearance into gasoline} + \text{disappearance into light gases} + \text{disappearance into coke}
\]
Also cracking of gasoil is seconder order so \( n = 2 \)
\[
R1 = \frac{dy1}{dt} = (-k12*\Phi*y12) + (-k13*\Phi*y1) + (-k14*\Phi*y12)
\]
Production and disappearance of gasoline
\[
R2 = \frac{dy2}{dt} = \text{production of gasoline from gas oil} + \text{disappearance of gasoline into light gases}
\]
\[
R2 = \frac{dy2}{dt} = (k12*\Phi*y12) - (k23+k24)*\Phi*y1
\]
Since cracking gasoline is first order
Production of light gases
\[
R3 = \frac{dy3}{dt} = \text{production of light gases from gasoline} + \text{production of light gases form gasoline}
\]
\[
R3 = \frac{dy3}{dt} = (k13*\Phi*y12) + (k23+k24)*\Phi*y1
\]
Production of coke
\[
R4 = \frac{dy4}{dt} = \text{production of gas oil} + \text{production of gasoline}
\]
\[
R4 = \frac{dy4}{dt} = (k14*\Phi*y12) + (k24*\Phi*y1
\]
These are four differential equations. These equation accounts form the rate of reactions. These equations can be incorporated into the material balance equation of plug flow. Input rate = Output rate + rate of reaction + accumulation
Accumulation is zero
Input rate = output rate + rate of reaction
This equation is applied to four lumps turn by turn. Rate of reaction term appearing in the above equation is derived on basis of lump model. Input will be weight fraction \( yi \) and output will be
yi+Δ1 when applying these equations to a plug flowing in riser. If Inlet is ‘I’ and outlet is be ‘i+Δ1’
So applying these analogies to y1, y2, y3 and y4
For gas oil
Gasoil input rate = gasoil output rate + rate of reaction of gas oil
yi/i = (yi + Δi)/(ti + Δi) = (k12*Φ*yi12) + (-k13*Φ*yi12) + (-k14*Φ*yi12)
By definition of derivative term of right hand side = dyi/dt
So dy1/dt = (-k12*Φ*y12) + (-k13*Φ*y12) + (-k14*Φ*y12) (3)
Applying same procedure of all of remain three lumps we get
dy2/dt = (k12*Φ*y12) - (k23+k24)*Φ*y1 (4)
dy3/dt = (k13*Φ*y12) + (k24*Φ*y1) (5)
dy4/dt = (k14*Φ*y12) + (k24*Φ*y1) (6)

2.3. Modeling of catalyst activity
Catalyst activity has been incorporated into above equations. This approach is right since production or consumption of any pseudo component is related to catalyst activity. As the process of fluidized catalytic cracking proceeds in riser reactions happen. Coke is produced according to above reactions. This coke is basic cause of catalyst deactivation. Because catalyst that is used in fluidized catalytic cracking are ZEOLITES. Zeolites are alunna silicates. They have negatively charged macromolecular framework. They are micro porous structure. The porous structure makes them able to hold large number of cations like Na+, etc. These ions are readily accepted and transferred due to protonation.
Zeolite porous structure contains defined lattice structure. It is composed of silica and alumina tetrahedral frame work. Each tetrahedron contains silica or alumina atoms with oxygen atom at corner. This results in the pore structure. The pores diameter is in range of 8 angstrom. The internal surface area is 600 square meter/grams. This enormous surface area is due to extreme porous structure. Now what happened during fluidized catalytic reactions? As reaction proceeds with passage of time the coke is formed. Since all these reactions are happening on the catalyst surface.

a) Reactant is moved from bulk to catalyst.
b) Reactants get adsorbed on the surface of catalyst
c) Reaction takes place on catalyst surface
d) Product are formed and desorbed
e) Product is moved to bulk.
As you have seen this entire scheme of reaction that reaction basically happens on catalyst surface. Since coke is also formed. These coke particles are UN desirable. This is due to reason because they block the pores structure and active sites of catalyst.
Due to this barriers reactant are not able to adsorb on catalyst surface. And reaction stops. Thus catalyst gets deactivated. It is in therefore necessary to model catalyst activity. Following are the approaches used in modeling catalyst activity.

2.4. Time decay model of catalyst activity
This represents that coke rate formation is independent of reactant composition and extent of conversion of hydrocarbon. Catalyst deactivation has been modeled as exponentially decay.
Following are two law that are used
Φ = e (-α*t)
Φ = t-n
Where ‘t’ is time domain
Alpha and n are constant of catalyst decay function.
Another approach used form modeling catalyst decay function is based on coke content. It is exponential relation of coke content on the active sites.
Φ = e (λ*c)
Where ‘λ’ is constant and ‘c’ is coke content.
Time approach is better since it give deactivation of catalyst as function of time. Coke content is subjected to variations in highly random way.

3. Simulation of riser using Euler method
The Φ (catalyst activity) is incorporated in the modeling equations and then the new modeling equation becomes; Since Φ = e (-α*t)
dy1/dt = (-k12*c (-α*t)*y12) + (-k13*c (-α*t)*y12) + (-k14*c (-α*t)*y12) (7)
dy2/dt = (k12*c (-α*t)*y12) - (k23+k24)*c*y1 (8)
dy3/dt = (k13*c (-α*t)*y12) + (k24*c*y1) (9)
dy4/dt = (k14*c (-α*t)*y12) + (k24*c (-α*t)*y1) (10)
‘α’ is activity constant. It is given by following formula
α = α0*e(-E/(R*T))
Where α0 is frequency factor. ‘E’ is activation energy in kJ ‘R’ is ideal gas constant in kJ/(mol*K) and ‘T’ is temperature in kelvins

4. Arrhenius equation
It is observed that rate of reaction dependent upon temperature & activation energy as follow k = k0*e(-E/(R*T))
This is equation that is incorporated at place of rate of reactions in above equations. So final form of this system of equation is
dy1/dt = [-k120*e(-E/(R*T))*e(α0*e(E/(R*T))*t*y12)] + [(-k130*e(-E/(R*T))*e(α0*e(E/(R*T))*t*y12)] + [-k140*e(-E/(R*T))*e(α0*e(E/(R*T))*t*y12]]
dy2/dt = [k120*e(-E/(R*T))*e(α0*e(E/(R*T))*t*y12)] + [k230*e(-E/(R*T))*e(α0*e(E/(R*T))*t*y12]] + [k240*e(-E/(R*T))*e(α0*e(E/(R*T))*t*y12)]
dy3/dt = [k130*e(-E/(R*T))*e(α0*e(E/(R*T))*t*y12)] + [k240*e(-E/(R*T))*e(α0*e(E/(R*T))*t*y12)]
dy4/dt = [k140*e(-E/(R*T))*e(α0*e(E/(R*T))*t*y12)] + [k240*e(-E/(R*T))*e(α0*e(E/(R*T))*t*y12)]
This is our system of differential equation. These equations are relating weight fraction of vacuum gas oil, gasoline, light gases and coke to the time. Time here is residence time. Residence time is average time which this gaseous mixture is going to spent in the riser. And we have to find out this time. For finding out time we need to solve this non homogenous and nonlinear system of differential equation. Every differential system is affiliated with initial conditions or boundary contains in numerical analysis. This system is initial value problem Following are initial conditions for above mentioned system.
At inlet condition when time is $t_0$ that is when reaction has not yet been started. Then only reactant we have is vacuum gas oil having weight fraction equal to 1. While gasoline, light gases and coke are zero at that time. We will find time at point when 80% of gasoline has been formed. This will be done by Euler method.

Table 1: “Activation Energy & Frequency factors of various reactions”

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Activation energies (KJ)</th>
<th>Frequency factors</th>
</tr>
</thead>
<tbody>
<tr>
<td>SGO to gasoline</td>
<td>68250</td>
<td>$K_{12}$ $7.968 \times 10^6$</td>
</tr>
<tr>
<td>SGO to light gases</td>
<td>89216</td>
<td>$K_{13}$ $4.595 \times 10^6$</td>
</tr>
<tr>
<td>SGO to coke</td>
<td>64575</td>
<td>$K_{14}$ $3.756 \times 10^4$</td>
</tr>
<tr>
<td>Gasoline to light gases</td>
<td>52718</td>
<td>$K_{23}$ $3.255 \times 10^3$</td>
</tr>
<tr>
<td>Gasoline to coke</td>
<td>63458</td>
<td>$K_{24}$ $7.975 \times 10^3$</td>
</tr>
</tbody>
</table>

5. Results and Discussion

Below are the results of our MATLAB Simulation.

Table 2: Riser Model

The Simulation was carried out at different temperatures. The residence time corresponding to each temperature vary from 0.0001 hrs. to 0.0011 hrs. While during these different temperature composition of SGO, gasoline, Coke and dry gases were different. It was observed that maximum formation of gasoline was at $T = 890k$ equal to 0.866 wt. fraction. From further decrement of temperature the gasoline production was reduced. Due to endothermic nature of reaction, it was observed that at 430K temperature there was no formation of gasoline.

6. Conclusion

First of all for our ease we need to visually understand the results in form of graph. So the column graph was used. On the $y$ axis is yield of different product while the $x$-axis is use to represent the products obtained from cracking. We can see form the figure the following main observations: maximum production or yield correspond to naphtha or gasoline range; minimum yield in product is of H2S; LCO is second highest in term of yield; lights gases names propane, propylene and n butane etc. are in range of 5 to 10% in term of yield; bottoms are ranging up to 10% of yield; coke yield is acceptable in range of 5% yield. Since required cut is Naphtha, we maximized the production of our desired fraction to 40%.

Post Riser cracking can occur due to which Gasoline or Naphtha can further convert into secondary products. These are undesirable reactions and we can minimize rate of these reactions by taking into account modeling the rate equation of SGO cracking and gasoline secondary cracking. From these rate equations and with the help of CRE, we can also minimize the post riser cracking residence time mathematically.
<table>
<thead>
<tr>
<th>PRODUCT</th>
<th>YIELDS (WEIGHT PERCENT %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂S</td>
<td>0.3286</td>
</tr>
<tr>
<td>Fuel gas</td>
<td>6.1201</td>
</tr>
<tr>
<td>Propane</td>
<td>3.6246</td>
</tr>
<tr>
<td>Propylene</td>
<td>6.0672</td>
</tr>
<tr>
<td>N butane</td>
<td>1.7824</td>
</tr>
<tr>
<td>i-butane</td>
<td>4.2146</td>
</tr>
<tr>
<td>Butenes</td>
<td>7.6942</td>
</tr>
<tr>
<td>Naptha</td>
<td>40.00</td>
</tr>
<tr>
<td>LCO</td>
<td>13.426</td>
</tr>
<tr>
<td>Coke yield</td>
<td>6.5127</td>
</tr>
<tr>
<td>Bottoms</td>
<td>10.2976</td>
</tr>
</tbody>
</table>

Table 4: Product cuts and yield

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References


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