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Modelling, Simulation And Control Of An Fcc Unit

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Abstract

The riser and regenerator of industrial FCC is modelled using five lump kinetic model. Here riser is considered as adiabatic plug flow since riser operates in between fast and pneumatic fluidization. The regenerator is assumed as CSTR as catalyst to be well mixed for removing coke from pores of catalyst. The model is simulated using MATLAB obtaining the data from literature. The model results are in good agreement with plant data obtained from MRPL.

Keywords: FCC, riser, regenerator, dense bed, dilute bed, five lump kinetics

I Introduction

Fluid catalytic cracking (FCC) is one of the most important processes in the petroleum refinery; employed for the conversion of straight-run atmospheric gas-oil, vacuum residues, and other related heavy stocks, into a broad spectrum of products in the presence of a catalyst. The products of catalytic cracking include fuel gases, liquefied petroleum gas, high-octane gasoline, light fuel oil, diesel fuel, heavy fuel oil, etc. FCC unit consists of a reaction section and a fractionating section that operates together as an integrated process unit. The reaction section has two reactors: (i) the riser-reactor where almost all the endothermic cracking reactions and coke deposition on the catalyst occur, and (ii) the regenerator-reactor, where air is used to burn-off the accumulated coke on the catalyst. The catalyst-regeneration process also provides the heat required for the endothermic cracking reactions in the riser-reactor.

In the FCC unit, the catalyst enters the riser-reactor as a dense bed and is pneumatically conveyed upwards by the dispersing steam and vaporizing gas-oil feed. It is during this period of conveying the catalyst that catalytic cracking of gas-oil takes place through efficient catalyst and gas-oil contact. The spent catalyst is separated from the product stream through the spent-catalyst slide-valve in the riser-reactor and enters the top of the regenerator. The major purpose of the regenerator is to oxidize the coke on the spent catalyst with oxygen to form CO, CO2, and H2O, thereby reactivating the catalyst. Compressed combustion-air enters the regenerator from the bottom through a grid distribution pattern designed to provide efficient mixing of air with deactivated catalyst, resulting in a fluidized-bed catalyst-regeneration operation. The regenerated catalyst passes through the regenerated-catalyst slide-valve and is mixed with gas-oil at the riser-reactor's base and the cycle is repeated. Provisions are made for adding fresh catalyst makeup to maintain inventory and for withdrawal of aged and contaminated catalyst. The FCC unit is quite complex from both the process modelling/simulation and control points of view. The complexity of the FCC unit is attributed to the strong interaction between the riser and the regenerator reactors, and the uncertainty in the cracking reactions, coke deposition, and coke burning kinetics. The objective of FCC is to maximize the yield of high octane gasoline and minimize coke formation to make it economically attractive.

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II FCC chemistry

The main reaction in the FCC is the catalytic cracking of paraffin, olefins, naphthenes and side chains in aromatics. A network of reactions occurring in the FCC is illustrated in Figure. The VGO undergoes the desired 'primary cracking' into gasoline and LCO. A secondary reaction also occurs, which must be limited, such as hydrogen transfer reaction which lowers the gasoline yield and causes the cyclo-addition reaction. The latter could lead to coke formation (needed to provide heat for catalyst regeneration).

Primary cracking occurs by the carbenium ion intermediates in the following steps:

I. Olefin is formed first by the mild thermal cracking of paraffin
II. Proton shift
III. Beta scission:
Carbon–carbon scission takes place at the carbon in the position beta to the carbenium ions and olefins.

The newly formed carbenium ion reacts with another paraffin molecule and further propagates the reaction. The chain reaction is terminated when (a) the carbenium ion losses a proton to the catalyst and is converted to an olefin; or (b) the carbenium ion picks up a hydride ion from a donor (e.g. coke) and is converted to paraffin. Besides paraffins, other hydrocarbons which are formed by primary cracking include the following:

- Olefins – smaller olefins
- Alkylaromatics – Dealkylation
- Alkylaromatics – Side chain cracking

Hydrogen transfer plays a key role in the gas oil cracking process. It reduces the amount of olefins in the product, contributes to coke formation, and thereby influences the molecular weight distribution of the product. Through intermolecular (bimolecular) hydrogen transfer, highly reactive olefins are converted to more stable paraffins and aromatics as in the following reaction:

Further loss of hydrogen to olefins by aromatics or other hydrogen-deficient products results in more paraffins and coke.

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III Primary Mechanism

When feed contacts the regenerated catalyst, the feed vaporizes. Then positive-charged atoms called *carbocations* are formed. Carbocation is a generic term for a positive-charged carbon ion. Carbocations can be either *carbonium* or *carbenium* ions.

A carbonium ion, CH_5^+, is formed by adding a hydrogen ion (H^+) to a paraffin molecule. This is accomplished via direct attack of a proton from the catalyst Bronsted site. The resulting molecule will have a positive charge with 5 bonds to it.

$R — CH_2 — CH_2 — CH_2 — CH_3 + H^+$ (proton attack)

$R — C^+H — CH_2 — CH_2 — CH_3 + H_2$

The carbonium ion's charge is not stable and the acid sites on the catalyst are not strong enough to form many carbonium ions. Nearly all the cat cracking chemistry is carbenium ion chemistry.
A carbenium ion, $R\text{-}CH_2^+$, comes either from adding a positive charge to an olefin or from removing a hydrogen and two electrons from a paraffin

$R — CH = CH — CH_2 — CH_2 — CH_3 + H^+$ (a proton @ Bronsted site)

$R — C^+H\ CH_2 — CH_2 — CH_2 — CH_3$

$R — CH_2 — CH_2 — CH_2 — CH_3$ (removal of H^- @ Lewis site)

$RC^+H\ CH_2 — CH_2 — CH_3$

Both the Bronsted and Lewis acid sites on the catalyst generate carbenium ions. The Bronsted site donates a proton to an olefin molecule and the Lewis site removes electrons from a paraffin molecule. In commercial units, olefins come in with the feed or are produced through thermal cracking reactions.

The stability of carbocations depends on the nature of alkyl groups attached to the positive charge. The relative stability of carbenium ions is as follows with tertiary ions being the most stable:

One of the benefits of catalytic cracking is that the primary and secondary ions tend to rearrange to form a tertiary ion (a carbon with three other carbon bonds attached). As will be discussed later, the increased stability of tertiary ions accounts for the high degree of branching associated with cat cracking.

Once formed, carbenium ions can form a number of different reactions. The nature and strength of the catalyst acid sites influence the extent to which each of these reactions occurs. The three dominant reactions of carbenium ions are:

- ❖ The cracking of a carbon-carbon bond
- ❖ Isomerization
- ❖ Hydrogen transfer

Cracking, or beta-scission, is a key feature of ionic cracking. Beta- scission is the splitting of the C-C bond two carbons away from the positive-charge carbon atom. Beta-scission is preferred because the energy required to break this bond is lower than that needed to break the adjacent C-C bond, the alpha bond. In addition, short-chain hydrocarbons are lessreactive than long-chain hydrocarbons. The rate of the cracking reactions decreases with decreasing chain length. With short chains, it is not possible to form stable carbenium ions.

The initial products of beta-scission are an olefin and a new carbenium ion. The newly-formed carbenium ion will then continue a series of chain reactions. Small ions (four-carbon or five-carbon) can transfer the positive charge to a big molecule, and the big molecule can crack. Cracking does not eliminate the positive charge; it stays until **two** ions collide. The smaller ions are more stable and will not crack. They survive until they transfer their charge to a big molecule.

$$R - C^{+}H — CH_2 — CH_2 — CH — CH_3$$
$$CH — CH = CH_2 + C^{+}H_2 — CH_2 — CH_2R$$

Because beta-scission is mono-molecular and cracking is endothermic, the cracking rate is favoured by high temperatures and is **not** equilibrium-limited.

IV Isomerization Reactions

Isomerization reactions occur frequently in catalytic cracking, and infrequently in thermal cracking. In both, breaking of a bond is via beta-scission. However, in catalytic cracking, carbocations tend to rearrange to form tertiary ions. Tertiary ions are more stable than secondary and primary ions; they shift around and crack to produce branched molecules (In thermal cracking, free radicals yield normal or straight chain compounds.)

Some of the advantages of Isomerization are:

- Higher octane in the gasoline fraction. Isoparaffins in the gasoline boiling range have higher octane than normal paraffins.
- Higher-value chemical and oxygenate feedstock in the $C, /C_4$ fraction. Isobutylene and isoamylene are used for the production of methyl tertiary butyl ether (MTBE) and tertiary amyl methyl ether (TAME). MTBE and TAME can be blended into the gasoline to reduce auto emissions.
- Lower cloud point in the diesel fuel. Isoparaffins in the light cycle oil boiling range improve the cloud point.

V. Hydrogen Transfer Reactions

Hydrogen transfer is more correctly called hydride transfer. It is a bimolecular reaction in which one reactant is an olefin. Two examples are the reaction of two olefins and the reaction of an olefin and a naphthene.

In the reaction of two olefins, both olefins must be adsorbed on active sites that are close together. One of these olefins becomes paraffin and the other

becomes a cyclo-olefin as hydrogen is moved from one to the other.
Cyclo-olefin is now hydrogen transferred with another olefin to yield paraffin and a cyclo-di-olefin. Cyclo-di-olefin will then rearrange to form an aromatic. The chain ends because aromatics are extremely stable. Hydrogen transfer of olefins converts them to paraffins and aromatics.
In the reaction of naphthenes with olefins, naphthenic compounds are hydrogen donors. They can react with olefins to produce paraffins and aromatics.

A rare-earth-exchanged zeolite increases hydrogen transfer reactions. In simple terms, rare earth forms bridges between two to three acid sites in the catalyst framework. In doing so, the rare earth protects those acid sites. Because hydrogen transfer needs adjacent acid sites, bridging these sites with rare earth promotes hydrogen transfer reactions.

Hydrogen transfer reactions usually increase gasoline yield and stability. The reactivity of the gasoline is reduced because hydrogen transfer produces fewer olefins. Olefins are the reactive species in gasoline for secondary reactions. Therefore, hydrogen transfer reactions indirectly reduce “over-cracking” of the gasoline. Some of the drawbacks of hydrogen transfer reactions are:

- Lower gasoline octane
- Lower light olefin in the LPG
- Higher aromatics in the gasoline and LCO
- Lower olefin in the front end of gasoline

VI. Simulation of Riser and Regenerator Model

A continuous riser reactor and regenerator model equations (7-12, 25-28, 54-58) have been coupled by generating a code in MATLAB.

The ordinary differential equations and nonlinear algebraic equations for material and energy balance are solved by using a RungeKutta fourth order and Successive Substitution methods respectively.

The calculation of these equations started with initial guess of regenerated catalyst temperature (T_{rgn}) and coke on regenerated catalyst (C_{rgc}), the product yields are calculated at the outlet of the reactor. Subsequently the temperature of spent catalyst and coke on spent catalyst are calculated.

Nomenclature

A_{rgn}= Regenerator cross-section area, m^2
A_{ris} = Riser cross-sectional area, m^2

CH= Weight fraction of hydrogen in coke, (kg H_2)/(kg coke)
C_c= Coke on catalyst, kg coke /kg catalyst
C_i= Concentration of ith component, kmol/m^3
C_{pc}= Catalyst heat capacity, kj/kg·K
C_{pCO}= Mean heat capacity of CO, kj/kg·K
C_{pCO2}= Mean heat capacity of CO2, kj/kg·K
C_{pl} = Liquid feed heat capacity, kj/kg·K
C_{pv} = Vapor feed heat capacity, kj/kg·K
C_{pH2O} = Mean heat capacity of water, kj/kg·K
C_{pN2}= Mean heat capacity of N2,kj/kg·K
C_{pO2}= Mean heat capacity of O2,kj/kg·K
Crgc= Coke on regenerator catalyst, (kg coke)/kg cat
Csc= Coke on spent catalyst, (kg coke)/kg cat
E_β= Activation energy for CO/CO2at the catalyst surface
Ej = Activation energy of ithcracking reaction in the riser
E_{13c}= Activation energy for homogeneous CO combustion
E_{13h}= Activation energy for heterogeneous CO combustion
f_C= Molar flow rate of carbon in the regenerator, kmol/ sec
f_{CO}= CO molar flow rate in the regenerator, kmol/sec
f_{H2O}= H2O molar flow rate in the regenerator, kmol/sec
f_{CO2}= CO_2 molar flow rate in the regenerator, kmol/sec
f_{N2}= N_2molar flow rate in the regenerator, kmol/sec
f_{tot}= Total gas molar flow rate in the regenerator, kmol/sec
f_{O2}= O_2molar flow rate in the regenerator, kmol/sec
F_{air}= Air flow rate to the regenerator, kmol/sec
Q_{ent}= Heat input to the dense bed from entrained catalyst returning from cyclone, kj/sec
Q_H= Heat released by the hydrogen combustion, kj/sec
Q_{rgc}= Heat flow with regenerated catalyst, kj/sec
F_j= Molar flow rate of jthlump, kmol/sec
F_{rgc}= Catalyst Circulation Rate (CCR), kg/sec

F_{sc}= Spent catalyst flow rate, kg/sec

F_{feed}= Oil feed flow rate, kg/sec

Z = Dimensionless riser height of riser

H_{ris}= Riser height, m

ΔH_{evp}= Heat of vaporization of oil feed, kj/kg

H_f= Heat of Formation of oil feed, kj/kmol

H_{CO2}= Heat of formation of CO_2, kj/kmol

H_{H2O} = Heat of formation of H_2O, kj/kmol

ΔH_i = Heat of cracking ofith lump, kj/kmol

i = total no. of reactions in the reactor

j = Total no. of kinetic lumps

K_{i0}= Frequency factor for ith reaction in the riser

K_{C0}= Frequency factor for coke combustion, 1/(atm) (s)

K_{13c0}= Frequency factor in heterogeneous CO combustion expression, kmol CO/(m^3) (atm^2) (s)

K_{13h0}= Frequency factor in homogeneous CO combustion expression, kmol CO/ (m^3) (atm^2) (s)

MW_j= Molecular weight of jth lump, kg/kmol

MW_c= Molecular weight of coke, kg/kmol

MW_g= Average molecular weight of gas oil feed, kg/kmol

MW_{H2}= Molecular weight of hydrogen, kg/kmol

P_{ris}= Riser pressure, atm

P_{rgn}= Regenerator pressure, atm

P_{O2}= Average mean oxygen partial pressure, atm

Q_{air}= Heat flow rate with air, kj/sec

Q_C= Heat released by the carbon combustion, kj/sec

Q_{SC}= Heat flow rate with spent catalyst, kj/sec

Q_{sg}= Heat flow rate with gases from the regenerator dense bed, kj/sec

$Q_{loss,rgn}$= Heat losses from the regenerator, kj/sec

$Q_{loss,\ ris}$= Heat losses from the riser base, kj/sec

r_i = Rate of the ith reaction, kmol/kg.cat.sec

R = Universal gas constant

R_{OT} = Riser outlet temperature, K

T = Riser temperature at any axial height, K

T_{air}= Temperature of the air to the regenerator

T_{base}= Base temperature for heat balance calculations, K (866.6 K)

T_{feed}= Gas oil feed temperature, K

T_{rgn}= Regenerator dense bed temperature/Regenerated catalyst temperature, K

T_{sc}= Temperature of spent catalyst, K

W = Catalyst inventory in the regenerator, kg

ρ_{den} = Catalyst density in the dilute phase of the regenerator, kg/m^3

ρ_g= Molar gas density in the regenerator, kmol/m^3

ρ_v= Oil vapor density, kg/m^3

φ = Catalyst activity

X_{pt}= Relative catalytic CO combustion rate

X_j= Mole fraction of jth component

Z = Axial height from the entrance of the riser or regenerator, m

Z_{bed}= Regenerator dilute bed height, m

Z_{dil}= Regenerator dilute phase height, m

Z_{rgn}= Regenerator height, m

β_c= CO/CO_2 ratio at the surface in the regenerator

β_{co} = Frequency factor in $\beta_c$expression

ε= Riser or regenerator void fraction

ρ_{dil}= Catalyst density in the regenerator dilute bed, kg/m^3

ρ_{den}= Catalyst density in the regenerator dense bed, kg/m^3

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