Continuous Lumping Model of an Industrial Refinery Isomax Reactor

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Abstract

Hydrocracking is an important secondary process in the petroleum industry, generally used to process heavy oil cuts. The process is tailored to various needs of refineries in order to maximize middle distillates, gasoline, LPG and similar products. Therefore, kinetic modeling of hydrocracking reactors applied to upgrade vacuum heavy oil (Isomax) is important and needs to be investigated. In this work, following a brief comparison of continuous lumping model in contrast to discrete lumping model, the former was chosen to model an operational Isomax reactor in Tabriz refinery, located in the North West of Iran. In order to categorise various unknown components True Boiling Point (TBP) of the mixtures were employed as the key parameter. Hence, the hydrocracking rate constant was assumed to be an even function of true boiling point. This would facilitate reformulation of mass-balance equations in terms of rate constant as a continuous variable. In order to determine the fraction yield distribution of the species, a specific distribution function was formulated. The resulting model equations were solved numerically and the yield of various fractions as a function of reactor residence time were estimated. A comparison between model predictions and experimental data shows it can predict the weight percent of light and heavy fractions well with an acceptable accuracy.

Keywords: *Hydrocracking, Continuous Lumping Model, Isomax Reactor*

1- Introduction

Hydrocracking is an important process endeavouring to upgrade the quality of heavy oil cuts. The aim is to retrieve more products of middle distillates having a better quality through adding hydrogen to the heavy cuts. Limited oil resources and a countable portion of crude oil as heavy bottom distillate have drawn more attention to hydrocracking as a justifiable process in recent decades.

Environmental aspect is another reason to look at the hydrocracking process. Heavy oil cuts usually contain sulphur, nitrogen, oxygen and heavy metals that need to be refined before consumption in order to prevent environmental pollution. Thermal and catalytic processes can facilitate elimination of the agents. The process of adding hydrogen is possible either in catalytic form (Catalytic Hydro Processing)

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or in thermal form (Thermal Hydro Processing). In catalytic processes, usually nickel oxide and molybdenum oxide catalysts based on alumina in 400 to 450 °C and 140bar are used. The catalysts play an important role in removing heteroatom components. On the other hand, thermal reactions break heavy components into lighter ones. In thermal hydrocracking, additives are added in order to control coke formation. Since hydrocracking is used as a prime process to enhance oil quality, the demand of having a kinetic model, especially for heavy cuts, has become more significant. Prediction of desired and undesired products at different operating conditions, optimisation and control of the process, design and selection of catalyst type would be easier having a kinetic model. A reliable kinetic model of a chemical reaction can describe the unique behaviour of each component based on the reaction mechanism. Due to the numerous components that exist in heavy oil cuts, modelling the composition and behaviour of such complex mixtures is not an easy task. Hence, determination of the complete molecular composition is not feasible with current analytical techniques. A modelling approach called structure oriented lumping (SOL) can be a solution to model the composition and chemistry of the complex mixture at a molecular level [1]. The main concept of the method is to represent an individual molecule or a set of closely related isomers as a mathematical construct of certain specific and repeating structural groups. Thus, the complex hydrocracking mixture can be represented as thousands of distinct molecular components, each having a mathematical identity. This enables construction of large complex reaction networks with tens of thousands of specific reactions simulating the chemistry of the mixture. The method provides a convenient framework for incorporating molecular physical property correlations, existing group contribution methods, molecular thermodynamic properties, and the structured activity relationships of chemical kinetics in the development of the model [2]. Detailed reaction network of the process can be taken into account in a newly proposed method called single event microkinetics (SEMK) [3]. The method underlying the classical carbenium ion chemistry occurring on the Brønsted acid sites of zeolitic catalysts has been shown to be effective in modelling acid catalyzed processes or the catalytic cracking process [4, 5]. It employs the rate coefficients applicable to any feedstock composition that can be estimated through the cracking of relatively simple and representative model molecules [6]. Catalyst properties such as acid strength were not explicitly accounted for in the early version of the SEMK model[7]. The SEMK simulations can be performed at the molecular level for hydrocarbons with small carbon numbers. However, having higher carbon numbers, the reaction network can be so large that the solution of the resulted equations becomes almost impossible [4, 8]. Moreover, a full detail analysis of the reaction products is not viable with today's analytical tools. The SEMK model needs to be modified to the so called relumped form to describe the system, while preserving the fundamental character of the model [9]. Artificial neural network (ANN) modelling is another tool investigating the steady-state

behaviour of the process [10]. A large set of real data is needed to develop, train and check the model. Due to the complexity of hydrocracking however, modelling the process is a great challenge. The ANN model proved to be capable of predicting the volume percent of conversion based on six input variables [11]. The optimum architecture of the ANN model was investigated by the authors and it was claimed to be superior to an existing non-linear statistical model.

In a more simple approach, a range of components are conventionally selected as a bulk instead of studying each component. The behaviour of the bulk in the reactions will be analysed for overall process studies. A range of the components is called a pseudo component. The range may be categorised based on boiling point, molecular weight, number of carbon atoms and other quantitative properties. Different lumping models were developed in order to analyse the kinetics of hydrocracking reactions for complex mixtures. The models can be used in discrete lumping methods [12-15] as well as continuous lumping methods that have attracted more attention [16, 17]. In discrete models, since the components are defined in lump (group), individual reactions of species can be ignored. Moreover, the conversion in lumped boundaries can be used to describe chemical conversion as well as conversion of one lumped component to another. Any number of lumped components can be assumed, in which distribution of the mixture changes due to reaction. Continuous models were basically developed in the 1980's and proved to be useful by recent researches. In all the above methods, the main challenge is

to relate the feed composition to the product yields and quality for a wide range of operating conditions. In this paper the continuous lumping concept was applied to model the Tabriz refinery Isomax reactor.

2- The continuous lumping model

A continuous mixture is so complex that individual chemical species present in the mixture are no longer worth being distinguished independently. Instead, an index such as TBP or reactivity may be chosen. In contrast to the discrete lumping approaches that are usually based on pseudo components such as products slate, TBP cuts, carbon number or molecular weight, in the continuum theory of lumping, the reactive mixture is considered to form a continuous mixture with regard to its species type, boiling point, molecular weight or other applicable physical properties.

The idea of continuous mixture has found many applications since it was first introduced in 1931 [18]. The concept is used when a system consists of numerous components having physical properties close to each other. For such mixtures a continuous variable such as boiling point, molecular weight or other mixture characteristics may be used to describe the mixture composition. This method is used in the mathematical modelling of different phenomena including distillation [19], thermodynamics, isomers distribution [20], polymerization [21] as well as reaction of continuous mixtures [22-25]. In order to apply a continuous model, a continuous distribution function for the reactants mixture based on one of their properties needs to be defined. The aim of modelling is to analyze the continuous

function finding its final values after the reaction. In this research, a model for hydrocracking of an oil mixture based on the continuous lumping theory [26] is developed. The oil mixture is fundamentally defined by TBP curves. A first order reaction between the components is assumed which is an acceptable assumption for hydrocracking of heavy cuts [27]. However, the model is flexible enough to be applied for other reaction orders. Moreover, TBP curves are employed as the key variable describing the mixture characteristics. Therefore the mixture composition at any given time of the reaction is known by TBP curves. The TBP distribution function for the reactants mixture varies with reaction time. More heavy components are converted to lighter ones as residence time (reaction time) increases. The distribution function of the mixture changes in a way that lighter components increase with more residence time. Similar to any other kinetic model, the model is expect to predict the distribution of reactant mixture composition at any given residence time. The TBP curves can be converted to a weighted composition distribution function as $C(\theta, t)$ is relative to the normalized temperature defined as follows:

$$\theta = \frac{TBP - TBP_l}{TBP_h - TBP_l} \tag{1}$$

Where, TBP_h and TBP_l indicate the higher and lower boiling point possible in the reactant mixture and represent the heavier and lighter components in the mixture respectively. $C(\theta,t)$ is the value of concentration distribution function, corresponding to a normalized $TBP(\theta)$ at any

given time (t). Therefore, $C(\theta, t)d\theta$ is the concentration of the components having a boiling point between θ and $\theta+d\theta$ in the normalized TBP curve. Here, we assume a simple relation for reaction rate constant k versus θ as:

$$\frac{k}{k_{max}} = \theta^{(\frac{1}{\alpha})} \tag{2}$$

α is a model parameter and k_{max} is the rate constant of the component with the highest *TBP* for which $\theta = 1$. Another assumption in the above equation is that when $k = 0$ then $\theta = 0$. That means the cracking rate of the component with the smallest boiling point is zero. This is a reasonable assumption since the smallest component would not break and remains intact. The above function was chosen since it confirms many experimental data from previous studies [28, 29, 30, 31, 32]. Other functions having the same assumptions may also be applied. Conversion of discrete mixture (i coordinate) to continuous mixture (k coordinate), in which i transforms to k coordinate system, and a description of the reactor performance in the continuous system are formulated by Chou et al [24]. The component type distribution function $D(k)$ can be obtained as a Jacobian of *i-k* coordinate transformation in mathematical form as follows:

$$D(k) = \frac{di}{dk} = \frac{di}{d\theta} \frac{d\theta}{dk} \tag{3}$$

Where i is the component index in discrete system. In this work however, pseudo components were used that are defined

relative to θ and equally spaced along the i coordinate axis. N is the total number of components ($N \rightarrow \infty$), and $\dfrac{di}{d\theta}$ can be estimated by the N components. From the above equation we can write the following relation:

$$D(k) = \frac{N \alpha k^{(\alpha-1)}}{k_{max}^{\alpha}} \tag{4}$$

2.1- Mass balance equation

Mass balance equation for the component with reactivity k in direction t can be derived as:

$$\frac{dc(k,t)}{dt} = -k\,c(k,t) + \int_{k}^{k_{max}} P(k,K)\,K\,c(K,t)\,D(K)\,dK \tag{5}$$

The yield distribution function $P(k, K)$ represents the amount of the components produced with reactivity k resulting from the cracking of the components with reactivity K. Since the mass balance is written in k space, the component type distribution function $D(K)$, accounts for cracking of all components with reactivity K required to inscribe the conservation law. From the above equation, a similar relation for non-linear kinetic reactions can also be deduced. This requires incorporation of the rate models of $k\,c(k,t)$ and $K\,c(K,t)$ that can be easily substituted for other complex nonlinear reaction rates.

Equation 5 can be used in general to find outlet product distribution from the reactor (as a function of residence time) choosing an appropriate $P(k, K)$ function. The function

should be chosen in a form that satisfies the experimental results. From the experimental data, the $P(k, K)$ function is presented as follows [26]:

$$P(k,K) = \frac{1}{S_0\sqrt{2\pi}}\left[exp-\left[\left\{(k/K)^{a_0}-0.5\right\}/a_1\right]^2 - A + B\right] \tag{6}$$

The terms A and B in the above equation are redefined as:

$$A = exp\left[-\left(0.5/a_1\right)^2\right] \tag{7}$$

$$B = \delta\left(1-\left(\frac{k}{K}\right)\right) \tag{8}$$

a_0 and a_1 are model parameters. Therefore, the distribution function is computed from the following relation.

$$S_0 = \int_0^K \frac{1}{\sqrt{2\pi}}\left[exp-\left[\left\{(k/K)^{a_0}-0.5\right\}/a_1\right]^2 - A + B\right]D(k)\,d(k) \tag{9}$$

Although first order hydrocracking reaction is assumed, the model can be easily extended to other kinetic forms. This is possible since the component type distribution function for complex continuous reaction mixtures has the same condition as discrete mixtures [33].

2.2- Solving the continuous model

Since there is no analytical solution for the continuous model, numerical methods are employed in order to solve equation 5. This is done by solving the integral part and then computing the resulting differential equation

using a direct method. The integral part is solved for each pseudo component as follows. The *K* space axis is divided into *N* equal distance points and the differential equation for each point with small time step *δt* is derived as shown in equation 10. Moreover, the relation between any two points in the function *c(k,t)* is assumed to be linear [26, 33].

$$\frac{c(k_i,t) - c(k_i,t-\delta t))}{\delta t} = c(k_i,t)[-k_i + I_1(k_i,k_{i+1})] +$$

$$\sum_{j=i+1}^{N-1} c(k_j,t)I_1(k_j,k_{j+1}) + \sum_{j=i+1}^{N-1} c(k_j,t)I_2(k_j,k_{j+1})$$

(10)

Where:

$$I_1 = (k_j,k_{j+1}) = \int_{k_j}^{k_{j+1}} P(k_i,K)\frac{(K-k_{j+1})}{(k_i-k_{j+1})}D(K)dK$$

(11)

$$I_2 = (k_j,k_{j+1}) = \int_{k_j}^{k_{j+1}} P(k_i,K)\frac{(K-k_j)}{(k_{j+1}-k_i)}D(K)dK$$

(12)

The first numerical solution would be in the *N*'th point in which the heaviest molecule with the highest reactivity is cracked into lighter ones. Therefore at each time step we can write:

$$c(k_N,t) = c(k_N,t-\delta t)e^{-k_N \delta t}$$

(13)

The difference equation is solved for all points and *c(k,t)* would be obtained. Next, the concentration of the slices is determined by the following integral equation.

$$C_{1,2}(t) = \int_{k_1}^{k_2} c(k,t)D(k)dk$$

(14)

The above concept was applied to model the operational isomax reactor of Tabriz refinery and simulation results are presented in TBP curves predicting the processes behaviour.

3- Plant description and data collection

Tabriz refinery isomax plant is designed to convert 18000 barrels per day (bbl/d) of low quality gasoil from the vacuum tower producing 8255kg/hr butane (C_4), 1022 bbl/d light naphtha, 1418 bbl/d heavy naphtha, 9781 bbl/d kerosene and 7456 bbl/d gasoil (diesel fuel). The plant consists of four identical catalytic fixed bed reactors placed in two pairs of reactor series as shown in Fig. 1. The feed and hydrogen are fed into the system via two streams entering both reactor series, while additional hydrogen enters between the beds to supply the required hydrogen and to control the operating temperature. The product streams are then combined at their exit from the reactors.

The catalyst used in the reactors is supplied by a Holland company (Akzo Nobel) with the commercial name "KF-1015" that contains cobalt and molybdenum oxide on γ-alumina bases. Due to the soaring heat of the reaction, hydrogen is launched between the catalytic fixed beds. The reactions take place at around 401°C, while the operating pressure is 190 bars.
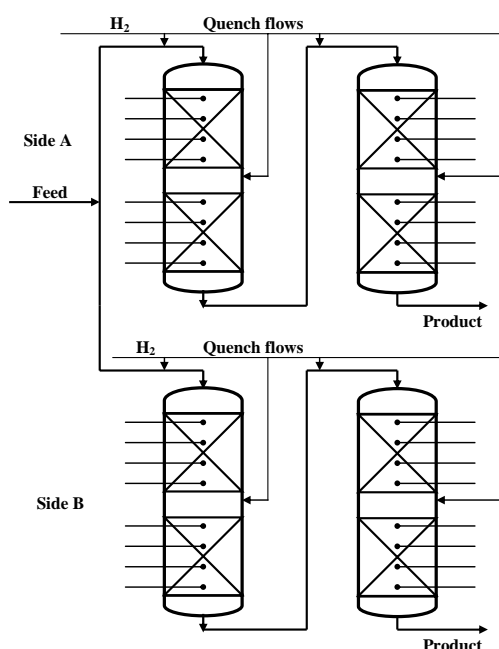
Figure 1. Schematic view of the reactors with temperature measurements on the beds

Since the model parameters are temperature dependant, it is important to make sure that the data collected are at an identical temperature. This ensures the accuracy and reliability of the plant data. The concept of weight average bed temperature (WABT) defined by the catalyst manufacturer was employed to monitor temperature variations during the sampling periods. The WABT is the linear average of temperatures measured along the reactors multiplied by percentage of weight fraction of the catalyst at the measuring positions. The WABT is an important parameter for temperature evaluation in catalytic reactor systems. Having 32 measured temperatures at the locations shown in Fig. 1, WABT was attained for both sides of A and B corresponding to the two series of reactors in the Tabriz plant. This shows that there is not a considerable temperature deviation during the sampling periods to affect the temperature dependant model parameters (Fig. 2).
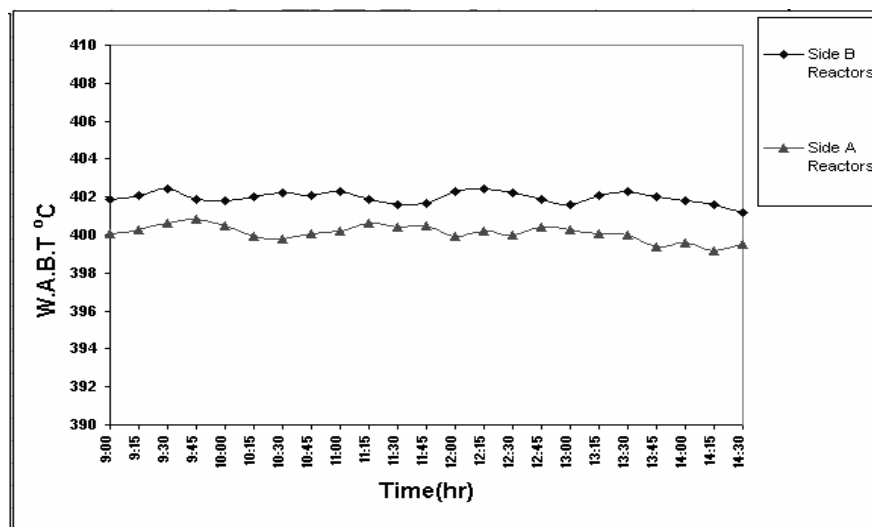

Figure 2. The weight average bed temperature (WABT) for Sides A and B during sampling period.

4- Results and discussion

Samples from products including gaseous products as well as light naphtha, heavy naphtha, kerosene, gasoil and offtest were taken at the specified sampling time. The gaseous product compositions were measured by a GC analyzer, while ASTM-D86 was used for light naphtha, heavy naphtha, kerosene and gasoil. Moreover, offtest samples were tested using ASTM-D1160 and specific gravity. In this way, based on the sample data, the TBP curve for feed and products at different reaction times could be attained [34].

Samples of the inlet and outlet streams of the refinery isomax reactors were taken from the plant and the standard ASTM tests were done in order to draw the θ curves for each stream. The experimental data include specifications of feed as well as products at three different residence times of reaction. TBP curves for feed and products at the three residence times of 0.22, 0.26 and 0.3 hours were attained from the collected samples. Note that equivalent variable LHSV (Liquid Hourly Space Velocity) can also be used instead of residence time. The resulted values from the feed sample are shown in Fig. 3, which illustrate weight fraction distribution of the feed with respect to normalised TBP (θ), while Fig. 4 shows the specification of the products having 0.22 hour for the residence time of reaction.

Having the above experimental data, optimal values for model parameters were computed. The optimum values of the five independent tuning parameters of the model were calculated using the Levenberg-Marquardt algorithm as follows:

$\alpha = 0.1718$

$a_0 = 1.009 \times 10^{-5}$

$a_1 = 100$

$k_{max} = 1.932 \ h^{-1}$

$\delta = 1.72 \times 10^{-4}$

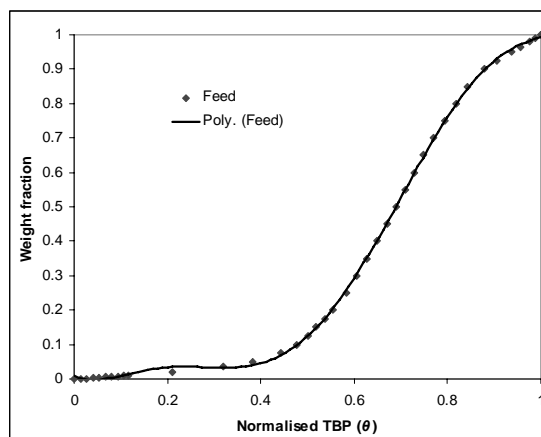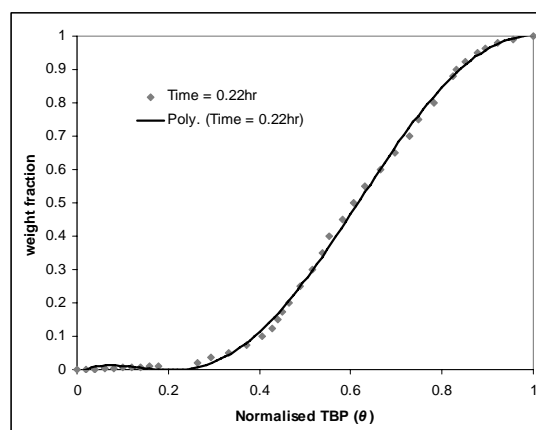**Figure 3.** The θ curve for feed stream specification

Figure 4. The θ curve for product stream with residence time of 0.22 hour

The above steps were repeated having the 2nd and 3rd round of samples taken from the reactor. On the other hand, the model results were obtained having the above mentioned estimated parameters and considering the inlet reactor feed specification. The

experimental data were compared to the model results for these two sets of the plant data. It can be seen from the results that typical hydrocracking trends with respect to the residence time are well predicted by the model. This shows that as the hydrocracking proceeds, a wider distribution results that is more evident toward lower TBP components. Model predictions and experimental data from the second and third sets of samples having residence times of 0.26 and 0.3 hours are evaluated. Fig. 5 compares the model predictions and experimental data from the second set of samples having residence times of 0.26, while the third set of samples having residence times of 0.3 hour along with other sets of experimental data are compared in Fig. 6.
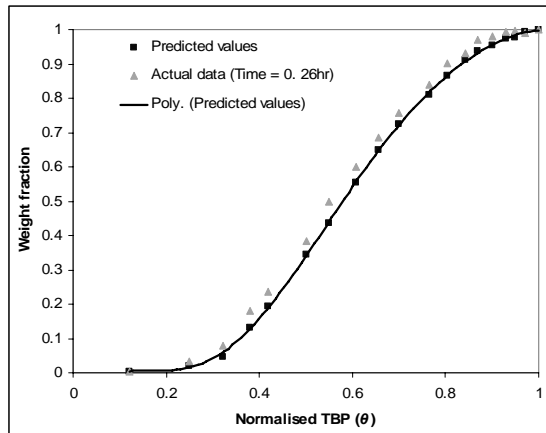
normalized TBP (θ) values. By fitting a simple *n*th order rate expression to the concentration data, it can be found from the model results and experimental data that the overall apparent order of the reaction in this process is 2. Hence the reaction order for individual component is 1, which confirms the finding of other researchers [35, 36].

Fig. 7 shows the errors for different hydrocarbon cuts predicted by the model in two specified residence times.
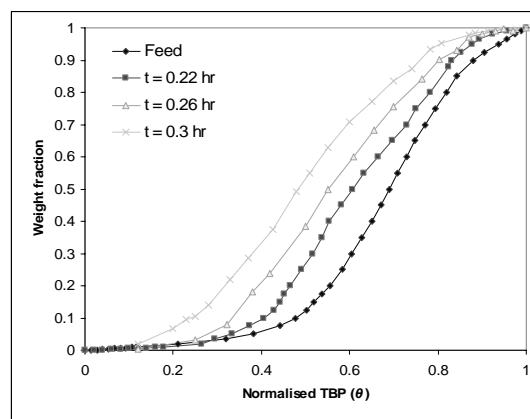

Figure 6. Comparison of the experimental data including feed and products in residence time of 0.22, 0.26 and 0.3 hour

Figure 5. Comparison of the values of model prediction and experimental data in residence time of 0.26 hour

The results show that the model could well predict the experimental data. A polynomial trend line was also depicted on the figures having an order of 6 that can be used for estimation of the weight fraction at any given
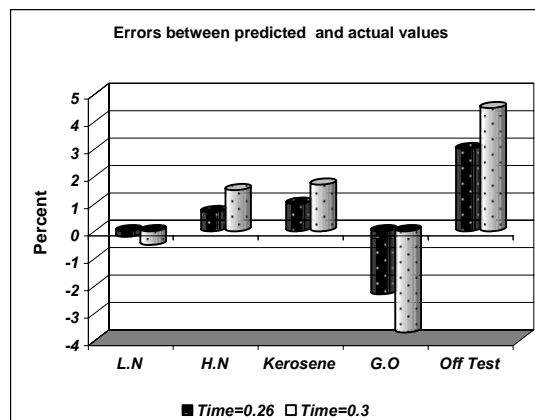

Figure 7. Model prediction error for product values with residence time of 0.26 and 0.3 hours

This shows that while the model prediction is acceptable with less than 5% relative error, it has greater accuracy for lighter components and less residence time. This is reasonable since more conversions for heavier components can be expected in higher residence times. Overall, the model is reliable to a reasonable extent, for predicting the complex hydrocracking process.

5- Conclusions

The method of continuous lumping model was successfully applied in modelling hydrocracking kinetics of an industrial isomax plant. The model presented in this paper, based on TBP curves and reactor residence time, was validated by three sets of experimental data. The model was able to come up with the complex hydrocracking kinetics showing an acceptable accuracy in predicting the product yield. The model prediction was more accurate for lighter components with smaller residence time. Moreover, it provides the framework for a more general and flexible model to be used for predicting complex nonlinear kinetics in simulation of hydrocrackers.

6- Acknowledgment

7- Nomenclature

a_0, a_1	model parameters
A	parameter defined in equation 7
B	parameter defined in equation 8
C_i	concentration of species i
$D(k)$	distribution function
E	activation energy (cal)
I_1	parameter defined in equation 11
I_2	parameter defined in equation 12
k_i	reactivity of species i (h^{-1})
K_{max}	rate constant of heaviest species (h^{-1})
N	number of equal distance points
$P(k, K)$	yield distribution function
R	gas constant (J/mole.K)
S_0	parameter defined in equation 9
T	temperature (K)
TBP_h	true boiling point of heaviest species (K)
TBP_i	true boiling point of species i (K)
TBP_l	true boiling point of lightest species (K)
α, δ	model parameters
θ_i	normalized TBP of species i
Poly	6th order polynomial trendline that best fit the data in figures
t	reactor residence time (h)

Indices

i	coordinate axis
j	component index
k	coordinate axis

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