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Industrial hydrocracker model based on novel continuum lumping approach for optimization in petroleum refinery

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Abstract

Hydrocracking is widely practiced by the refiners to convert heavy petroleum feedstocks into desired lighter products. There are many process variables and catalyst formulations for optimization of hydrocracker performance with respect to yield pattern, products' quality and catalyst life. A user-friendly steady state hydrocracker model (HC-MOD) has been developed based on novel continuum theory of lumping approach for simulating hydrocracking kinetics and heat effects in a commercial hydrocracker. The model formulation includes skewed Gaussian type primary yield distribution function to describe yield and selectivity of the hydrocracking components. The model provides excellent prediction of commercial units' performance, as it incorporates hydrocracking kinetics of paraffins, naphthenes, and aromatics. The capabilities of HC-MOD include prediction of products' yields and qualities, reactor bed temperature profile, estimation of chemical hydrogen consumption, etc.

In the present paper, case studies from operating refineries are presented where HC-MOD has been successfully applied for optimization and troubleshooting, leading to better performance. The cases involve: (i) solving low conversion problem in a two stage hydrocracker, (ii) catalyst selection for maximum middle distillates, and (iii) increase in middle distillates selectivity through optimization of operating conditions. The paper also describes the knowledge-based solutions, which have led to the significant benefits to the operating refineries.

Keywords: Hydrocracking; Model; Continuum lumping; Optimization; Troubleshooting

1. Introduction

The environmental concern in the last two decades has set the agenda for development in the refining industry. Requirement of fuels with higher hydrogen, lower aromatics and low hetero-atoms, e.g., sulfur (S), nitrogen (N), etc. have been key factors, which are considered for the development of grass root projects as well as for revamps all over the world. In this scenario, hydroprocessing has emerged as the key technology to meet the challenges globally.

Hydroprocessing is a group of technologies where catalytic reactions take place in presence of hydrogen at elevated pressure to fulfill some or all of the following major objectives:

(i) Removal of hetero-atoms (e.g. S, N, metals, etc.) from hydrocarbon streams.
(ii) Saturation of unsaturated hydrocarbon compounds (e.g. olefins and aromatics).
(iii) Cracking of heavier hydrocarbon molecules to lighter ones for production of desired fuels and lubes.

In hydrocracking, apart from the hydrotreating reactions, cracking of the heavier molecules to lighter molecules also takes place with significant reduction of molecular weight. As practically no unsaturated compound and hetero-atoms are present in the products, the hydrocracked fuels are clean and environment friendly. The higher hydrogen content of the products provides better combustion characteristics making hydrocracking technology absolutely necessary to meet the current and future fuel specifications. Also, hydrocracking has the capability of processing a broad range of feedstocks of different characteristics ranging from naphtha to vacuum gas oil (VGO) to produce a wide range of products.

Hydrocracking reactions involve both cracking and hydrogenation and hence require dual functional catalysts

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consisting of a hydrogenation component dispersed on a porous acidic support for providing cracking activity. The cracking reactions in hydrocracking are similar to that taking place in conventional catalytic cracking. These involve carbenium ion intermediates and are characterized by extensive skeletal isomerization. The hydrogenation component of the reaction contributes to saturation of olefinic and aromatic hydrocarbons. The presence of excess hydrogen and of hydrogenation components in the catalyst results in hydrogenated products and inhibits some of the secondary reactions such as coke formation and secondary cracking. In the presence of hydrocracking catalyst, hydrogenation of aromatic compounds takes place followed by naphthene ring opening. Scission of the side chains of cyclic compounds, along with cracking of long chain paraffins and isomerization of paraffins take place in hydrocracking.

In this paper, a review on hydrocracking kinetic modeling has been presented followed by discussions on our model formulation for hydrocracker model (HC-MOD), based on continuum theory of lumping approach. The model provides excellent prediction of commercial units' performance with respect to prediction of products' yields and qualities, reactor bed temperature profile, estimation of chemical hydrogen consumption, etc. Three case studies from operating refineries are presented, where HC-MOD has been successfully applied for optimization and troubleshooting, leading to better performance.

2. Hydrocracking: kinetics and modeling

The major consideration for modeling of a commercial hydrocracking unit is to depict the chemistry of the different reactions taking place accurately. As different compound classes such as 'S' and 'N' compounds, paraffinic, naphthenic, olefinic, aromatics and polyaromatics react in different ways, some of which (mainly hydrogenation reactions) are equilibrium governed, it is important to consider a suitable kinetic modeling scheme to obtain a complete insight into the process phenomenon so that products' yields and qualities can be predicted satisfactorily.

As hydroprocessing reactions are mostly exothermic, it is imperative to predict the bed temperature profile in order to estimate the ΔT (changes in temperature) rise, locate hotspots, etc. for design and operation of reactors. The feed compositional changes have significant impact on heat of reaction and estimation of actual heat effects is an issue of major concern in a hydroprocessing reactor modeling. Also, heat effects are related to hydrogen consumption and its estimation would need a detailed hydrogen balance performed around the reaction network in order to arrive at a reasonable estimate. A choice of proper lumping approach depending on the process modeling requirements should be made in order to arrive at a reasonable model.

Deactivation plays an important role in hydrocracking as feed micro-constituents can deactivate the catalyst temporarily or permanently. A proper deactivation model would be needed for remaining life estimation of catalyst. Different mechanisms for deactivation exist and are available in literature [1]. Another major issue, which determines the reactor performance, is hydrodynamics. Hydrodynamics determines the extent to which hydrogen and oil are contacted for reaction. While the intraparticle diffusion is a result of catalyst design with respect to pore volume, pore size, etc., the availability of reactants on the catalyst surface is a phenomenon governed by hydrodynamics.

Following are the major issues involved in modeling:

(a) Detailed kinetics for prediction of products' yields and qualities.
(b) Heat effects for prediction of reactor bed temperature profile.
(c) Hydrogen consumption to account for hydrogen balance.
(d) Hydrodynamics effects to predict pressure drop.
(e) Deactivation effects for estimation of remaining life of catalyst.

Any accurate model should address the above aspects so as to reasonably model the hydrocracking phenomenon.

Different modeling approaches have been applied for hydrocracking, ranging from simple power law kinetic models to detailed molecular structure based kinetic approaches depending on the objectives of the modeling and availability of analytical and computational tools. The major approaches followed in hydrocracking are: (1) discrete lumping approach, (2) structure oriented lumping and single-event kinetics approach, and (3) continuum theory of lumping approach.

2.1. Discrete lumping approach

In this approach, the reaction mixture is divided into discrete pseudocompounds (lumps) based on their boiling range, molecular weight or C-number distribution, etc. The approach was initially developed by researchers to model catalytic cracking reactions. The classical examples for discrete lump approach are Weekman's 10 lump model [2] to model fluid catalytic cracking (FCC) reactions and Strangeland's model [3] for hydrocracking reactions. In discrete lumping approach, for a typical reaction network of hydrocracking [4], it can be found that to obtain more resolution, there is a requirement of increased number of lumps, which in turn would require large number of model parameters and experimental data to obtain a reasonably accurate model. The discrete lumping approach based models use relatively coarse lumped kinetics to describe the mixture and has following inherent limitations:

(a) This approach often fails to extrapolate to different feedstocks because of compositional differences within the same defined lumps.
(b) Actual composition of lumps in terms of molecular components may change with overall conversion of the system and vary from the true kinetics.
(c) Coarsely lumped models cannot be utilized to interpret the effects of catalyst properties because fundamental catalytic reaction mechanisms are not incorporated into the kinetic scheme.
(d) Insufficient details exist in the above models to predict changes in products' properties.

2.2. Model compounds/structure oriented lumping approach

The structure oriented lumping approach was originally proposed by Jaffe (1974) [5] where the lumping was based on bond kinetics, i.e. reactions involved with sigma and pi bonds. Later, Gray (1990) [6] developed the analogous group kinetics in which lumps carbon types are based on NMR analysis. These approaches however are not formulated to predict the details of product composition or properties. McDermott et al. (1990) [7] developed technique for construction of reaction of molecules through Monte Carlo methods and statistical analysis of mixture properties. Liguras and Allen (1989) [8] described a mixture with several hundred pseudocomponents where selection is based on a set of typical routine analytical data and whose reactions are based on group contribution methods. Quann and Jaffe (1992) [9] developed the detailed concept of structure oriented lumping. The basic concept involves description of hydrocarbon molecules as a vector, with elements of vector representing structural features sufficient to construct any molecule. This approach would require large experimental data bank and computational power to build a reasonable model. However, this approach is a detailed approach and a promising one to be adopted in some form or the other by the refiners in coming years. Many research laboratories worldwide are putting efforts to develop reactor models based on such a detailed approach.

Fundamental kinetic approaches such as single-event kinetic models have promising applicability as they have the feature of reducing the large data bank requirement [10]. However, this approach is still in a developing stage.

2.3. Continuum theory of lumping approach

The continuum theory of lumping considers the reactive mixture to form a continuum mixture with respect to its species type, boiling point, molecular weight, etc. The continuum mixture is so complex that it is no longer worth distinguishing individual chemical species, instead an index is chosen (e.g. TBP, reactivity, 'C' number, molecular weight, etc.).

Continuum description of first-order reactions in thermal cracking has been presented in the classic paper by Aris (1968) [11]. Further research in this direction had been carried out by several researchers, viz. Ho and Aris (1987) [12], Aris (1989) [13], Aris and Astarita (1989) [14], Astarita (1989) [15], Astarita and Nigam (1989) [16], Astarita and Ocane (1988, 1989) [17,18], Chou and Ho (1988, 1989) [19,20], Li and Ho (1990) [21], and Li and Rabitz (1989) [22].

Application of continuum theory of lumping has been described by Laxminarasimhan et al. (1996) [23] for hydrocraking of vacuum gas oil. This approach basically tries to represent basic chemistry. For example, observation such as heavier paraffins crack faster than lighter paraffins lead to representation of this relationship in a mathematical form by a monotonic function relating 'k' (reactivity) and 'C' number, etc. Such mathematical representation of reactivity relationships, chemical species type distribution, reaction network and primary yield distribution make the modeling of kinetics elegant leading to reduction of the number of model parameters drastically and at the same time following the process chemistry accurately. Continuum theory of lumping can improve structure oriented lumping in many ways.

3. Hydrocracking model based on continuum theory of lumping

The model formulation of our HC-MOD is based on continuum theory of lumping approach. The complex reaction mixture is classified into continuous boiling mixtures of paraffinic (P), naphthenic (N) and aromatic (A) compounds. In other words, the feed characterization involves TBP analysis and analysis of PNA for each narrow TBP fraction to generate separate TBP curves for P, N and A. Based on the above feed characterization and reaction trends of model compounds reported in literature, following reaction scheme has been assumed for hydrocracking:

- Hydrocracking of aromatics:

$$\mathrm{A}_i \rightarrow (\mathrm{A}_{i-1} + \mathrm{A}_{i-2} + \cdots + \mathrm{A}_1) + (\mathrm{N}_i + \mathrm{N}_{i-1} + \cdots + \mathrm{N}_1) + (\mathrm{P}_i + \mathrm{P}_{i-1} + \cdots + \mathrm{P}_1) \quad (1)$$

- Hydrocracking of naphthenes:

$$\mathrm{N}_i \rightarrow (\mathrm{N}_{i-1} + \mathrm{N}_{i-2} + \cdots + \mathrm{N}_1) + (\mathrm{P}_i + \mathrm{P}_{i-1} + \cdots + \mathrm{P}_1) \quad (2)$$

- Hydrocracking of paraffins:

$$\mathrm{P}_i \rightarrow (\mathrm{P}_i + \mathrm{P}_{i-1} + \cdots + \mathrm{P}_1) \quad (3)$$

where A^i, N^i and P^i represent the yield distribution of aromatic, naphthenic and paraffinic components, respectively.

The individual component material balance and the constraints thereof for the continuous mixture are described in details in one of our earlier publications [24]. The yield distribution function, $P(k, K)$ (described later) determines the yields of species with reactivity k from hydrocracking of components with reactivity K. It follows a skewed Gaussian type distribution function.

3.1. Model formulation for continuous description of feed from discrete data

The model formulation involves consideration of reaction mixture by a characterization parameter called true boiling point (TBP). The mixture composition at any particular stage of the reaction is represented by its distillation (TBP versus weight percent) curve. During the course of the hydrocracking of a particular feed, the TBP distribution curve of the reaction mixture (corresponding to the feed TBP curve at the start of the reaction) changes continuously with the changing residence time of the reaction mixture in the reactor. As the residence time of reaction increases, more of the heavier components in the reaction mixture are converted in to lighter components. As a result, the distribution curve of the mixture changes with the increased length of residence time, and shows an increased bias toward the lighter components. Like any other kinetic model, the present model formulation also attempts to determine the concentration distribution of the reaction mixtures at any given residence time (reaction time).

The TBP curve can be converted into a distribution function with the weight fraction of any component as a function of normalized TBP, θ, which is defined below

$$\theta = \frac{\text{TBP} - \text{TBP(l)}}{\text{TBP(h)} - \text{TBP(l)}} \tag{4}$$

where TBP(h) and TBP(l) are, respectively, the highest and the lowest possible boiling points of the reaction mixture, which corresponds to the heaviest and lightest possible component present in the mixture.

The mixture composition changes with reaction time, and is duly represented by the continuous function $C(\theta, t)$ at any given instant t. Thus $C(\theta, t)\,\mathrm{d}\theta$ is a fraction of the species with a boiling point corresponding to the normalized TBP range of θ and $\theta + \mathrm{d}\theta$. If the species (pseudocomponents) index in the reaction mixture is chosen as i, then the concentration of any pseudocomponent, i, can be designated as $C_i(t)\,\mathrm{d}i$, which is equal to $C(\theta, t)\,\mathrm{d}\theta$. For all practical purposes, i's are assumed to be equally spaced along the i-axis. Hence $C_i(t)\,\mathrm{d}i = C(\theta, t)\,\mathrm{d}\theta$. It has been widely reported in the literature that the hydrocracking rate constant is a monotonic function of TBP. In other words, molecules with a higher boiling point (heavier molecules) crack faster than molecules with a lower boiling point. Accordingly, the species of normalized TBP θ_i will have a rate constant defined as k_i. Since the components are treated as a continuum (as mentioned earlier) of normalized TBP, the rate constants can also be treated as continuous variables, and the concentration of species i can also be expressed as a function of the rate constant variable. Although the model is formulated for a single characterization variable, the approach could be extended to develop models with multiple characterization variables.

3.2. Estimation of hydrogen consumption

Hydrogen consumption is estimated based on hydrogen balance equations using dynamic C/H (carbon/hydrogen) ratio approach for hydrocracking. C/H ratio, which is a function of boiling point and PNA distribution in reaction mixture, changes along the bed length of the reactor. As the C/H ratio changes monotonically with the boiling point of a mixture (which is represented in terms of P, N and A), it is defined for individual components as follows:

$$(\text{C/H})(k) = X_i + \beta_i(k) \tag{5}$$

where X_i depends on the compound class and the values are 12, 6 and 3 for i = A, N and P respectively and β_i depends on maximum C/H ratio components present in the mixture and get dynamically updated with hydrocracking. Hydrogen consumption $h(k)$ is estimated based on the following equation along the length (z) of the reactor.

$$\begin{aligned}
\frac{\mathrm{d}h(k)}{\mathrm{d}z} = {} & \int_0^{k_a} P_{\text{AA}}(k_\text{A}, K_\text{A}) K_\text{A} C(k_\text{A}, z) \\
& \times \left[\frac{1}{1 + (\text{C/H})(k_\text{A})} - \frac{1}{1 + (\text{C/H})(K_\text{A})}\right] \\
& \times D(k_\text{A})\,\mathrm{d}k_\text{A} + \int_0^{k_n} P_{\text{NN}}(k_\text{N}, K_\text{N}) K_\text{N} C(k_\text{N}, z) \\
& \times \left[\frac{1}{1 + (\text{C/H})(k_\text{N})} - \frac{1}{1 + (\text{C/H})(K_\text{N})}\right] \\
& \times D(k_\text{N})\,\mathrm{d}k_\text{N} + \int_0^{k_p} P_{\text{PP}}(k_\text{P}, K_\text{P}) K_\text{P} C(k_\text{P}, z) \\
& \times \left[\frac{1}{1 + (\text{C/H})(k_\text{P})} - \frac{1}{1 + (\text{C/H})(K_\text{P})}\right] \\
& \times D(k_\text{P})\,\mathrm{d}k_\text{P} \\
\bar{h} = {} & \int_0^{k_{\max}} h(k) D(k)\,\mathrm{d}k
\end{aligned} \tag{6}$$

where, $\bar{h}$ is the average hydrogen consumption, $P_{ii}(k_i, K_i)$ (for i = P, N, A) the species type distribution function described later, and $D(k)\,\mathrm{d}k$ denotes the number of species with reactivity between k and $k + \mathrm{d}k$. As hydrocracking progresses, the parameters β_A, β_N and β_P are updated for

every reactor bed element as follows:

$$\beta_A^{new} = \beta_A^{old} \times \frac{\text{Total } H_2 \text{ concentration in aromatics}^{old}}{\text{Total } H_2 \text{ concentration in aromatics}^{new}},$$
$$\beta_N^{new} = \beta_N^{old} \times \frac{\text{Total } H_2 \text{ concentration in naphthenes}^{old}}{\text{Total } H_2 \text{ concentration in naphthenes}^{new}},$$
$$\beta_A^{new} = \beta_A^{old} \times \frac{\text{Total } H_2 \text{ concentration in paraffins}^{old}}{\text{Total } H_2 \text{ concentration in paraffins}^{new}} \quad (7)$$

3.3. Estimation of heat effects

Hydrocracking is an overall exothermic reaction. The heat effects vary for different components, e.g. aromatic components generate more heat. The temperature dependency of each species is determined by following Arrhenius type expression:

$$k = k_0 \exp\left[-E/R(1/T - 1/T_0)\right] \quad (8)$$

where E is the activation energy, T the temperature, and subscript 0 refers to the reference value.

The respective reactivities for different species are set in the kinetic expressions and generation of heat is linked to hydrogen consumption. HDS and HDN reactions are also considered in this step. Considering all of the above reactions, the reactor heat balance is carried out, the details of which are described by Laxminarasimhan et al. [25].

3.4. Solution methodology

The 1D model is a set of coupled integro-differential equations, which are solved using numerical techniques. Integration is performed by Gaussian quadrature using non-linear interpolation techniques for the $c(k, z)$ functionalities. The differential equation is solved using standard Runge–Kutta technique based explicit ODE solvers with feed concentration, initial bed temperature, and reactor top bed pressure as initial conditions for each of the bed reactor systems. Quench hydrogen is introduced at the top of every bed which is considered in the mass balance. The model has six skewed Gaussian functions to describe the primary yield distribution of hydrocracking of paraffins to lower paraffins, hydrocracking of naphthenes to lower naphthenes and lower paraffins and hydrocracking of aromatics to lower aromatics, naphthenes and paraffins. The skewed Gaussian function is formulated as follows:

$$P(k,K) = \frac{1}{S\sqrt{2\pi}} \exp\left[\frac{[(k/K)^{a_0} - 0.5]^2}{a_1^2}\right] - A + B,$$
$$A = \exp\left(-\left(\frac{0.5}{a_1}\right)^2\right), \qquad B = a_2\left[1 - \left(\frac{k}{K}\right)\right] \quad (9)$$

where a_0, a_1, a_2 are the parameters to be estimated for each yield distribution function. As there are six yield distribution functions, 18 parameters need to be estimated through regression of experimental data. S_0 is estimated from material balance constraints imposed on yield distribution functions. In addition to the above parameters three more parameters need to be estimated from species type distribution functions $D(k)$. In all there are 21 parameters for this complex model. Parameter estimation is carried out using the conversion data as responses applying Levenberg–Marquardt algorithm, which is a non-linear least square regression technique with multiple responses. The parameters have been found to be feed invariant for VGO range feedstocks. However, these are catalyst dependent.

3.5. Hydrodynamics

The basic understanding of the hydrodynamics of three phase trickle bed reactors used for hydrocracking reactions is essential for their design, scale-up, and prediction of performance. Liquid holdup and pressure drop have been identified as the most important parameters in hydrodynamics and it is vital to predict these as functions of the operating variables and the reactant physical properties.

A phenomenological hydrodynamic model has been developed [26] which predicts pressure gradient and liquid holdup at high pressures. The model consists of 1D force balance equations incorporating particle–gas drag, particle–liquid drag, and gas–liquid interactions. The model takes into account the tortuosity effect (the measure of tortuous path the fluid would take) in a unique way. The tortuosity effect is included into the force balance in terms of gravity. This factor takes the extra energy losses (and, hence pressure drop) into account. The model has been tested with major available experimental data and the predictions have been found to be satisfactory. The dimensionless expression given in Eqs. (10) and (11) represent the expression for pressure drop:

$$\alpha(1-\alpha)\tau + F_{PG}^*(1-\alpha) - \alpha F_{PL}^* + F_I^* = 0 \quad (10)$$

$$\left\{-\frac{dP}{dz} + \rho_G g\tau\right\}\alpha\varepsilon = F_{PG} + F_I \quad (11)$$

where α is the gas saturation, τ the tortuosity factor, dP/dz the pressure gradient and ε the porosity of bed. F_{PG} is the particle–gas drag, F_{PL} the particle–liquid drag and F_I the gas–liquid interaction and * denotes dimensionless drag.

A model for estimation of external wetting efficiency of the catalyst in hydrocracking reactor has also been developed [27] based on 1D force balance equations incorporating drag forces in three phase system. The external wetting efficiency has been calculated from the square root of the effective diffusivities in two-phase and liquid filled operation. The model predictions for catalyst wetting efficiency lie within an average confidence limit of ±15%.

After integration of the hydrodynamic model with hydrocracking kinetic model, the following parameters can be realistically estimated for improvement in reactor performance:

(i) Pressure drop, which determines the partial pressure of hydrogen in the reactor.
(ii) Catalyst wetting efficiency, which is a measure of the effective surface area available for the reaction.

3.6. Deactivation effects

The basic aim of modeling the catalyst deactivation is to assess the catalyst health and to predict its remaining life along with selectivity of products. Catalyst deactivation can be both reversible and irreversible which are normally known as temporary deactivation and permanent deactivation, respectively.

In HC-MOD, the effect of temporary deactivation (through nitrogen) has been accounted through preliminary deactivation model, developed through (i) in-house correlation based on long duration pilot plant testing (processing feedstocks containing nitrogen at different levels) and (ii) catalyst specific data (given by catalyst vendors). The effect of deactivation on remaining life has been considered through the following simplistic relation:

$$k = f(\text{catalyst activity, days on stream}) = k_0\, e^{-at} \qquad (10)$$

where k_0 is the kinetic constant at SOR, a is a constant (depending upon catalyst properties), and t denotes time on stream. The performance of HC-MOD for prediction of remaining life of the catalyst in a commercial hydrocracker unit is shown in Fig. 1.

The model has been tuned with increasing number of days on stream and the activity of the catalyst system deteriorated, as expected. One can see from Fig. 1 that the present activity (represented by location D) estimated by HC-MOD is higher than k_{EOR} (represented by location E). On linear interpolation of HC-MOD predicted activity data from k_{SOR} (location A) to $k_{present}$ (location D), the intermediate activities have been found to match satisfactorily (locations B and C). This shows the effectiveness of the deactivation modeling approach in HC-MOD. On assuming a linear deactivation profile from present time period (location D) to k_{EOR} (location E) it can be estimated that the catalyst remaining life is another four months from the time of study, provided the hydrocracking unit processes similar kind of feedstocks. The life predicted from HC-MOD has been found to match exactly with the commercial plant.

Further, rigorous deactivation kinetic model is developed for detailed understanding of catalyst behaviour. The kinetic parameters for tuning of the rigorous model are being generated through extensive pilot plant testing; the following effects are studied:

(i) Effect of ammonia in recycle gas (modeled through L–H adsorption kinetics).
(ii) Effect of operating conditions (temperature, liquid hourly space velocity, hydrogen partial pressure, etc.)

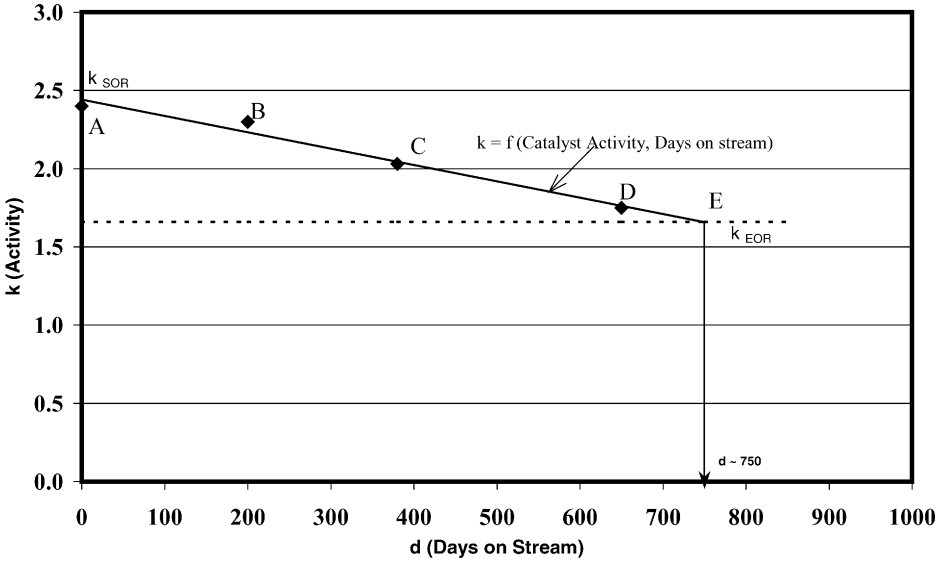

Fig. 1. Estimation of remaining life of HCU catalyst (application of HC-MOD deactivation module). Catalyst activity vs. days on stream. A, B, C, D, and E represent the different values of activity with various days on stream.

on rate of coke formation through accelerated deactivation testing (modeled through non-linear kinetics).

(iii) Effect of feed composition (like, asphaltenes, Conradson carbon residue, etc.) on nature of coke formation.

The deactivation model, on integration with hydrocracker kinetic and hydrodynamic model can result in accurate performance prediction of commercial unit.

3.7. Model validation

The model has been validated [28] with published data of Bennett and Bourne [29]. Subsequently, HC-MOD has been extensively tuned for commercial VGO hydrocracking units. Initially, the model tuning parameters are obtained through pilot plant studies at different operating severities and using the same, it is tuned with historic commercial plant operating data to take care of deviations between scale of operation between the pilot and commercial scales. After that, the model satisfactorily predicts the commercial units' performance.

The model has the capability to predict the following:

(a) Prediction of products' yields and qualities.
(b) Estimation of chemical hydrogen consumption.
(c) Prediction of reactor bed temperature profile and products' concentration profile.
(d) Prediction of consolidated TBP curve for products.
(e) Temporary deactivation effects due to nitrogen in feed.
(f) Prediction of the effect of varying operating conditions — throughput, feed temperature, pressure, quench and make-up gas flow and quality, recycle rates for gas and liquid, etc.
(g) Prediction of the effect of varying feed mix with different properties, e.g. variation in PONA (paraffins, olefins, naphthenes, aromatics), micro-constituent levels, etc.
(h) Estimation of pressure drop, etc. (through hydrodynamic module).
(i) Remaining life assessment (through deactivation module).

The user-friendly Graphic User Interface (GUI) based HC-MOD, depicted in Fig. 2 (for once-through configuration), can be handled by plant operating personnel quite easily. HC-MOD has been configured, tuned and installed in several refineries for both once-through as well as two-stage

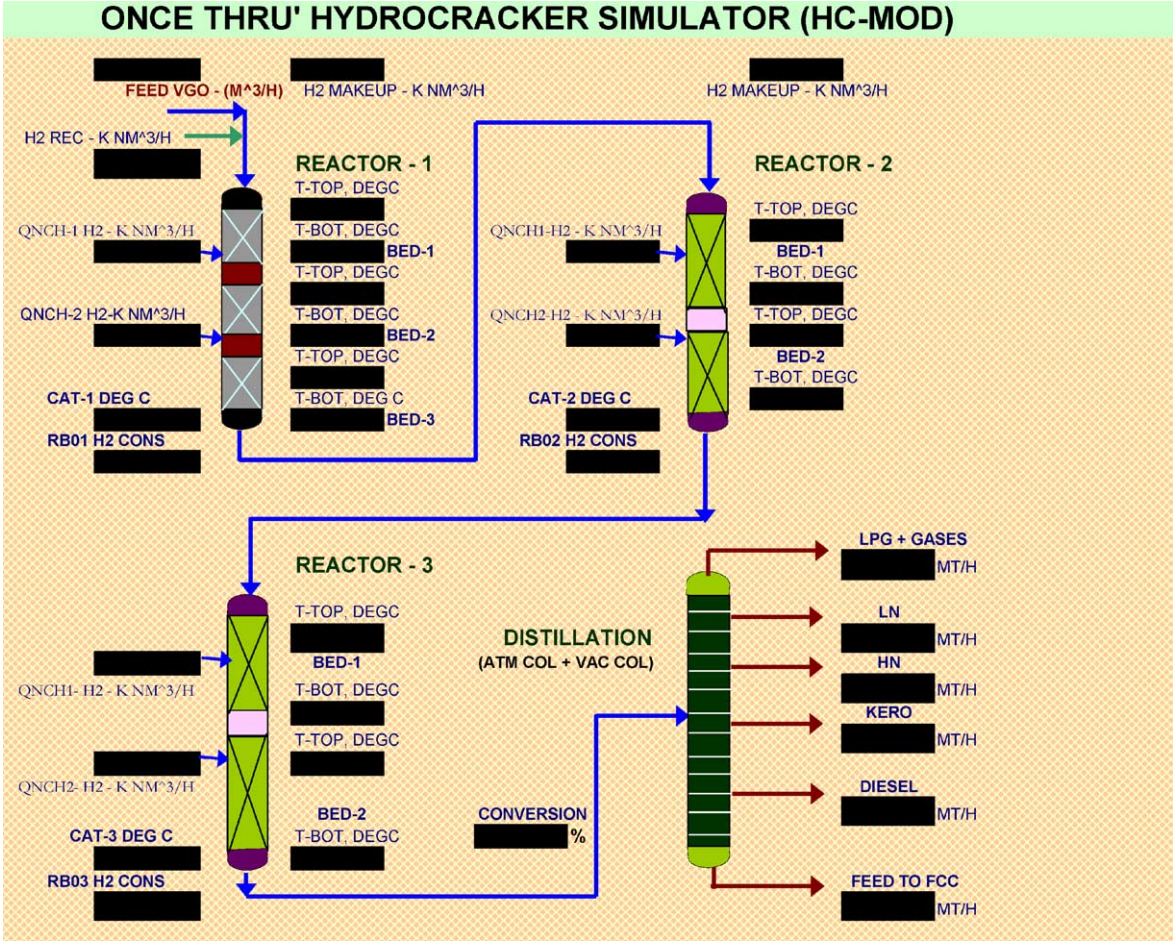

Fig. 2. User-friendly Graphic User Interface (GUI) of hydrocracker model (HC-MOD).

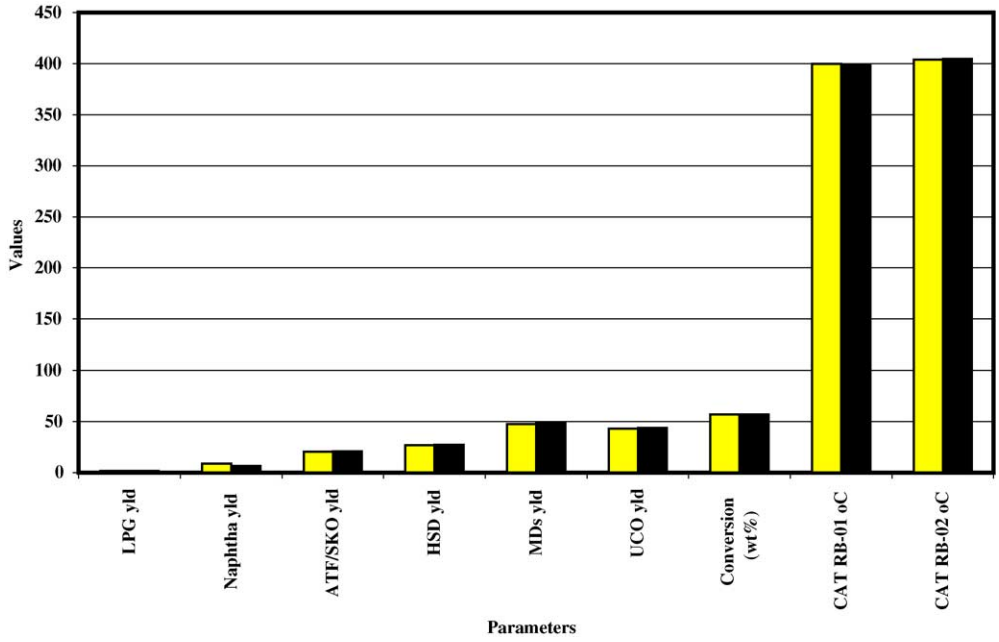

Fig. 3. HC-MOD historic data prediction vis-à-vis commercial performance.

recycle configurations. The models are being used for the following applications:

(a) Commercial hydrocracker troubleshooting.
(b) Commercial hydrocracker optimization.
(c) Catalysts evaluation and selection.
(d) Day to day performance monitoring.
(e) Optimum feed mix selection.
(f) Exhaustive data generation for tuning of refinery-wide LP model.

Detailed application of the model for scale-up of pilot plant data has been discussed in a recent conference [30]. The performance of the model vis-à-vis commercial units' performance is depicted in Fig. 3. Typically, the maximum deviation between the yields is of the order of ±2% and temperature profile matches within ±2 °C.

4. Results and discussion

Case studies are discussed in this section where HC-MOD has been utilized in the refineries for successful optimization, troubleshooting, and catalyst selection, leading to significant benefits.

4.1. Case 1: Troubleshooting of a commercial hydrocracker unit

4.1.1. Background

A refinery commissioned a hydrocraking unit (two-stage recycle configuration) of 1.1 MMTPA capacity. The design conversion has been 40% in the first stage and 60% per pass conversion (PPC) in the second stage leading to total conversion of feed. The objective of the unit has been the production of high quality middle distillates.

The design start of the run (SOR) and end of the run (EOR) temperatures for first stage had been specified by the licensor at 396 and 407 °C and that for second stage at 349 and 382 °C respectively. Since commissioning, the hydrocracker unit was facing problem with respect to the second stage conversion. The feed processed in the unit had been a combination of VGO and Coker Distillates, as specified in the design. In spite of increasing the second stage reactor catalyst average temperature (CAT) in steps from SOR condition to 360 °C, the increase in conversion was negligible. Further, the refinery tried to increase conversion by decreasing the throughput by about 50%. However, the problem of very low conversion in second stage could not be identified despite a lot of efforts.

4.1.2. Experimental studies and model findings

The feed and reactor exit samples were analysed in details followed by rigorous process simulation studies. The samples analyses results are presented in Table 1. The major observations from analyses of samples and operating conditions are as follows:

(i) Conversion was low only in the second stage. There had been no problem with regard to first stage operation, which was operated at about design conversion of 40%.
(ii) Due to high conversion in first stage reactor, it was evident that the first stage catalyst system had been functioning properly and not deactivated. To determine whether there had been any leak(s), second stage feed had been analysed for total nitrogen content, which was

Table 1
Important properties of commercial hydrocracker feed and product samples (used for troubleshooting)

Sample description	Total nitrogen (ppm)	Total sulfur (ppm)	Polycyclic index (PCI) (g/g)	Aromatics (%, w/w)	Saturates (%, w/w)
First stage reactor feed	–	1910	0.2277	44.5	55.5
First stage effluent (product)	0.4	138	0.0032	12.5	87.5
Second stage reactor feed	0.5	–	0.0035	<1	~100
Second stage effluent (product)	0.4	68	0.0011	<1	~100

found to be well within the tolerance limit. Hence, the possibility of deactivation of second stage catalyst due to nitrogen slippage was ruled out.

(iii) Polycyclic index (PCI), which is a measure of multi-ring compounds in hydrocarbon, was lowered by about 1/3 indicating good hydrogenation activity of second stage catalyst.

(iv) Feed micro-constituents were well within the tolerable limits of the catalyst system.

(v) Aromatics content in the fresh feed was different from typical feed composition. Further, the second stage feed was lighter and much more paraffinic.

Apparently, there was no component in feed that could lead to catalyst deactivation. Hence, the feed/products' analyses could not solve the problem of low conversion in second stage. Following were the salient observations from simulation studies through HC-MOD, which was tuned with same catalyst system and configuration:

(a) HC-MOD predicted the hydrocracker yield pattern within reasonable accuracy but suggested a much higher CAT than specified in SOR condition to achieve desired conversion (both for design as well as actual cases).

(b) As the second stage feed was lighter and paraffinic, the required CAT for second stage to achieve 60% PPC was found to be about 35–40 °C higher than that indicated by the licensor during design. It may be pointed out that it is always difficult to crack the lighter fractions in heavy VGO range feed. Fig. 4 depicts a typical activity-species relationship curve for VGO hydrocracking, which is a function of feed composition and catalyst characteristics. It can be seen that the overall relative reaction rate constant (k) increases strongly with an increase in the boiling range in a non-linear fashion. Hence, if the feed is relatively lighter, then higher reaction temperature is required to achieve the same level of conversion.

Because of incorporation of PNA kinetics in HC-MOD, it could identify clearly that the problem faced by the hydrocracker unit had been due to significantly light and highly paraffinic feed in the second stage which requires about 35–40 °C higher than design CAT for the conversion levels envisaged in the design.

4.1.3. Implementation of recommendations

Based on the simulation study findings, it was recommended to the refinery to increase the hydrocracker CAT of second stage by 35–40 °C. The refinery increased the CAT and once the reactor temperatures reached the model predicted values, the conversion in second stage gradually increased from negligible value to more than 55%, which is quite close to the design value of 60%. Hydrocracker overall throughput was increased from about 50% to more than 95%. Fig. 5 depicts the summary of commercial hydrocracker performance vis-à-vis model predictions after

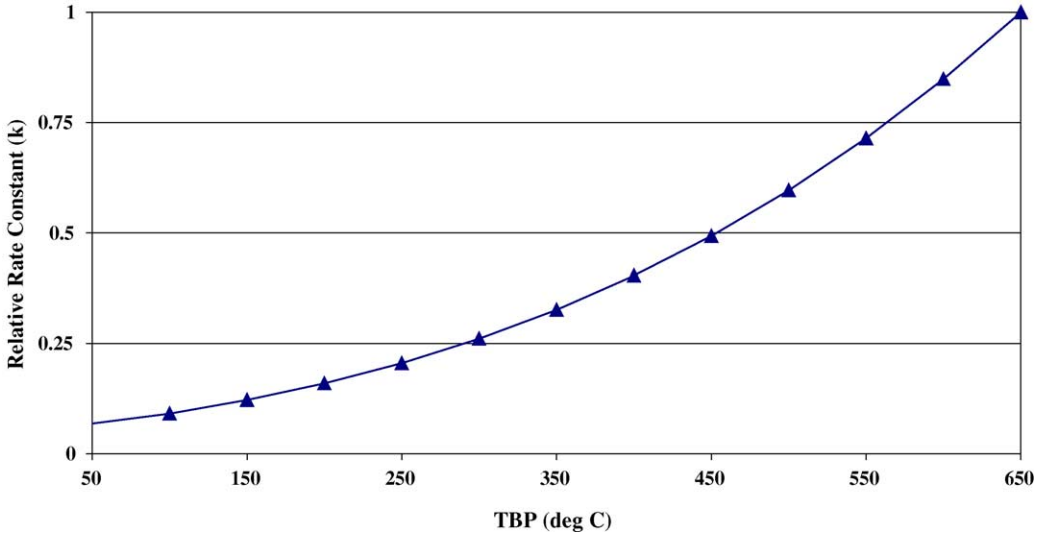

Fig. 4. Typical activity–species relationship in VGO hydrocracking.

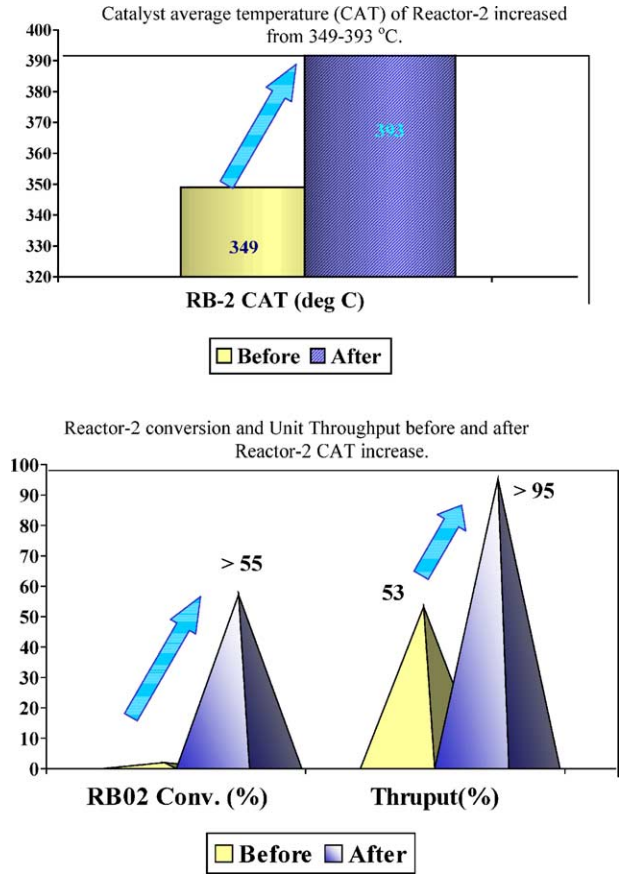

Fig. 5. Summary of a commercial hydrocracker troubleshooting.

increasing second reactor CAT. Since then, the unit has been running smoothly without any problem of conversion or throughput. Significant economic benefit of the order of INR 1.80 billion (about US$ 37 million) per annum could be obtained due to this study.

4.2. Case 2: Catalyst system selection for middle distillates maximization

4.2.1. Background

A study was conducted to identify better catalyst system from among the proven catalyst systems of different reputed licensors for replacement in a two-stage recycle hydrocracker unit which almost reached the end-of-run condition. Initial groundwork, previous data bank and experience had been used for selection of three catalyst systems, which showed higher middle distillates selectivity apart from stability and higher tolerance to micro-constituents. Hence, the basic objective of the study has been to select a catalyst system for a commercial hydrocracker unit which can perform the following functions:

(i) Middle distillate maximization preferably with higher diesel yield.
(ii) Processing more difficult feedstocks with higher end point, sulfur, nitrogen, etc.

As most of the catalyst systems studied are robust enough to handle more difficult feedstocks, the primary focus of the work has been identification of catalyst systems with highest possible middle distillate selectivity.

4.2.2. Experimental studies and model findings

The pilot plant studies had been carried out using same feed (VGO), configuration and units' constraints as commercial unit for generation of data on products' yield pattern and quality at different levels of conversion. Typical yield pattern and hydrogen consumption are reported in Table 2. It has been observed that for all the catalysts, the middle distillate selectivity as a function of first stage conversion passes through a maxima. Optimization studies have been carried out using HC-MOD to locate the optimum point (first stage conversion) through interpolation of the experimental data, as it would not be feasible to carry out costly and time-consuming experiments for large number of data points. Analysis of the HC-MOD findings showed that all the catalyst systems are middle distillate selective by 5–9 wt.% and are expected to provide edge over the existing commercial catalyst system (base case). Fig. 6 shows the middle distillate selectivity of the two-stage (with extinction) recycle hydrocracker system at various first stage conversions for different catalyst systems. Maximum overall middle distillate forms at 40% first stage conversion for catalyst B and 35% for catalyst A and catalyst C. Hence, in

Table 2
Overall yield pattern and hydrogen consumption with different catalyst systems through experimental studies and HC-MOD for commercial catalyst selection

Serial number	Product name	Catalyst A yield (% FF)	Catalyst B yield (% FF)	Catalyst C yield (% FF)	Base case yield (% FF)
1	LPG and gases	5.17	7.49	6.02	8.52
2	Light naphtha	5.75	8.01	3.36	8.85
3	Heavy naphtha	1.59	2.04	4.13	4.38
2 + 3	Total naphtha	7.34	10.05	7.49	13.23
4	Kero	47.26	46.57	40.82	41.27
5	HSD (diesel)	42.19	39.31	48.63	39.57
4 + 5	Middle distillate	89.45	85.88	89.45	80.84
	Hydrogen consumption (% fresh feed basis)	1.96	2.44	1.96	2.59

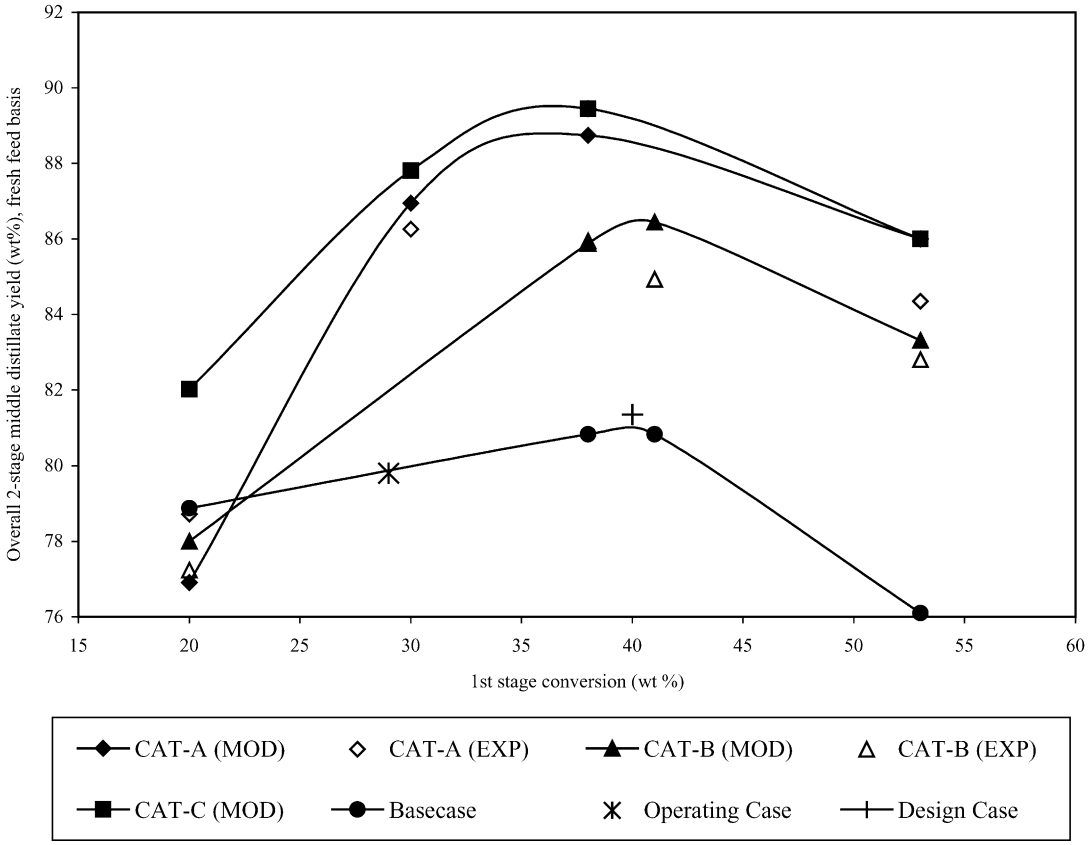

Fig. 6. Simulator and pilot plant studies on middle distillate selectivity with variation of first stage conversion for different Licensors' catalyst systems for two-stage hydrocracker unit.

commercial operation, the operating conditions should be set so as to obtain the optimum first stage conversion for maximum overall middle distillate selectivity. It has been observed that diesel selectivity also follows the same trend as that for middle distillates. All the catalyst systems A, B, and C perform better than the existing catalyst.

4.2.3. Implementation of recommendations

Based on preliminary economic analysis with the yield patterns obtained through HC-MOD, all the catalyst systems have been found to have low payback periods between 1 and 2 years. It has been found that catalyst system C is the best techno-economic option followed by A and B. Potential economic benefit of the order of INR 0.50 billion (US$ 11 million) per annum could be obtained due to this study.

4.3. Case 3: Optimization of operating conditions for middle distillates maximization

4.3.1. Background

A single stage once-through hydrocracking unit was being operated at 52–54 wt.% overall conversion. A study has been carried out using pilot plants and model for optimization of operating conditions for maximization of high demand middle distillates.

4.3.2. Experimental studies and model findings

Pilot plant has been operated at various conversion levels using the same feed, configuration, catalyst, and base case operating conditions as commercial unit. Thereafter, HC-MOD has been tuned using pilot plant data and the model has been applied to locate the optimum operating point for middle distillates maximization. It has been observed that the existing operation of the unit could be improved on running the unit at about 60% once-through conversion thus providing an increase of about ∼5% middle distillates yield improvement (overlap free basis). The optimized case indicates an increase of ATF by 3–4% and even though it indicates a slight reduction of diesel by about 1.5%, its quality has been observed to be relatively excellent (e.g. high cetane and low pour point). A summary of the base case and the optimized case are provided in Table 3.

The products' properties for the optimized case are excellent and critical product properties like diesel pour point and diesel cetane number are found to improve with increase in once-through conversion level due to improved aromatic saturation and ring opening.

4.3.3. Implementation of recommendations

On changing the operating conditions (particularly, reactor severity), the actual increase of middle distillates

Table 3
Optimization of operating conditions of a once-through hydrocracker unit with HC-MOD for middle distillates maximization

Parameters	Base case	Optimized case
Conversion (%)	52	60
Catalyst average temperature, CAT (°C)	X	$X + 3$
Yield pattern (overlap free basis)		
Light naphtha (wt.%) (C_5 − 85 °C)	L	L + 0.49
Heavy naphtha (wt.%) (85–127 °C)	H	H + 1.54
Total naphtha yield (wt.%)	N	N + 2.03
ATF/Kero (wt.%) (127–293 °C)	A	A + 4.85
Diesel (wt.%) (293–370 °C)	D	D − 1.55
Total middle distillates (wt.%)	MD	MD + 3.30
Product critical properties		
Light naphtha RON (research octane number)	76.5	79.7
Heavy naphtha RON (research octane number)	75.9	76.6
Kero smoke point (mm)	29	29
Diesel cetane number	58.3	67
Diesel pour point (°C)	6	−2

yield over base case has been observed to be about 3 wt.%. All products' properties have improved significantly. Since then the unit is operated at high conversion levels without any significant loss in cycle length. Economic benefit of the order of INR 40 million (US$ 0.9 million) per annum could be obtained due to this study.

5. Conclusion

A hydrocracker model has been developed based on continuum theory of lumping approach, incorporating PNA hydrocracking kinetics, hydrodynamics and deactivation effects. Hence, it has been found to match commercial reactors' performance appreciably. The model has been successfully applied for various commercial optimization and troubleshooting exercises, which shows the efficacy of the model formulation. Case studies have been discussed for HC-MOD application in three commercial hydrocracker units. In the first case study, the second stage conversion (to design values) could be achieved by increasing reactor temperature by 40 °C over the design values; in the second case, state-of-the-art catalyst could be selected for higher middle distillates selectivity (by 5–9 wt.%) along with optimum operating regime with respect to first sage conversion and in the third case, the operating conditions had been optimized for maximization of middle distillates (by 3–4 wt.% over base case). These exercises have led to significant refinery profitability.

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