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Mathematical Modeling of an Industrial Naphtha Reformer with Three Adiabatic Reactors in Series

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ABSTRACT: *A mathematical model for commercial naphtha catalytic reformer of Tehran refinery was developed. This model includes three sequencing fixed beds of Pt/Al_2O_3 catalyst at the steady state condition using detailed kinetic scheme involving 26 pseudo-components connected by a network of 47 reactions, in the range of C6 to C9 hydrocarbons. The reaction network consisted dehydrogenation, hydrogenation, ring expansion, paraffin and iso-paraffin cracking, naphthene cracking, paraffin isomerization and hydrodealkylation of aromatics. The kinetic model was fine tuned against industrial plant data using a feed characterized by PIONA (Paraffin, Iso-paraffin, Oleffin, Naphthene and Aromatics) analysis. The final outlet results of the reformer such as RON (Research Octane Number), yield and outlet reformate compositions have shown good agreement with actual conditions of Tehran Refinery reforming unit.*

KEY WORDS*: Kinetic model, Modeling, Naphtha reforming, Fixed bed reactor.*

INTRODUCTION

The catalytic reforming process is one of the most critical operations in petroleum refineries to produce gasoline with high octane number [1-6].

To design new plants and optimize the existing ones, an appropriate mathematical model for simulation the industrial catalytic reforming process is needed. However using simple lump kinetic models could not show reasonable and appropriate results in scaled up reforming processes, therefore introduction of new kinetic lumps and reaction networks are still being the interested research and development subjects in the field of modeling and simulation of reforming processes.

The applied reaction and their kinetics reported in the literature are different and usually simplified to the three lumps of paraffin, naphtane and aromatic. However these kinetic models could not be a proper tool for modeling and simulation of a commercial process, in the case of Tehran refinery naphtha reforming. In this study, an appropriate kinetic model was developed and fine tuned for Tehran refinery catalytic reformer to process the straight run naphtha. The feed was characterized by naphthenes, isoparaffins, paraffins and aromatics lumps of each carbon number from C6-C9 consisting 26 pseudo-components. The major reforming reactions such as dehydrogenation, dehydrocyclization, isomerization, hydrocracking and hydrodealkylation were considered in the model. The kinetic equations and their initial parameter estimations were taken from the literature [3,5,7].

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The kinetic parameters were fine tuned by direct search (Nealder-Mead simplex) method. Suitable coupling of optimization method with a fast ODEs solver, choosing proper reactions, kinetics, objective function and weight factors for a special commercial process are critical stages of the present kinetic modeling.

MODEL DEVELOPMENT

The schematic of the reforming process modeled in this work is shown in Fig. 1. The feed to the reforming unit is hydrotreated straight run naphtha. It consists of naphthenes (Alkyl cyclohexanes (ACH) and Alkyl cyclopentanes (ACP)), paraffins (normal paraffins (nP) and isoparaffins (iP)) and aromatics (A), containing lumps of carbon number from C_6-C_9. The major reforming reactions are endothermic causing temperature decrease of the reaction stream and catalyst along the bed. To prevent reaction rate reduction caused by temperature decrease, the catalyst is distributed in three adiabatic reactors in presence of heaters installed between the reactors. As shown in Fig. 1, the naphtha feed is mixed with hydrogen and heated to desired temperature before entering the first reactor. In order to delay coke formation of the catalysts in the fixed bed reformers, the process should work at high pressure of hydrogen.

In reforming, a bifunctional catalyst is used in which an acidic function provided by a cholorinated alumina carrier which is combined with a metal function provided by platinum. [4,7]. Table 1 exhibits the catalyst properties of Tehran reforming process. The operational conditions of Tehran refinery reformer and naphtha feed characterization are shown in table 2.

The reaction network considered in this study is introduced by various reactions such as Dehydrogenation, Ring expansion, Isomerization, Hydrocracking, Naphthene cracking, Hydrodealkylation, for C6 to C9 hydrocarbons which were totally 47 reactions. [3, 5, 7].

The kinetic models of the above reactions were incorporated into a non-isothermal plug flow reactor model. The partial mass balances of each component were written as follows for 26 components consisting liquid hydrocarbons, LPG and Hydrogen:

$$\frac{dF_i}{dW} = \sum_{j=1}^{47} \left(R_j \times StCo_{j,i} \right) \quad ; \quad i = 1, 2, 3, ..., 26 \qquad (1)$$

Table 1:Catalyst characterization.

Kind of Catalyst	Pt/γ-Al_2O_3
Size and shape	Spherical-1.8 mm diameter
Particle density	690 kg/m^3
Particle porosity	0.6

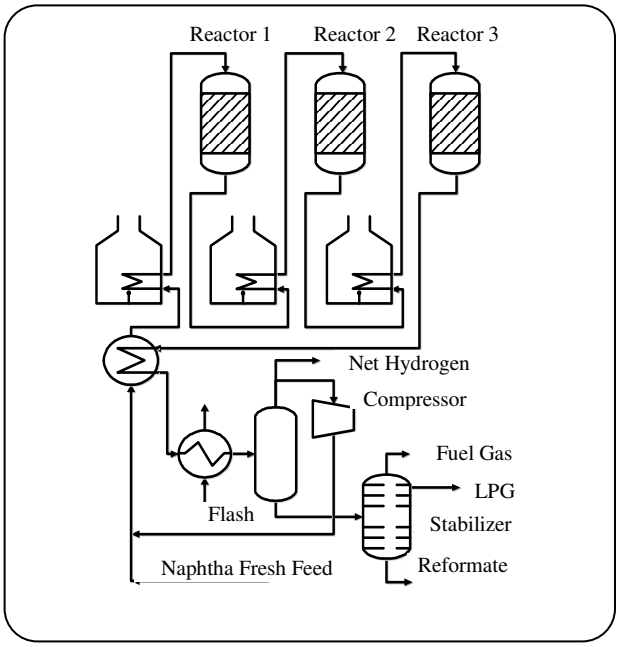

Fig. 1: Schematic of naphtha reforming process.

The partial pressure of each component, in thereaction rate equation, was related to the molar flow rate by the following equation:

$$Pi = \left(\frac{F_i}{\sum_{i=1}^{26} Fi} \right) \times Pt \quad ; i = 1, 2, 3, ..., 26 \qquad (2)$$

The homogeneous energy balance of each adiabatic reactor was written as:

In which the reaction enthalpies and component heat capacities were replaced from *Sinnott* [8].

Ordinary differential equations of mass and heat balances were solved simultaneously by variable order solver based on the numerical differentiation formulas (NDFs) method with MATLAB 7.3 software. Inlet conditions of each reactor were set to outlet conditions of prior reactor in except of temperature that is changed because of intermediate heaters. The input to the model were feed flow rate and composition of all lumps in the

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Table 2: Naphtha feed and operating conditions of Tehran refinery reforming plant.

Operating Condition		Values
Inlet temperature of the reactors (°C)	T1	493
	T2	493
	T3	493
Pressure (kPa)	P1	3075.6
	P2	2920.5
	P3	2799.9
No. of Reactors		3
Total catalyst weight (kg)		45693.5
Catalyst loading (wt%)	R1	20
	R2	30
	R3	50
Feed flow rate (kg/hr)		65341.7
H_2/HC molar ratio		5.6
Fresh feed composition (mole %)	ACH6	2.261
	ACH7	5.952
	ACH8	3.878
	ACH9	2.852
	ACP6	5.866
	ACP7	0.821
	ACP8	4.156
	ACP9	0.724
	nP6	4.925
	nP7	9.315
	nP8	8.582
	nP9	5.263
	iP6	2.063
	iP7	7.880
	iP8	10.930
	iP9	10.674
	A6	0.944
	A7	4.915
	A8	5.217
	A9	2.782
Feed RON		69.44

feed, catalyst loading, recycle gas composition, inlet temperatures and pressures. The output of the model included temperatures and concentration profiles of reformate as a function of catalyst distribution for each reactor, gas composition and temperature drop. In addition the octane number of the feed and liquid reformate obtained from a data base of several pure components of naphtha by a subroutine program.

The initial guess values for the frequency factors and activation energies were obtained from the literature [3] and optimized using the commercial plant data of first few days data, by a direct search algorithm (Nealder-Mead simplex method) due to the minimization of an objective function. This function is introduced as the sum of absolute relative deviations of the reactors temperature drop, outlet compositions and liquid reformate yield as observed in Eq. 4. The weight factors were introduced for each term of objective function (OF) in order to approach to desired convergence of model and experiment.

Objective Function (OF)

$$= \sum_{i=1}^{24}\left(100 * w_i \left|\frac{Z_i^{Calculated} - Z_i^{Exprimental}}{Z_i^{Exprimental}}\right|\right)$$

$$= \sum_{i=1}^{20}\left(100 * w_i \left|\frac{x_i^{Calculated} - x_i^{Exprimental}}{X_i^{Exprimental}}\right|\right) +$$

$$\left(100 * w_{21} \left|\frac{LY\%^{Calculated} - LY\%^{Exprimental}}{LY\%^{Exprimental}}\right|\right) +$$

$$\sum_{r=1}^{3}\left(100 * w_{21+r} \left|\frac{\Delta T_r^{Calculated} - \Delta T_r^{Exprimental}}{\Delta T_r^{Exprimental}}\right|\right)$$

RESULTS AND DISCUSSION

The pre-exponential Arrhenius constants and activation energies were determined after fine tuning with experimental data. Table 3 gives the predicted and the plant output results of Tehran refinery reforming plant. The predicted temperature drop of the reactors and the reformate yield, compositions and RON from the last reactor are compared with actual results of the plant, in this table.

As can be seen, temperature differences in all reactors are in good consistency with reality. Reformate composition, yield and research octane number are also close to actual values. The maximum deviation of the tuned model from operational values is less than 2 %.

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Table 3: Comparison of predicted and experimental results of the reforming unit.

Parameters		Tehran Refinery		
		Experimental	Predicted	Absolute Relative
Temperature drop in the reactors (°C)	ΔT1	54	53.889	0.206
	ΔT2	19	18.951	0.258
	ΔT3	5	4.986	0.280
Composition (mole %) of reformate at the outlet of reactor no.3	ACH6	0.058	0.058	0.059
	ACH7	0.098	0.098	0.119
	ACH8	0.081	0.081	0.030
	ACH9	0.010	0.010	0.167
	ACP6	0.912	0.913	0.093
	ACP7	0.468	0.468	0.047
	ACP8	1.160	1.161	0.034
	ACP9	0.010	0.010	0.000
	nP6	4.681	4.666	0.333
	nP7	2.660	2.659	0.023
	nP8	0.010	0.010	0.040
	nP9	5.398	5.426	0.522
	iP6	10.863	10.750	1.040
	iP7	10.033	10.029	0.040
	iP8	2.640	2.639	0.042
	iP9	0.370	0.370	0.016
	A6	5.675	5.675	0.004
	A7	21.723	21.734	0.051
	A8	19.705	19.795	0.457
	A9	13.445	13.448	0.022
LY (wt %)		80.24	78.699	1.920
RON		96.8	96.824	0.0248

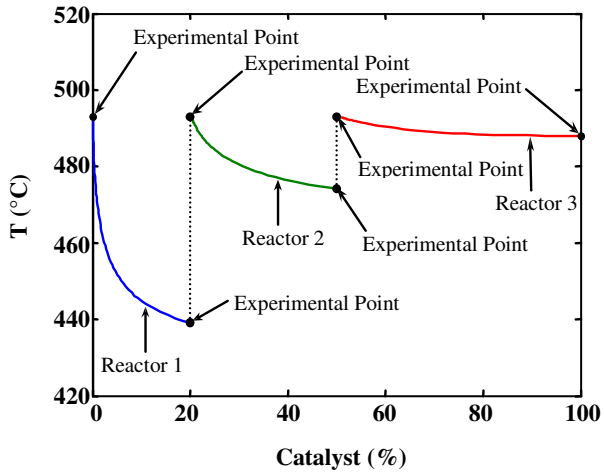

Fig. 2: Temperature profiles in three reforming reactors.

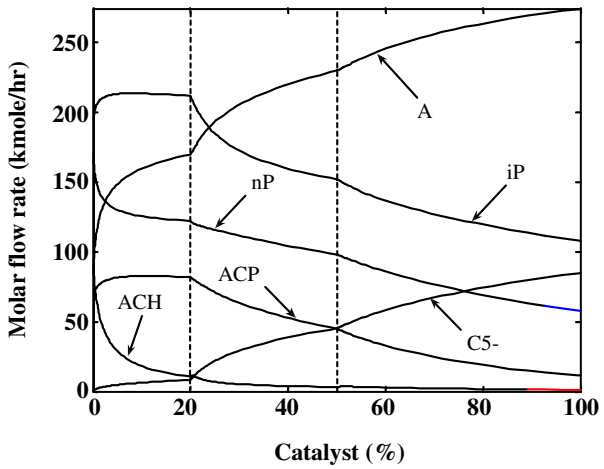

Fig. 3: Lumped component molar flow rate versus catalyst percent.

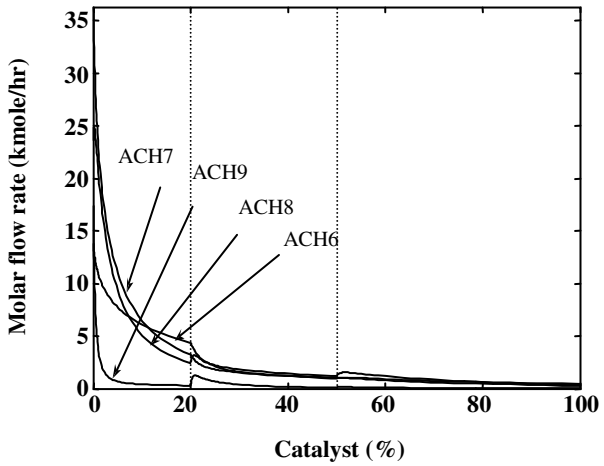

Fig. 4: Alkylcyclohexanes (ACH) molar flow rates versus catalyst percent.

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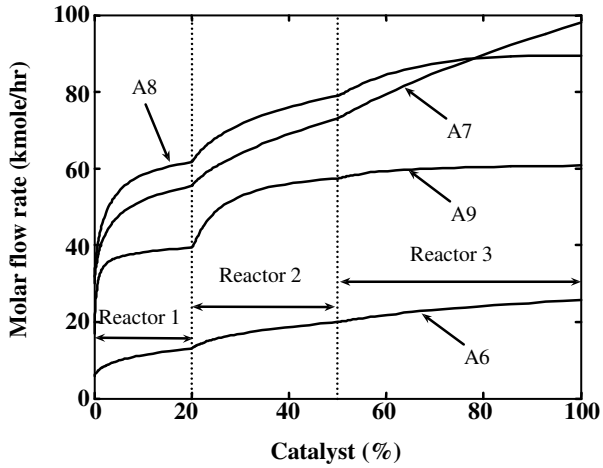

Fig. 5: Aromatic (A) molar flow rates versus catalyst percent.

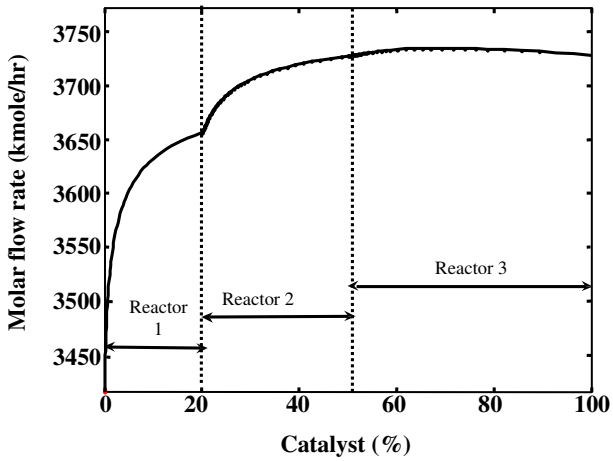

Fig. 6: Hydrogen molar flow rates versus catalyst percent.

The presented model can also predict the trends of the liquid products, LPG, H_2 and other necessary outputs. The present model shows production of the reformate of 96.8 RON from a feed around 69 RON. The model shows around 79 wt % yield of reformate against 21 wt % LPG which is considered in the acceptable range for such a high pressure process. The predicted temperature and component profiles along the catalyst weight are shown in Figs. 2 to 6.

CONCLUSIONS

Nowadays production of gasoline with high octane number from naphtha produced from crude oil refining through catalytic reforming reactions, attracts great attention. In this research naphtha reforming reactor of Tehran refinery was kinetically modeled, in high pressure fixed bed reactors, using 47 reactions network with 26 pseudo-components which enables modeling of hydrogen, C1 to C5 production, liquid reformate composition and temperature variations.

The kinetics was fine tuned by direct search (Nelder-Mead simplex) method. This study showed that using fast ODE solver of variable order based on the numerical differentiation formulas (NDFs) is suitable for coupling to optimization method and can handle large number of components and reactions.

The final outlet results of the reformer such as RON, yield and outlet reformate composition have shown good agreement with actual conditions of Tehran Refinery reforming unit with global absolute deviation of less than 2 %. The reforming model contains a rich set of model features and the confrontation of simulation results with experimental observations suggests that the model is well founded and is a good platform for additional process specific refinement.

Nomenclatures

C_p	Specific heat capacity (KJ/kmol.K))
F_t	Total molar flow rate (kmol/hr)
F_i	Molar flow rate of i th component (kmol/hr)
LY %	Reformate liquid mass yield percent
P_t	Total pressure (kPa)
P_i	Partial pressure (kPa)
R	Gas constant (J/mol.K)
R_j	j th reaction rate (kmol/(hr.kg_{cat}))
$StCo_{i,j}$	Stochiometry coefficient of componet i in j th reaction
T	Temperature (K)
W	Catalyst weight (kg)
w_i	i th weight factor
X_i	Mole fraction of the ith component
ΔH_j	Reaction enthalpy(kJ/kmol)
ΔT_r	Temperature difference across the reactor no. r

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