

Steady-State Modeling of An Industrial Hydrocracking Reactor by Discrete Lumping Approach

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Abstract--In this study, a steady-state model of an industrial hydrocracking reactor was developed by using discrete lumping approach. Discrete lumping considers the reaction mixture to be composed of discrete pseudo-compounds (lumps) based on their true boiling points. The model parameters were estimated by using real data from an industrial hydrocracking unit. The effects of catalyst deactivation on model parameters were investigated and temperature sensitivity was introduced to the model. Since the model consists of a set of ordinary differential equations and algebraic equations which have to be solved simultaneously, a code was written by using MATLAB. It was shown that the model predictions for temperature profile, product distribution and hydrogen consumption were in good agreement with real plant data.

Index Terms-- reactor modeling, steady-state model, hydrocracking, discrete lumping, parameter estimation

I. INTRODUCTION

Hydrocracking is a catalytic process used in refineries for converting heavy oil fractions into high quality middle distillates and lighter products such as diesel, kerosene, naphtha and LPG. The process takes place in hydrogen-rich atmosphere at high temperatures (260-420 °C) and pressures (35-200 bar). The main hydrocracking reactions are cracking and hydrogenation. A bi-functional catalyst is used in the process in order to facilitate both the cracking and hydrogenation. The cracking reaction is slightly endothermic while the hydrogenation reaction is highly exothermic. Hence, the overall hydrocracking process is highly exothermic.

A hydrocracker unit (HCU) in a refinery consists of mainly two sections; the reactor section and the fractionation section. The reaction takes place in the reactor section and the products are separated in the fractionation section.

The feedstock is generally vacuum gas oil (VGO) or heavy vacuum gas oil (HVGO). The feed and high-pressure hydrogen are heated in a fuel-fired heater before entering the first reactor of the reactor section. This first reactor is called the hydrotreater in which organic sulfur and nitrogen are transformed into H₂S and NH₃ respectively. At the same time, the olefins and aromatics in the feedstock are hydrogenated. Hydrogen is consumed in all treating reactions. A negligible amount of cracking occurs in the hydrotreater. After the hydrotreater, the sulfur and nitrogen free feedstock goes to the hydrocracker reactors where the cracking reactions take place and the feedstock is converted to products. The effluent from the reactor section is sent to a wash water separator (WWS) where most of NH₃ is removed. During this process, a negligible amount of H₂S is also lost. The stream then is routed into a high-pressure separator (HPS) for separation into three phases: hydrogen-rich gas, hydrocarbon liquid and water. The hydrogen-rich gas is mixed with hydrogen make up and recycled back to the reactor section. The hydrocarbon liquid is sent to low-pressure separator (LPS). The reduction in pressure partially vaporizes the liquid. H₂S is recovered from the resulting vapor. The liquid hydrocarbon is then fed into the fractionation section to be separated into products.

Modeling of hydrocracking is a difficult task due to the complexity of the process. The modeling approaches in the literature can be classified as mechanistic and lumped kinetic modeling. Mechanistic kinetic models consider the reaction mixture at molecular level. Although theoretically independent of feedstock, the application of mechanistic models to industrial processes is still far from being achieved due to analytical complexity and modeling limitations [1]. When compared with mechanistic modeling, the lumped kinetic modeling is simpler and therefore easier to implement. Continuous lumping considers the reactive mixture to form a continuum mixture with respect to its species type, boiling point, molecular weight, etc. [2]. The idea of continuous mixture was originally proposed by DeDonder [3]. Chou and Ho [4] have provided a procedure for continuum lumping of nonlinear reaction. Application of continuous lumping to hydrocracking of vacuum gas oil was described by Laxminarasimhan et al [5]. It is reported that continuous lumping has good prediction ability and gives satisfactory results. However, discrete lumping has been widely used in hydrocracking modeling. In this approach, the reaction mixture is divided into discrete pseudo-compounds (lumps)

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based on their boiling range, molecular weight or carbon number distribution [2]. Stangeland [6] developed a four-parameter model. Mohanty et al. [7] implemented Stangeland's model for a two-stage hydrocracking unit. In this study the starting point is this model. Some modifications were introduced to simplify and improve the model. The modeling details are presented in the following sections.

II. MODEL DEVELOPMENT

In order not to overcomplicate the model, the reactor is assumed to be a plug flow reactor operating under adiabatic and steady-state conditions. The hydrocracking is assumed to be first order pseudo-homogeneous reaction [6, 8] and the components having a boiling point less than 400 °K are assumed not to undergo cracking [7]. A pseudo-component cannot crack into an adjacent pseudo-component but it can crack into at least once removed pseudo-component. For instance, pseudo-component 60 cannot crack into pseudo-component 59 but it can crack into pseudo-component 58 and lighters. The polymerization, hydrodesulfurization and hydrodenitrogenation reactions are negligible. Due to excess amount of hydrogen, the rate of hydrocracking is taken to be independent of hydrogen concentration. Make-up and recycle gases are assumed to be pure hydrogen and the total mass flowrate of liquid feed is constant. With these assumptions, the following mass (1) and energy (2) balance equations were solved simultaneously by using MATLAB ODE solvers.

$$M_{total} \times \frac{dC_i}{dW} = [-k_i \times C_i] + \left[\sum_{j=r}^N k_j \times P_{ij} \times C_j \right] \quad (1)$$

The first term on the right hand side of equation (1) shows the disappearance of component i due to cracking reaction and the second term represents the formation of component i from cracking of component j. M_{total} represents total mass flow rate of liquid feed in kg/h, C_i stands for mass fraction of components, W is the catalyst weight in kg, $k_{i,j}$ is the first order rate constant in kg-reactant/(kg-catalyst×h) and P_{ij} is the probability of formation of component i from cracking of component j [6].

The feed characterization, dividing the reaction mixture into pseudo-components, was performed by ASPEN HYSYS. The rate constant $k_{i,j}$ and the probability function P_{ij} were evaluated by the correlations given in [9, 10].

$$\sum_{i=1}^{N+1} (m_i \times Cp_i) \times \frac{dT}{dW} = \sum_{j=p}^N (\Delta H_R)_j \times k_j \times C_j \quad (2)$$

In equation (2), m_i is the mass flow rate of component i, Cp_i is the heat capacity of component i, T is the temperature, W is the catalyst weight, N is the number of pseudo-components, N+1 stands for hydrogen, p is the smallest component that undergoes cracking, $(\Delta H_R)_j$ is the heat of

reaction for cracking of component j, k_j is the first order rate constant and C_j is the mass fraction of component j.

Here, heat capacity of components and heat of reaction were calculated first by the same procedure given in [7]. When the results were investigated, it was observed that some simplifying modifications could be performed in heat capacity and heat of reaction calculations. The modifications were presented in the following sections.

A. Evaluation of Heat Capacity

Since the temperature difference between inlet and outlet streams is small (around 10.5 °C) enough, it is reasonable to neglect the temperature effect on heat capacities of individual pseudo-components. Therefore, instead of calculating heat capacity with respect to temperature, an average heat capacity value would serve our purpose. Mohanty [7] evaluated heat capacity of components by using Peng-Robinson equation of state and excess enthalpy. Following the same procedure, the calculated heat capacities can be plotted versus true boiling point of components as in Fig 1.

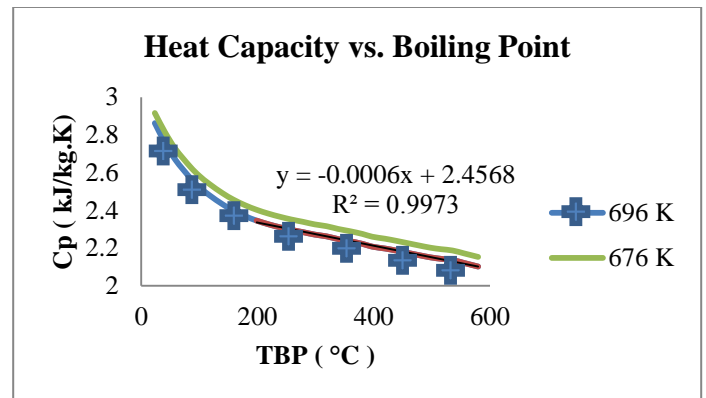


Fig 1. Heat capacity profile of components by procedure [7].

It can easily be observed from Fig 1 that the heat capacity decreases with increasing boiling point. Since hydrocracking process maximizes middle distillates, it would be more important to propose an average heat capacity describing middle distillates than light distillates. Hence, the range between 200 and 600 °C in Fig 1 was used to generate a relation for heat capacity. As can be seen from Fig 1, this portion of the graph has a linear trend. Hence, heat capacity of components was determined by a linear relationship as follows.

$$Cp_i = A \times TBP_i + B \quad (3)$$

The constants A and B were estimated by least squares using real plant data.

B. Evaluation of Heat of Reaction

The pressure along the reactor beds was assumed to be constant. Moreover, the temperature effect can be neglected as stated in heat capacity case. Under these conditions, the standard heat of reaction dominated over the other terms in the

heat of reaction equation. Therefore, standard heat of reaction can be taken as the total heat of reaction. The standard heat of reaction evaluated by equations given in [7] was plotted in Fig 2.

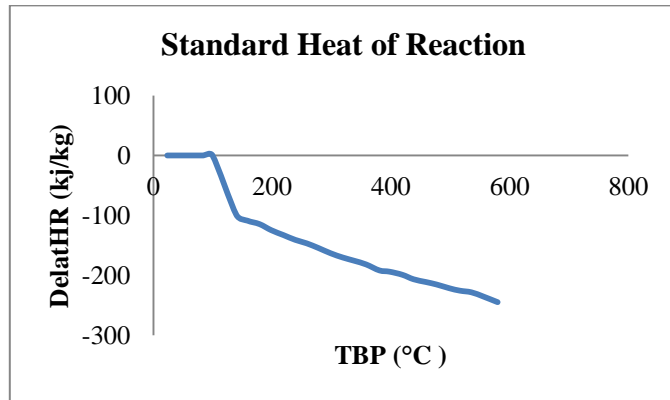


Fig 2. Standard heat of reaction by procedure [7].

In figure above, a linear trend is observed. In fact this is not surprising because standard heat of reaction depends on consumed hydrogen which is a function of C/H ratio. And C/H ratio increases with an increasing boiling point. Therefore, the components having higher boiling points will have higher standard heat of reaction. The values are negative due to the exothermic nature of the reaction. On the other hand, in cracking reactions, there is a cracking limit. The components having lower boiling point than that cracking limit do not undergo cracking. Hence, in Fig 2, the standard heat of reaction is zero for these components.

Due to the linearity of observed in the figure above, the heat of reaction can be expressed as

$$(\Delta H_R)_i = HR1 \times TBP_i + HR2 \quad (4)$$

Again, the constants were found by least squares using real plant data.

III. PARAMETER ESTIMATION

Parameter estimation is the process of determination of model parameters by matching the model-based calculated values with the experimental (real) data. In this study, parameter estimation was performed by using MATLAB fminsearch solver. This solver uses the Nelder-Mead Simplex algorithm which is one of the derivative-free methods. The unknown model parameters are determined by minimizing a function called objective function. It is the overall departure of model outputs from real data. In this study, the minimization of objective function was performed by least squares (LS) estimation in which weighted sum of least squares of errors (WSSE) was minimized. Model predicts the final product composition (for 59 pseudo-components), the outlet temperatures of beds (4 beds), the amount of quench flows (3 quench flows) and the amount of total consumed hydrogen. Hence, the objective function consisted of these items. Since

the units of outputs differ, the normalized values of items were used in objective function as given below.

$$F = \text{Min} \left[w_1 \times \sum_{i=1}^{59} \left(1 - \frac{f_{C_{i,M}}}{f_{C_{i,R}}} \right)^2 + w_2 \times \sum_{i=1}^4 \left(1 - \frac{T_{i,M}}{T_{i,R}} \right)^2 + w_3 \times \sum_{i=1}^3 \left(1 - \frac{Q_{i,M}}{Q_{i,R}} \right)^2 + w_4 \times \left(1 - \frac{H_{2,M}}{H_{2,R}} \right)^2 \right] \quad (5)$$

In the above equation, w_1, w_2, w_3 and w_4 are elements of weighting matrix, the subscript M and R represent model predictions and real data respectively. The first term stands for product composition, the second one for bed outlet temperature, the third one for quench flows and the last one for total hydrogen consumption.

Although it is not clear how to select the weights, it is obvious that the highest weight should be given to the term that has highest priority. The total hydrogen consumption depends on C/H ratio and final composition. The quench flows are cold hydrogen flows to cool the bed effluent and depend on both the outlet temperatures and intermediate composition between beds. Therefore, when the outlet temperatures and final composition are achieved, the quench flows and total hydrogen consumption will also be achieved. Hence, the weight for them was selected as 1. As final composition and outlet temperatures are equally important, their weights are to be equal as well. After many trials, the weight for them was chosen as 100.

In this study, the sensitivity analysis of model parameters was also performed in order to evaluate the impact of parameters on model outputs. It was observed that the rate constant parameters have the largest effect on the outputs.

IV. RESULTS

A. Constant Conversion Operation

As can be seen in Fig 3, the plant has constant conversion operation. It should be noted that the data presented here were manipulated due to confidential issues.

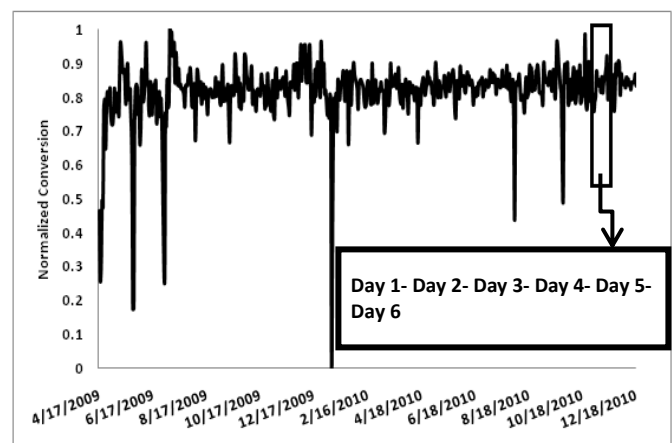


Fig 3. Plant conversion data with the selected data window.

The model parameters were found by matching three days of operation data (Day 1-Day 2 and Day 3) simultaneously

and then predictions were performed for Day 4, Day 5 and Day 6. The predictions were in good agreement with real data as can be seen in Fig 4.

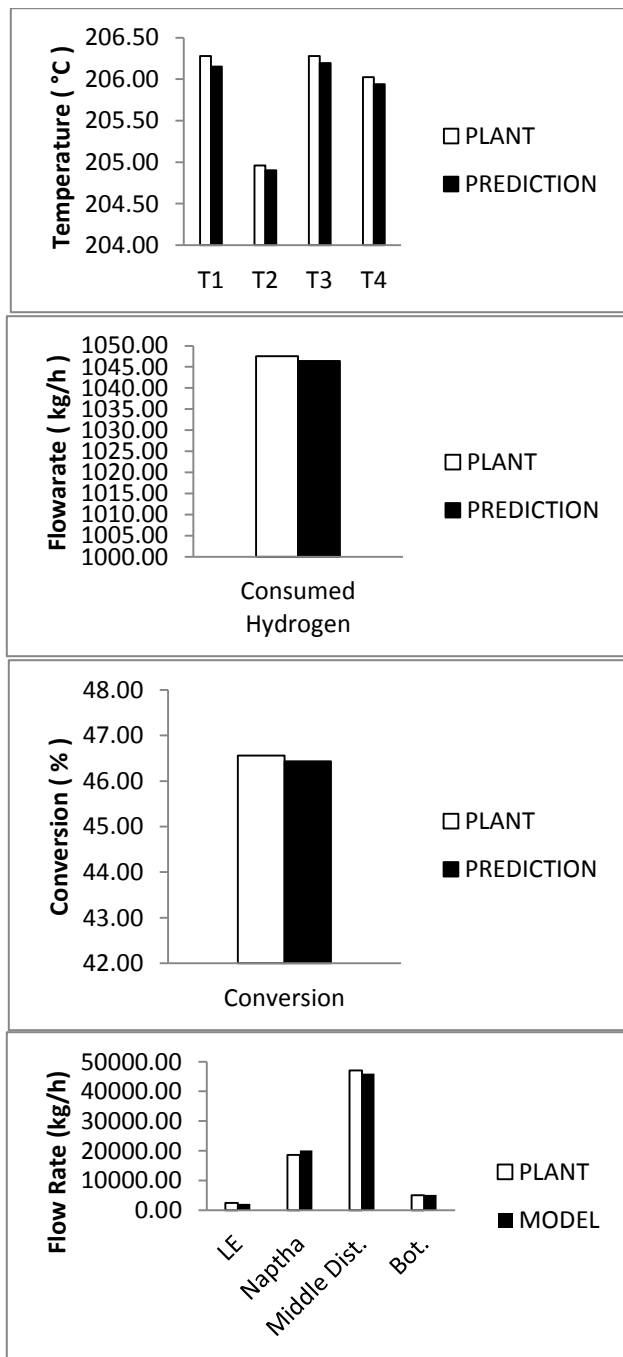


Fig 4. Comparison of model predictions and plant data for Day 4 operation.

B. Temperature Sensitivity

Although economic optimization is not in the scope of this study, the model was still tested whether it can be used in an optimization process or not. It is known that the changes in inlet temperatures will affect the conversion. In order to observe the temperature effect on conversion of the model, simulations were performed by changing bed inlet temperatures by 1 °C. It was observed that the temperature change made very insignificant difference on conversion. That is, the conversion remained nearly constant. In fact, it was not surprising because the data used for model was from constant conversion operation. Therefore, the model was insensitive to temperature. The aim of the optimization is to find the optimum inlet temperatures which will provide higher conversion, hence higher profit. Hence, the developed model was not proper for an optimization process because higher conversions would only be achieved by higher temperatures. In order to overcome this limitation, the parameter estimation was re-performed by six data sets where the conversion was at two different levels as can be seen in Fig 5.

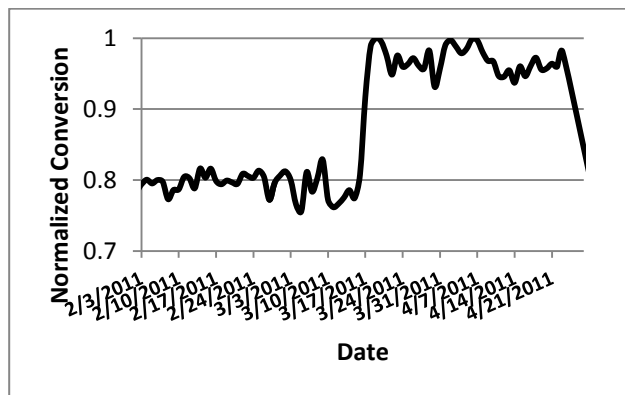


Fig 5. Plant operation at two different conversion levels.

The predictions showed that this updated model has temperature sensitivity. That is, it reacts against the changes in inlet temperatures as can be observed in Fig 6.

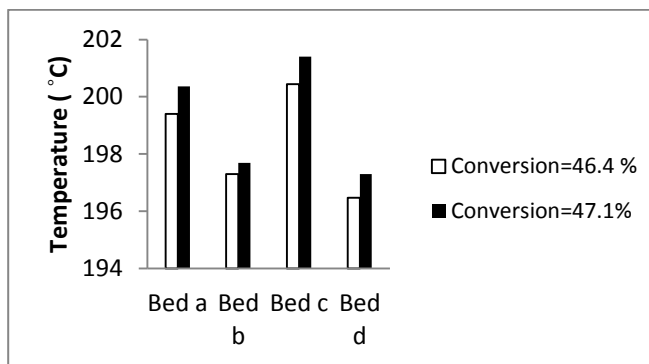


Fig 6. Effect of bed inlet temperatures on conversion.

C. Effect of Catalyst Deactivation on Model Parameters

As the plant operates, the catalyst loses its activity. In fact, catalyst activity determines the temperature that is required to obtain a fixed conversion. When the catalyst is deactivated, higher inlet temperatures are needed to achieve the same conversion as can be observed in Fig 7.

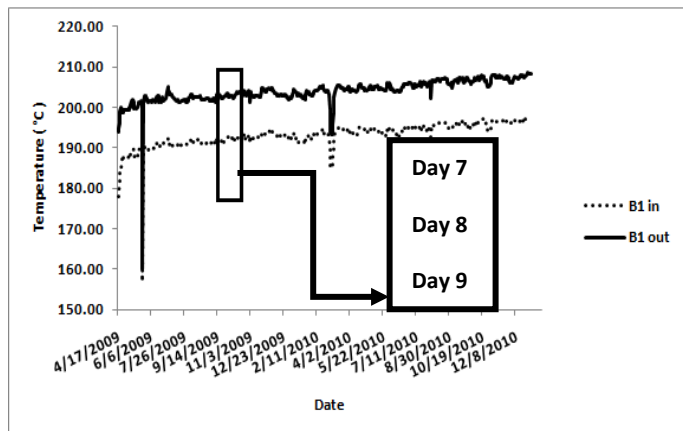


Fig 7. Plant data for the first bed inlet and outlet temperatures.

Since operating conditions change, the model parameters should be updated as well. When the new parameter set was compared with the previous set, it was seen that the product distribution parameters were similar. It is reasonable because the plant produces the same products. It was also observed that the reaction rate parameters were higher when the catalyst was fresher. The higher the activity, the higher the reaction rate is. Hence, the catalyst activity affects the model parameters.

V. CONCLUSIONS

In this study, an industrial hydrocracker reactor model was developed by discreet lumping method and it was shown that under constant conversion operating conditions, model estimates matched the plant data closely. Besides, the effect of catalyst deactivation on model parameters was investigated and it was indicated that rate constant parameters correlated well with catalyst deactivation. Moreover, temperature sensitivity was introduced to the model by estimating the parameters using operating data at two different conversion levels. Simulations revealed that the model reacts against the change in inlet temperatures.

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