Dynamic Modeling and Simulation of Heavy Paraffin Dehydrogenation Reactor for Selective Olefin Production in Linear Alkyl Benzene Production Plant

G. Zahedi, and H. Yaghoobi

Abstract—Modeling of a heterogeneous industrial fixed bed reactor for selective dehydrogenation of heavy paraffin with Pt-Sn-Al$_2$O$_3$ catalyst has been the subject of current study. By applying mass balance, momentum balance for appropriate element of reactor and using pressure drop, rate and deactivation equations, a detailed model of the reactor has been obtained. Mass balance equations have been written for five different components. In order to estimate reactor production by the passage of time, the reactor model which is a set of partial differential equations, ordinary differential equations and algebraic equations has been solved numerically.

Paraffins, olefins, dienes, aromatics and hydrogen mole percent as a function of time and reactor radius have been found by numerical solution of the model. Results of model have been compared with industrial reactor data at different operation times. The comparison successfully confirms validity of proposed model.

Keywords—Dehydrogenation, fixed bed reactor, modeling, linear alkyl benzene.

I. INTRODUCTION

PARAFFIN dehydrogenation for the production of olefins has been in use since the late 1930s. During World War II, catalytic dehydrogenation of butanes over a chromia-alumina catalyst was practiced for the production of butenes, which were then dimerized to octane and hydrogenated to octane to yield high-octane aviation fuel [1, 2].

A different approach to catalytic dehydrogenation was first introduced in the mid-1960s for the supply of long-chain linear olefins for the production of biodegradable detergents.

Synthetic detergents, based on the use of branched alkyl benzene sulfonates derived from propylene tetramer and benzene, had been introduced in the 1940s [1, 3]. By the early 1960s, however, it became apparent that branched dodecylbenzene-based detergents, though very active and offering excellent performance characteristics, did not biodegrade readily and were accumulating in the environment. The need for biodegradable detergents prompted the

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development of catalytic dehydrogenation of long-chain linear paraffins to linear olefins. This was the basis for the UOP PacolTM process for the production of linear olefins for the manufacture of biodegradable detergents. In 1999, there were more than 30 commercial Pt-catalyzed dehydrogenation units in operation for the manufactures of detergent alkylate [1, 3].

Linear alkyl benzene (LAB) is a major compound for production of biodegradable detergents. Bisetoon petrochemical complex is the first LAB plant which was built in Kermanshah (Iran) for the Mashal Daran petrochemical company by IFP (French) company. This plant processes a kerosene cut containing n-paraffin C$_{10}$- C$_{13}$ [4]. In this plant, the main process is the dehydrogenation of heavy paraffin to mono olefin [4] due to low conversion of heavy paraffin, high cost of dehydrogenation catalyst and deactivation of catalyst at less than 3- 4 week [2, 4] which is performed by catalytic radial flow reactor [4].

The main reaction in catalytic dehydrogenation is the formation of mono-olefins (desirable product) from the corresponding feed paraffin. Other reactions include consecutive and side reactions. Various by-products can also form. In addition, the catalyst rapidly deactivates due to fouling by heavy carbonaceous materials. Therefore, the properties of platinum and the alumina support need to be modified to suppress the formation of by-products and to increase catalytic stability [1, 3]. Arsenic, tin, germanium, lead and bismuth are among metals reported as platinum activity modifiers [1, 3]. Fig. 1 illustrates Paraffin dehydrogenation on modified platinum catalyst.
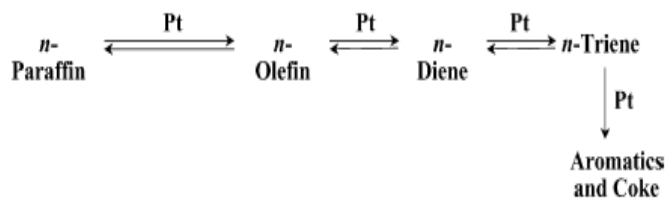

Fig. 1 Paraffin dehydrogenation on modified Pt catalyst [1]

The catalyst of paraffin dehydrogenation is deactivated rapidly; therefore for optimization of dehydrogenation reactor operation, we need a model, which can predict concentration

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profile. This reactor is a special type of catalytic reactor with radial feed flow. Any study about modeling of heavy paraffin dehydrogenation reactor has not been carried out until last of 2007 and this is first study about expressed reactor.

II. PROCESS DESCRIPTION

A. Dehydrogenation Reactor

IFP's catalytic dehydrogenation process typically makes use of radial flow adiabatic fixed-bed reactors with modified Pt-alumina catalysts [4]. The catalytic dehydrogenation reactor of IFP's process for selective long-chain paraffin dehydrogenation to produce linear mono olefin is shown in Fig. 2. Feed flow is consist of heavy paraffin & hydrogen (hydrogen / hydrocarbon= 6/1) [1, 4].

Gas flow is distributed by diffuser between the external cylinder and packed bed, at above the reactor. Feed flow from external cylinder is leaded to center of internal cylinder and has no axial velocity along the packed bed approximately, because end of packed bed is blocked, hence has no axial pressure drop. Paraffin dehydrogenation occurs in catalytic bed means from radius= 0.75 (m) to radius= 0.4 (m) [4].
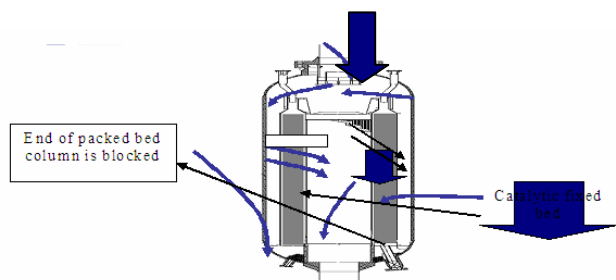

Fig. 2 The catalytic dehydrogenation reactor of IFP's process with radial feed flow [4]

TABLE I
FEED SPECIFICATION [4]

|	input	output
Temperature (K)	738.15	723.15
Pressure (bar)	2.7	2.5
Mass flow rate (Kg/hr)	55698	55698
Molar flow rate (Kmol/hr)	2131	2161

TABLE II
DEHYDROGENATION CATALYST SPECIFICATION [4]

type	DP- 805
Supplier	Procatalyse
Catalyst + Characteristics	Alumina impregnated with platinum and tin
Loading Method	Sock
Shape	Spherical
Average diameter	2.24 mm
Sock Loading	420 – 450 Kg/ m^3
Loaded quantity	3.33 m^3/ reactor

Long-chain paraffins are both valuable and highly prone to cracking. Therefore, in order to maintain high selectivity and yield, it is necessary to operate at relatively mild conditions, typically below 500 ◦C, and at relatively low per-pass conversions [4]. Feed specifications have been shown in Table I and Table II present catalyst specifications.
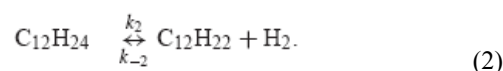
B. Kinetic Study

Literature on kinetics of higher paraffin dehydrogenation is very limited [3]. Studies by Krylova et al. (1980a) were based on H2–D2 exchange and dehydrogenation of n-decane and decene for Pt/Al2O3 and other promoted systems [3]. Stepwise dehydrogenation involving desorption of olefins and di-olefins as the rate determining step was proposed by Krylova et al. (1980b). However no mechanistic models were tested. Initially the rate expressions were derived for Pt–Li–W/Al2O3 catalyst and later extended to Pt–Sn/Al2O3 catalyst as well (Sadykhova et al., 1981). It has been established that relative to mono metallic Pt/Al2O3 catalyst, bi metallic Pt–Sn/Al2O3 promotes desorption of olefins and hence may follow a different mechanism (Sadykhova et al., 1984). Kinetic study of cock e formation in dehydrogenation of n-decane on Pt–Al2O3 catalyst was reported by Mart'yanaova et al. (1982). George (1991) studied the kinetics of n-dodecane dehydrogenation on Pt–Sn/Al2O3 catalyst but their study was limited to lower conversions and ignored the secondary dehydrogenation reactions [3]. K.K. Chaudhuri et al. (2005) studied the kinetics of n-dodecane dehydrogenation on Pt–Sn/Al$_2$O$_3$ catalyst and Various rate models based on Langmuir–Hinshelwood–Hougen–Watson (LHHW) and Eley Rideal mechanisms derived for the three dehydrogenation reactions and subjected to model discrimination and parameter estimation by using Box's complex optimization method. Of the 12 different models tested, model based on LHHW mechanism with surface reaction as rate-determining step fitted the experimental data well, that is employed as kinetic of reaction in this paper [3]. In accordance with the product distribution, the system can be described by the following reactions [3]:
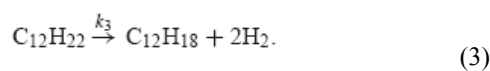
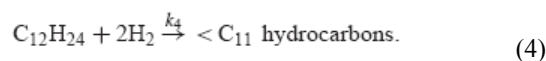Dehydrogenation, olefins formation:

$$C_{12}H_{26} \underset{k_{-1}}{\overset{k_1}{\leftrightarrow}} C_{12}H_{24} + H_2. \tag{1}$$
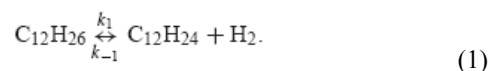
Secondary dehydrogenation, diens formation:

$$C_{12}H_{24} \underset{k_{-2}}{\overset{k_2}{\leftrightarrow}} C_{12}H_{22} + H_2. \tag{2}$$

Aromatics formation:

$$C_{12}H_{22} \overset{k_3}{\rightarrow} C_{12}H_{18} + 2H_2. \tag{3}$$

Olefins cracking:

$$C_{12}H_{24} + 2H_2 \overset{k_4}{\rightarrow} < C_{11} \text{ hydrocarbons.} \tag{4}$$

The rate of formation of each component can be expressed as [3]:

Rate of disappearance of paraffin (n-dodecane):

$$\frac{dX_P}{d\theta} = -r_1 \tag{5}$$

Rate of formation of olefins (dodecene):

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$$\frac{dX_O}{d\theta} = r_1 - r_2 - r_4 \qquad (6)$$

Rate of formation of dienes (dodecadine):

$$\frac{dX_D}{d\theta} = r_2 - r_3 \qquad \begin{matrix}(6)\\(7)\end{matrix}$$

Rate of formation of aromatics:

$$\frac{dX_A}{d\theta} = r_3 \qquad (8)$$

Rate of formation o flight paraffins *(<C11)*:

$$\frac{dX_{LP}}{d\theta} = r_4 \qquad (9)$$

Rate of formation hydrogen:

$$\frac{dX_{H2}}{d\theta} = r_1 + r_2 + 2r_3 - 2r_4 \qquad (10)$$

Where θ=W/F=g cat h/mol paraffin feed; r_i (i=1–4) is rate of ith reaction. Reaction rate is expressed in terms of partial pressure of the components [3].

$$r_1 = \frac{k_1 K_P (p_P - p_O p_H / K_{El})}{(1 + K_P p_P + K_O p_O + K_D p_D + K_A p_A + K_H p_H)^2} \qquad (11)$$

$$r_2 = \frac{k_2 K_O (p_O - p_D p_H / K_{E2})}{(1 + K_P p_P + K_O p_O + K_D p_D + K_A p_A + K_H p_H)^2} \qquad (12)$$

$$r_3 = \frac{k_3 K_D p_D}{(1 + K_P p_P + K_O p_O + K_D p_D + K_A p_A + K_H p_H)^2} \qquad (13)$$

$$r_4 = k_4 p_O \qquad (14)$$

III. MATHEMATICAL MODEL

For modeling on a reactor scale, which is of primary concern to us, only macroscopic variables are used. To derive macroscopic mass transport equations one evidently needs to know something about the fluid flow between the pellets. As the real fluid flow inside a packed bed is very complicated, especially at the high flow rates typical of reactors, it is impossible to rigorously derive equations for the macroscopic quantities, starting from known equations of change [5]. Therefore, instead of the averaging of fundamental equations and various simplifying assumptions, which are needed to make the problem mathematically tractable, we will first simplify the problem. To this end we will construct a physically acceptable transport model on a scale comparable

to the size of the pellets and according to the concepts of the kinetic gas theory. This model can be regarded as a microscopic model of dispersion process in a packed bed [5]. It is necessary to emphasize that we do not aim to achieve mathematical rigor, and that we adopt a style of reasoning which can be described as physical. The model has been developed on the basis of the following hypotheses:

1. One-dimensional cylindrical coordinate (radial) has been considered along with the feed flow.
2. Molecular diffusion is negligible by comparison bulk diffusion [5].
3. Due to the high ratio of the reactor to particle diameter in case of a technical fixed bed, axial gradient is neglected [5].
4. Thermal effects is negligible due to low conversion of paraffin, therefore temperature is constant along fixed bed reactor.
5. There is no axial & angular velocity.
6. There is no the effect of penetration resistance in catalyst, surface reaction is considered as rate determining step [6].
7. There is one phase (gas) in all of the bed.

All these assumptions have been suggested and justified by experimental observations.

A. Momentum Balance at Steady State Conditions

Based on the aforementioned assumptions the differential equations for the momentum balance of the gas phase are:

Considering negligible potential energy, Bernoulli equation can be expressed as [7]:

$$\frac{dP}{\rho} + d\left(\frac{u^2}{2}\right) + dh_{fs} = 0 \qquad (15)$$

Which expression of dh_{fs} define by following equation [7]:

$$dh_{fs} = f \frac{u^2}{2} \frac{dr}{R_H} \qquad (16)$$

Friction factor (f) for packed column is function of Reynolds number and for laminar flow and R_H is hydraulic radius, these are expressed as [7]:

$$f = \frac{(1-\varepsilon)^2}{\varepsilon^3} \frac{75}{(D_p \rho u / \mu)} \qquad (17)$$

$$R_H = \left(\frac{cross\ section\ available\ for\ flow}{wetted\ perimeter}\right) = \frac{\varepsilon}{\alpha} \qquad (18)$$

$$\alpha = (1-\varepsilon)\frac{6}{D_P} \qquad (19)$$

Pressure at Bernoulli equation has been expressed by equation of state. Peng-Robinson EOS has been employed for Z calculation. Due to low conversion, has been assumed that reactions in packed column have no effect in velocity profile

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and pressure drop calculations therefore ρ is expressed by continuity equation as [7]:

$$\frac{\partial \rho}{\partial t} + u\nabla . \rho = -\rho(\nabla . u) \qquad (20)$$

By the above assumptions we will have [7]:

$$\frac{\partial \rho}{\partial r} = -\frac{\rho}{u}\frac{\partial u}{\partial r} - \frac{\rho}{r} \qquad (21)$$

B. Mass Balance

Based on the aforementioned assumptions the differential equations for the molar balance of the gas phase are [5, 7]:

$$\frac{\partial C_P}{\partial t} = \frac{C_P u}{r\varepsilon} + \frac{u}{\varepsilon}\frac{\partial C_P}{\partial r} + \frac{C_P}{\varepsilon}\frac{\partial u}{\partial r} + d_{load}*ac*(-r_1) \quad (22)$$

Equation (36) can be rewritten for other component as following:

Molar balance for olefin:

$$\frac{\partial C_O}{\partial t} = \frac{C_O u}{r\varepsilon} + \frac{u}{\varepsilon}\frac{\partial C_O}{\partial r} + \frac{C_O}{\varepsilon}\frac{\partial u}{\partial r} + d_{load}*ac*(r_1 - r_2 - r_4) \quad (23)$$

Molar balance for diene:

$$\frac{\partial C_D}{\partial t} = \frac{C_D u}{r\varepsilon} + \frac{u}{\varepsilon}\frac{\partial C_D}{\partial r} + \frac{C_D}{\varepsilon}\frac{\partial u}{\partial r} + d_{load}*ac*(r_2 - r_3) \quad (24)$$

Molar balance for aromatic:

$$\frac{\partial C_A}{\partial t} = \frac{C_A u}{r\varepsilon} + \frac{u}{\varepsilon}\frac{\partial C_A}{\partial r} + \frac{C_A}{\varepsilon}\frac{\partial u}{\partial r} + d_{load}*ac*(r_3) \quad (25)$$

Molar balance for light paraffin:

$$\frac{\partial C_{LP}}{\partial t} = \frac{C_{LP} u}{r\varepsilon} + \frac{u}{\varepsilon}\frac{\partial C_{LP}}{\partial r} + \frac{C_{LP}}{\varepsilon}\frac{\partial u}{\partial r} + d_{load}*ac*(r_4) \quad (26)$$

Molar balance for hydrogen:

$$\frac{\partial C_H}{\partial t} = \frac{C_H u}{r\varepsilon} + \frac{u}{\varepsilon}\frac{\partial C_H}{\partial r} + \frac{C_H}{\varepsilon}\frac{\partial u}{\partial r} + d_{load}*ac$$
$$*(r_1 + r_2 + 2r_3 - 2r_4) \qquad (27)$$

C_P, C_O, C_D, C_A, C_{LP} and C_H are density of paraffin, olefin, diene, aromatic, light paraffin and hydrogen respectively. d_{load} is catalyst load density.

ac is activity of dehydrogenation catalyst which can be expressed as function of time [2, 6]. ac can be substituted by following equation [2, 6]:

$$t = \frac{1 - ac^{(1-n-E_d/E_A)}}{k_{d0}(1-n+E_d/E_A)} \qquad (28)$$

The numerical method of line is used to solve the above partial differential equations set [8]. These set of equations have been solved by programming in MATLAB. The method of lines is a general technique for solving partial differential equations (PDEs) by typically using finite difference relationships for the spatial derivatives and ordinary differential equations for the time derivative. This solution approach can be very useful with undergraduates when this technique is implemented in conjunction with a convenient ODE solver package such as MATLAB.

IV. RESULTS AND DISCUSSION

By combination of Bernoulli equation and continuity equation, velocity profile and pressure drop have been obtained that have been illustrated in Figs. (3) & (4) respectively. The 4th order Runge Kutta approach is used to solve the above set of equations. These set of equations have been solved by programming in MATLAB and Z calculation has been done separately [8].
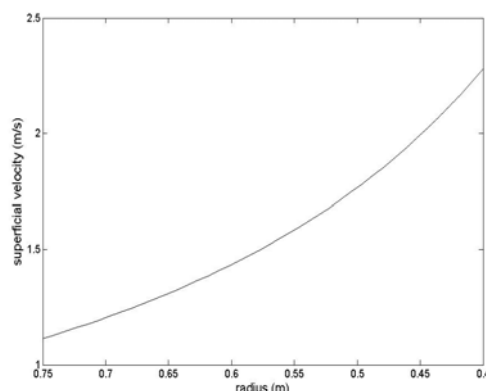

Fig. 3 Superficial velocity profile for fixed bed reactor with radial feed flow
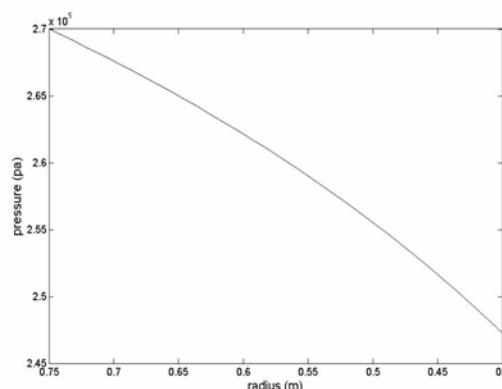

Fig. 4 Pressure drop for fixed bed reactor with radial feed flow

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According to Fig. 4, pressure drop for fixed bed reactor with radial feed flow has been predicted 0.23 bar. Industrial data for aforementioned reactor are 0.2- 0.25 bar approximately. This model has good accordance with experimental data; hence obtained velocity profile can be applied for calculations of concentration profile.

Results of simulation, in a wide range of reactor operation conditions are presented in Figs. 5-10.
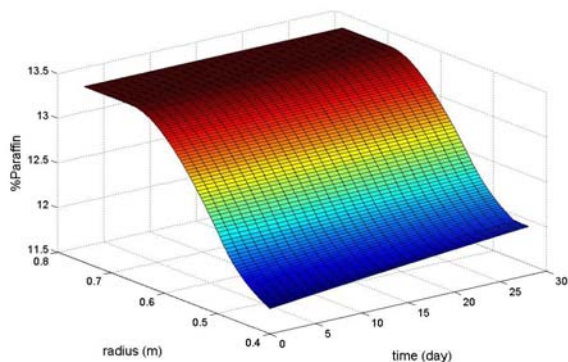

Fig. 5 Paraffin molar percent as a function of time and reactor radius

Fig. 5 illustrates the paraffin molar percent along catalytic fixed bed. According to Fig. 5, percent of paraffin decreases along the catalytic bed and due to deactivation of catalyst percent of paraffin increases at outlet, means conversion of paraffin decreases. It is obvious that changes of paraffin percentage is low initially, due to be reaction on catalytic surface as reaction determining step.
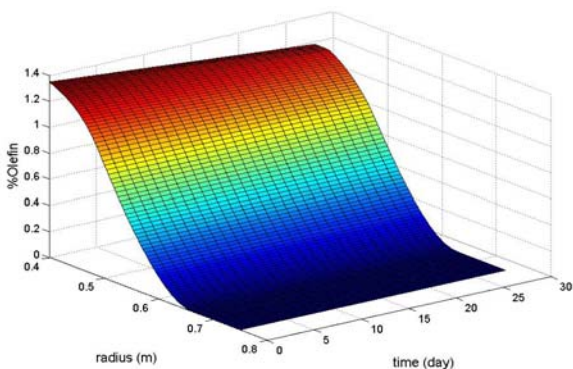

Fig. 6 Olefin molar percent for BPC dehydrogenation reactor

Fig. 6 illustrates the olefin molar percent along catalytic fixed bed. Changes of paraffin percentage are low initially, because conversion of paraffin is very low (zero approximately). After several days, due to coke formation activity of catalyst decreases hence amount of olefin decreases at outlet of reactor.

Fig. 7 illustrates the dienes molar percent along catalytic fixed bed. Rate of the dienes generation is very less than olefins generation due to presence of dehydrogenation catalyst promoter (Sn).
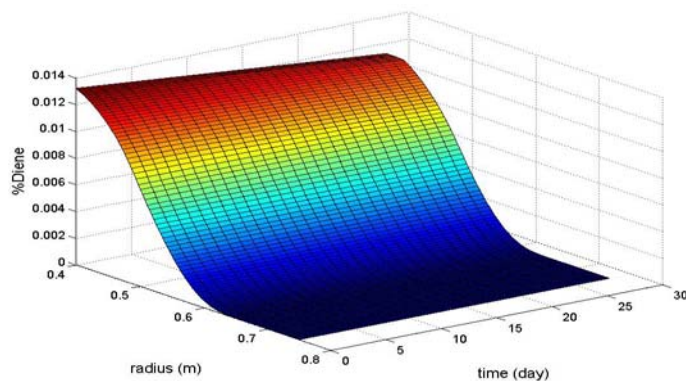

Fig. 7 Diene molar percent as a function of time across the BPC reactor

Diene concentration is near zero; hence by the increasing of diene concentration, the aromatics are generated by the dehydrogenation reaction of dienes. Fig. 8 illustrates aromatics molar percent along catalytic fixed bed.
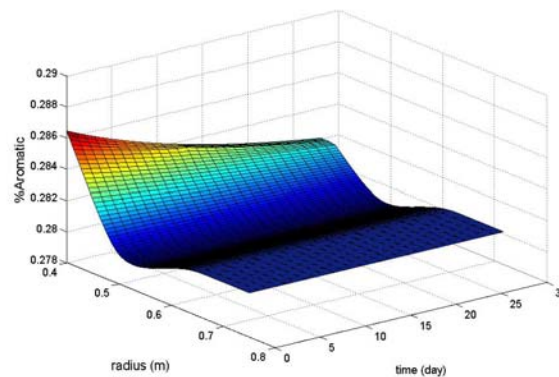

Fig. 8 Dynamic variation of aromatics across the BPC dehydrogenation reactor

By the cracking of the heavy paraffins, light paraffins are generated. High temperature is desirable for cracking of paraffin. Formation of cock on surface of catalyst and catalyst deactivation are caused cracking of heavy paraffin. Figure (9) illustrates light paraffin molar percent along catalytic fixed bed.
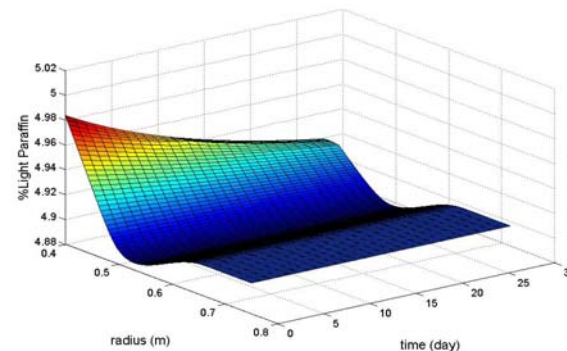

Fig. 9 Light paraffin generation

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Fig. 10 illustrates hydrogen molar percent along catalytic fixed bed. Concentration of hydrogen is function of dehydrogenation rate and cracking rate of olefin to light paraffin.
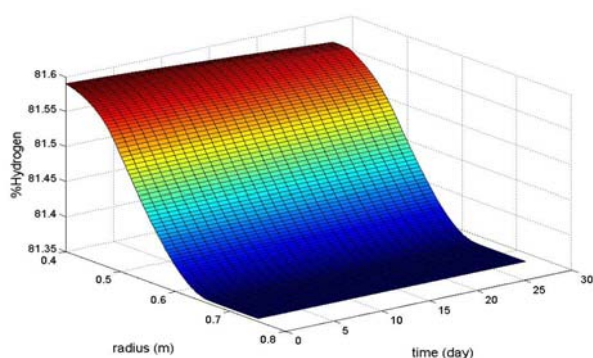

Fig. 10 Hydrogen molar percent as a function of time and reactor radius

Table III provides comparison of BPC reactor data and modeling at different operation times. As it is obvious good approach there are between model estimation and industrial data. As catalyst deactivates, accuracy of the model decreases.

TABLE I
COMPARISON OF SIMULATION RESULTS & INDUSTRIAL DATA

	%Paraffin (exp) [9]	%Paraffin (sim)	%Olefin (exp) [9]	%Olefin (sim)	%Hydrogen (exp) [9]	%Hydrogen (sim)
Start of run	11.99	11.77	1.22	1.35	81.57	81.59
After 10 day	12.09	11.87	1.09	1.29	81.55	81.58
After 16 day	12.18	11.94	1.02	1.25	81.54	81.58
After 22 day	12.22	11.99	0.98	1.21	81.53	81.57
After 28 day	12.29	12.03	0.92	1.19	81.52	81.57

V. CONCLUSION

A dynamic industrial model of dehydrogenation reactor in LAB plant has been presented in this study. Velocity change and pressure drop have been considered in modeling. Variations of paraffin, olefin, diene, hydrogen and aromatics with time and reactor radius have been investigated. The model has been validated with plant industrial data. The model will be implemented for dynamic optimization of the plant as a future work.

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