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Modeling and Simulation of Four Catalytic Reactors in Series for Naphtha Reforming

J. Ancheyta-Juárez,^{*,†,‡} E. Villafuerte-Macías,[‡] L. Díaz-García,[†] and E. González-Arredondo[†]

Instituto Mexicano del Petróleo, Eje Central Lázaro Cárdenas 152, México 07730 D.F., Mexico, and Instituto Politécnico Nacional, ESQIE, México 07738 D.F., Mexico

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In this work the modeling and simulation of catalytic naphtha reforming process is presented. The process model uses an extended version of the kinetic model reported by Krane et al. (Krane, H. G.; Groh, A. B.; Shulman, B. D.; Sinfeit, J. H. *Proceedings of the Fifth World Petroleum Congress*, 1959; pp 39–51). The new kinetic model utilizes lumped representation of the reactions that take place. These groups range from one to eleven carbon atoms for paraffins (P_1 – P_{11}), and from six to eleven atoms of carbon for naphthenes (N_6 – N_{11}) and aromatics (A_6 – A_{11}). Other reactions that this kinetic model considers are the cyclohexane formation via methylcyclopentane isomerization ($MCP \leftrightarrow N_6$) and paraffins isomerization ($nP_i \leftrightarrow iP_j$). The process model is used to predict temperature and reformate composition profiles in a commercial reforming unit consisting of a series of four catalytic reactors. The agreement between predicted and commercially reported results is very good.

Introduction

One of the major processes for producing high octane gasoline and aromatics in petroleum-refining and petrochemical industries is without any doubt the process of catalytic reforming. A variety of catalytic reforming processes are commercially available which differ in the type and composition of the catalyst, the regeneration procedure (cyclic, semiregenerative, or continuous), or the conformation of the equipment.^{1,2}

The normal commercial practice is to operate a system of 3 or 4 adiabatic reactors in series with intermediate preheaters. The feedstock is mixed with recycle hydrogen and heated to the desired temperature before it enters the first reactor. The fourth reactor is usually added to some units to allow an increase in severity of throughput while the maintaining the same cycle length, which in the case of those plants operating with semiregenerative mode is about one year.²

The hydrodesulfurized straight-run naphtha used as catalytic reforming feedstock has a very complex composition, which consists of normal and branched paraffins, five- and six-membered ring naphthenes, and single-ring aromatics, and each of them undergoes various reactions.

A detailed kinetic model considering all the components and reactions is also very complex. By this reason, it is common to assume that only three classes of hydrocarbons are present in naphtha (paraffins, naph-

thenes, and aromatics), and they are considered to have similar properties and kinetic behavior.^{3,4}

Various models for representing the kinetics of catalytic reforming reactions have been reported in the literature,^{5–20} which have also been widely discussed by other researchers.^{1,4,21}

The most important catalytic reforming models are ordered chronologically in Figure 1. Two periods of kinetic models developing can be distinguished, one by year 1975, and another after 1975.

* Author to whom correspondence should be addressed. Fax: (+52-5) 333-8429. E-mail: jancheyt@imp.mx.

[†] Instituto Mexicano del Petróleo.

[‡] Instituto Politécnico Nacional.

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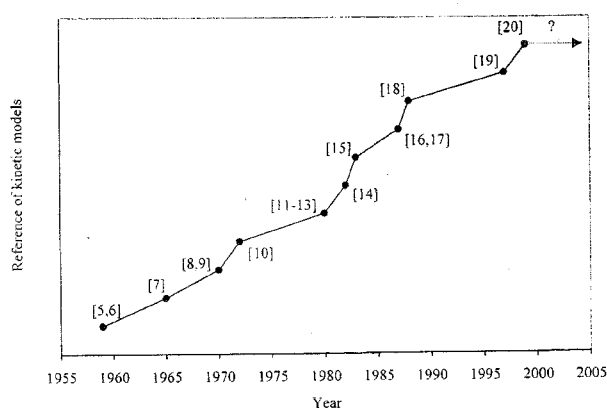


Figure 1. Evolution in kinetic modeling of catalytic reforming.

The level of sophistication of these models varies from a few lumps to detailed kinetic models, such as the rigorous pathways level approach for catalytic reforming modeling reported by Joshi and Klein.²¹ This level of sophistication is very related to the development of high-speed hardware and large-capacity computers.

On the other hand, the use of process models as a tool for simulation of commercial process has been growing rapidly. The advantage of using process models as compared to empirical approaches is related to the fact that the prediction accuracy of the models can be significantly superior over a wide operating range.²¹

In the case of the reforming process, a number of different process models of varying levels of sophistication have been developed in the past.^{3-4,21-23} Each of these models uses its own kinetic model or others already reported with or without some modifications. The accuracy of the process model depends on various aspects. One of the most important is the level of detail of the kinetic model used for predicting reformate composition.

In a previous work we reported an extension of the well-known and used Krane et al. model.^{6,24} In the present paper we incorporate this extended kinetic model in a process model to represent the reactions that take place in four fixed-bed, tubular, adiabatic catalytic reforming reactors.

The Kinetic Model

As it was mentioned before, the kinetic model used in this work is an extension of the one reported by Krane et al.,^{6,24} which utilizes lumped mathematical representation of the reactions that take place. The Krane et al. extended model is written in terms of isomers of the same nature (paraffins, naphthenes, or aromatics). These groups range from 1 to 11 carbon atoms for paraffins, and from 6 to 11 carbon atoms for naphthenes and aromatics.

To accurately predict benzene content in reformate, the assumption that all benzene is produced via cyclohexane dehydrogenation is considered, and additionally

Table 1. Reactions of the Proposed Kinetic Model^a

	number of reactions	E_A (kcal/mol)
paraffins		
$P_n \rightarrow N_n$	6	45
$P_n \rightarrow P_{n-i} + P_i$	26	55
subtotal	32	
naphthenes		
$N_n \rightarrow A_n$	6	30
$N_n \rightarrow N_{n-i} + P_i$	11	55
$N_n \rightarrow P_n$	7	45
subtotal	24	
aromatics		
$A_n \rightarrow A_{n-i} + P_i$	7	40
$A_n \rightarrow P_n$	5	45
$A_n \rightarrow N_n$	1	30
subtotal	13	
total	71	

^a n : Number of atoms of carbon ($1 \leq i \leq 5$).

to the benzene formation reaction reported by Krane et al. ($P_6 \leftrightarrow N_6 \leftrightarrow A_6$), the following path reactions were taken into account: cyclohexane formation via MCP isomerization ($MCP \leftrightarrow N_6$), and MCP production from P_6 ($P_6 \leftrightarrow MCP$).²⁵ Paraffins distribution is calculated by known equilibrium, because it is common to assume that the isomerization reactions are rapid enough to closely approach thermodynamic equilibrium at normal reforming conditions.²⁶

The following Arrhenius-type variation and a factor that accounts for the pressure effect on the rate constants are also considered in the extended model:²⁷

$$k_i = k_i^0 \left[\frac{E_{A,i}}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right) \right] \left(\frac{P}{P_0} \right)^{q_i} \quad (1)$$

The chemical reactions included in the extended model are summarized in Table 1. It can be observed that four more lumps can be directly predicted with this new model, P_{11} , N_{11} , A_{11} , and MCP, and by equilibrium calculations, six iso-paraffin lumps (i - P_5 , i - P_6 , i - P_7 , i - P_8 , i - P_9 , i - P_{10}) can also be estimated. In addition, benzene formation can be more accurately calculated, since the reactions between N_6 and MCP were incorporated to the model.

The Process Model

The kinetic model described in the last section was incorporated in a fixed-bed unidimensional pseudohomogeneous adiabatic reactor model. Mass and heat energy balance equations were solved at steady-state assuming constant catalyst activity for the calculation. The following ordinary differential equations were integrated through each reactor bed to describe reformate composition and temperature profiles along the length of the reactors.^{28,29}

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$$-\frac{dy_i}{dz} = \sum_{j=1}^m \frac{MW}{zWHSV} (r_j) \quad (2)$$

$$\frac{dT}{dz} = \frac{S \sum_{j=1}^m (r_j) (-\Delta H_{Rj})}{\sum_{i=1}^m F_i C_{P_i}} \quad (3)$$

Equations 2 and 3 were solved simultaneously with the kinetic model equations for each component (r_j) using a fourth-order Runge Kutta method. All reactions were assumed to be pseudo-first-order with respect to the hydrocarbon, and the kinetics were expressed by seventy-one first-order reaction steps, eight–ten steps more than the original model reported by Krane et al.⁶

All the reaction steps are combined into twenty-four rate reaction equations (r_j), one for each component, which comprise the kinetic model. Each rate reaction equation is function of the kinetic constants (k_j) and the component concentration (y_j), for instance, the differential equation for paraffins with six carbon atoms (P_6) is the following:

$$\frac{dP_6}{d(1/WHSV)} = 0.0191P_{11} + 0.0084P_{10} + 0.0068P_9 + 0.0025P_8 + 0.0014P_7 + 0.0148N_6 + 0.0005MCP - (0.0014 + 0.0018 + 0.0027 + 0.0042)P_6 \quad (4)$$

The values of the constants were taken from the kinetic model reported in a previous work.²⁴ In the case shown in eq 4, rate reaction describes how a lump of paraffins with six atoms of carbon is formed from hydrocracking of paraffins of higher carbon atoms (P_7 , P_8 , P_9 , P_{10} , and P_{11}), and how it disappears by hydrocracking to lighter paraffins (0.0014, 0.0018, and 0.0027 are the kinetic constant values to produce $P_5 + P_1$, $P_4 + P_2$, and P_3 , respectively). This rate equation also includes the hydrodeacyclization of naphthenes with six atoms of carbon (N_6), and the cyclization of paraffins P_6 to MCP .

Results and Discussion

Conditions for Simulation. The process model was tested on a commercial semiregenerative reforming unit with four reaction beds with interstage heaters. The operating conditions of this unit taken for simulation were the following: 495 °C inlet temperature, 10.5 kg/cm² reactor pressure, hydrogen-to-oil ratio of 6.3 mol/mol, and feedstock flow rate of 30 MBPD.

Some properties of the hydrodesulfurized straight-run naphtha used as feedstock are given in Table 2.

Operating conditions and feed were taken during a stable plant operation period of one month, and only average values are presented. The catalyst employed in the commercial reforming unit is the same as that used for developing the kinetic model previously described. This catalyst contains 0.29 wt % Pt, 0.29 wt % Re, and a particle diameter of 1.6 mm.

Length, diameter, catalyst-bed weight, and the corresponding weight hourly space velocities for each reactor are given in Table 3. As can be seen in this table the first reactor is always smaller than the other

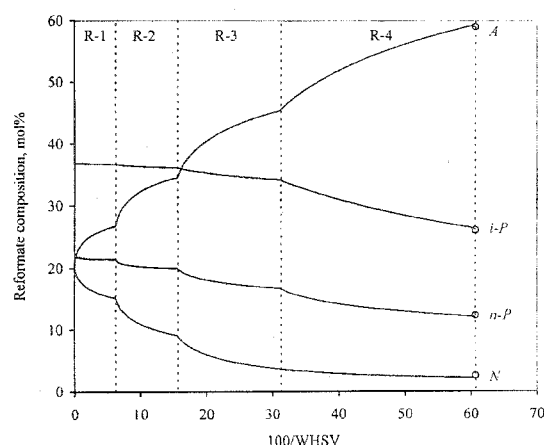


Figure 2. Predicted (—) and actual (○) composition profiles of total n-paraffins, iso-paraffins, naphthenes, and aromatics.

Table 2. Properties of the Feedstock

property	
specific gravity 60/60 °F	0.7406
molecular weight	104.8
ASTM distillation, °C	
IBP	88
10 vol %	101
90 vol %	155
FBP	180
total paraffins, mol %	59.11
total naphthenes, mol %	20.01
total aromatics, mol %	20.88

Table 3. Length, Diameter, and Catalyst-Bed Weight in Each Commercial Reactor

reactor	length (m)	diameter (m)	catalyst weight (Ton)	% of catalyst	WHSV (h ⁻¹)	100/WHSV
1	4.902	2.438	9.13	10.3	16.0	6.25
2	5.410	2.819	13.82	15.7	10.6	9.43
3	6.452	2.971	22.82	25.8	6.4	15.63
4	8.208	3.505	42.58	48.2	3.4	29.41
total	24.972		88.35	100.0	36.4	60.72

reactors and the last reactor is always the largest. This difference in reactor sizes is because some of the reactions that occur in the first reactors are very fast, and those that take place in the last stages of reactors are slow.

Simulation Results for Reformate Composition.

Reformate composition profiles of total n- and iso-paraffins, naphthenes, and aromatics obtained with the proposed model and those reported in the commercial unit at the exit of the fourth reactor are presented in Figure 2. Inverse of weight hourly space velocity ($WHSV$) was chosen as a convenient parameter for indicating the reactor positions as has been done by earlier workers.

Very good agreement can be observed between the simulated and reported values. That means that the process model predicts very well the total amount of lumped hydrocarbons present in reforming product (n - P , i - P , N , and A). The model is designed to give the reformate composition along the four reactors, however, since the available plant data do not provide this information, a comparison is not possible.

Heavy and light n-paraffins, and iso-paraffins along the reactor system as a function of catalyst distribution ($100/WHSV$) are shown in Figures 3 and 4, respectively.

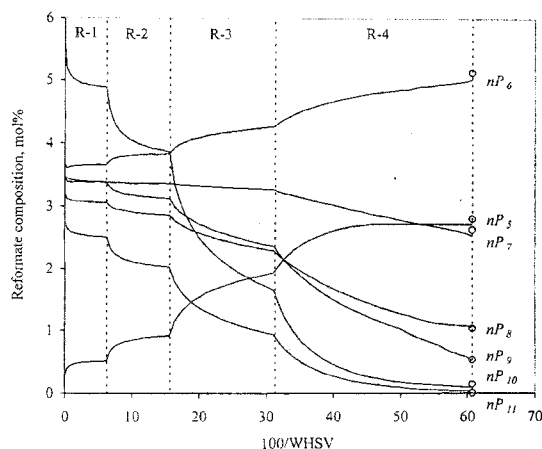


Figure 3. Predicted (—) and actual (○) heavy and light n-paraffins profiles.

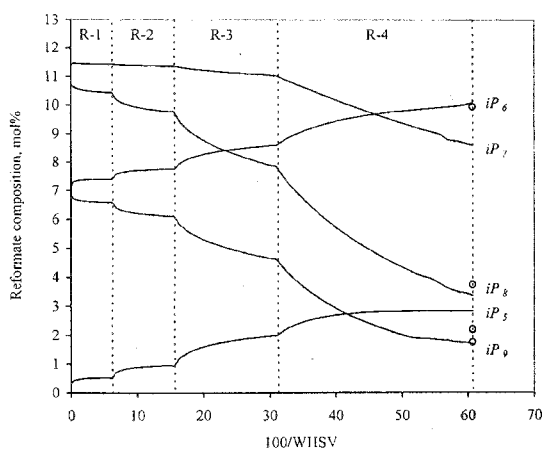


Figure 4. Predicted (—) and actual (○) iso-paraffins profiles.

Heavy and light naphthenes, and aromatic reformate compositions are presented in Figures 5 and 6, respectively. The solid lines represent the values calculated with the proposed model and the symbols the commercial data. Actual reformate composition values are found to agree with the plant reported values.

It can be observed that as the feedstock pass through the unit all aromatic hydrocarbon contents in reformate are higher. The most important increase is observed in lighter aromatics (A_6 , A_7 , A_8 and A_9), while the increase in A_{10} content is low, and aromatics with eleven atoms of carbon (A_{11}) remains essentially unchanged.

Naphthenes with six and more atoms of carbon, which are the most desirable components in reforming feedstocks, react relatively easily and their reactions proceed essentially to completion. Similar behavior was found with heavy paraffins, since P_{10} and P_{11} conversions were also very close to hundred percent. Paraffins with eight and nine carbon atoms (P_8 and P_9) also exhibited high levels of conversion, while percentage of some light paraffins is increased because they are produced by hydrocracking or hydrogenolysis.

The concentrations of N_6 – N_{10} and heavy paraffins (P_8 – P_{11}) decrease as they undergo conversion. A high rate of conversion of naphthenes was found in the first and second reactors. After third reactor, naphthenes concentration approaches a very low steady-state value. The relative rates of these naphthenes and paraffins

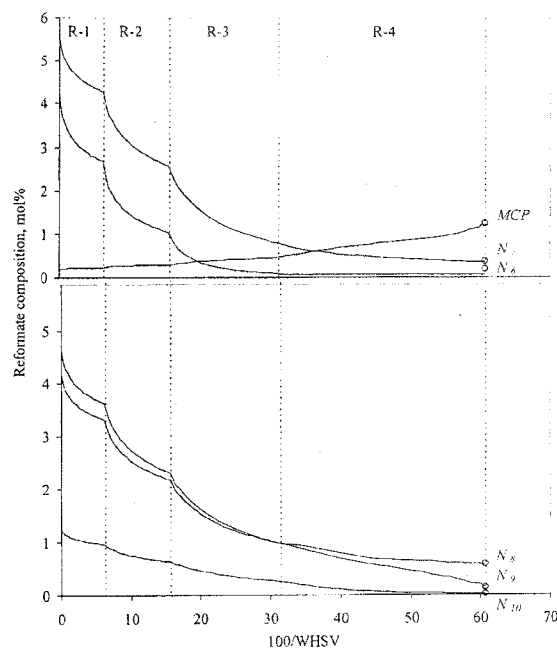


Figure 5. Predicted (—) and actual (○) heavy and light naphthenes profiles.

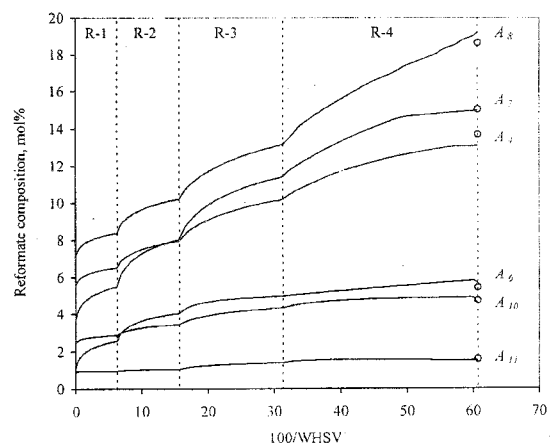


Figure 6. Predicted (—) and actual (○) aromatic profiles.

conversions are very different in the first two reactors. While N_6 and N_7 are almost totally converted in this section, paraffins have a very low conversion. There is an insignificant change in iso-paraffins content in the first and second reactors, and in the last two reactors the change is high. Similar behavior is found with light paraffins. This means that the increase in concentration of aromatics in the third and fourth reactors appears to be solely because of the disappearance of paraffins.

Table 4 shows the reformate composition obtained by simulation and those reported in the commercial reforming unit. It can be observed that the maximum absolute difference between these two values is 0.6 mol %. Lumps with 10 and eleven atoms of carbon and those involved in benzene formation (MCP , A_6 , P_6 , and N_6) as well as iso-paraffins are very well predicted. All these compounds were added to the original kinetic model reported by Krane et al., which was used in this work.

Simulation Results for Reactor Temperatures.

The major reforming reactions are highly endothermic producing a decrease in the temperature of the reaction

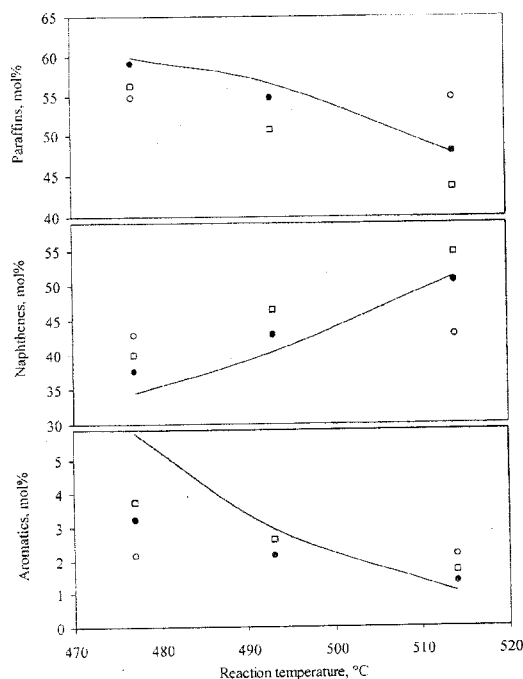


Figure 8. Comparison of predicted (symbols) and experimental data (lines). (O) Only pressure effect, (□) only temperature effect, (●) temperature and pressure effects.

Evaluation of the Process Model with Different Feedstock Composition. It is well-known that rate constants of kinetic models usually depend on feedstock and catalyst properties, and it is inappropriate to use them for simulating a process for new conditions, since they are specific for the feedstock and catalyst employed to obtain the kinetic data. However, there are some literature reports indicating that rate constants can be independent of initial feedstock composition, such as the ten-lump model for catalytic cracking reported by Jacob et al.³⁰ It means that if the kinetic model is detailed enough, it may be used to simulate a process outside the conditions it was derived.

A problem when using more detailed models is that the simplicity of kinetic representations used in models with small number of lumps is partially lost, since the use of kinetic models with large numbers of lumps where the number of parameters is significantly increased means that greater amounts of experimental data are also required.

In the case of our naphtha reforming process model, we have reviewed the changes in feed composition reported in the commercial plant in order to use this information for comparison with model predictions. Because of refiners' production policies, the feedstock quality was not drastically changed. Despite this, we found various cases that were used for simulation.

Figure 9 shows a comparison of reported and simulated results for total paraffins, naphthenes, and aromatics. It can be clearly seen that reformate composition is sufficiently well predicted when feedstock composition is changed.

Advantages and Limitations of the Proposed Model. The feedstock used for catalytic reforming has

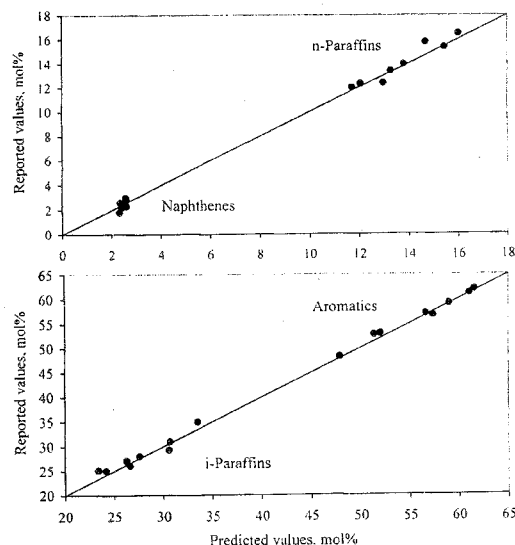


Figure 9. Comparison of reported and simulated results for different reforming feedstocks.

a very complex composition, in which each component undergoes several reactions. Due to this complexity, a detailed kinetic model considering all the components and reactions is also very complex. By this reason, lumps model are commonly used to describe the kinetics of complex reaction scheme processes, such as catalytic reforming, to reduce the broad spectrum of feedstock and products. These lumps are considered to have similar properties and kinetic behavior.

Following this criterion in the present work we assumed that only three classes of hydrocarbons are present in naphtha: paraffins (n- and iso-), naphthenes, and aromatics, which range from 1 to 11 carbon atoms for paraffins, and from 6 to 11 carbon atoms for naphthenes and aromatics. With this carbon distribution we are including more lumps than other previous models, which is an advantage of the proposed model.

Although we do not use all the pure components included in reforming feed and product, such as molecular models, reformate composition and temperature drop along the reactors are predicted with enough detail since mass and energy balances were properly predicted, as was confirmed with results of simulation.

Another important advantage of the proposed model is that benzene content in reformate is more accurately predicted. This was achieved by taking into account the following path reactions: benzene production via cyclohexane dehydrogenation ($P_6 \leftrightarrow N_6 \leftrightarrow A_6$), cyclohexane formation via MCP isomerization ($MCP \leftrightarrow N_6$), and MCP production from P_6 ($P_6 \leftrightarrow MCP$).

One limitation of lump models is that the relative concentrations of the species making up individual kinetic lumps can change as the reaction proceeds and thus these models may not be extrapolated to new conditions or feedstocks, and they are specific for the feedstock, catalysts, and operating conditions used to obtain the kinetic information. Despite this, we have shown that our model predicts sufficiently well reformate composition when feedstock composition is changed. Another limitation of the proposed model is that it does not take into account catalyst deactivation.

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Table 4. Actual and Simulated Reformate Composition

	actual	simulated	absolute difference
n-paraffins			
nP ₁₁	0.01	0.01	0.00
nP ₁₀	0.15	0.16	0.01
nP ₉	0.54	0.52	0.02
nP ₈	1.04	1.07	0.03
nP ₇	2.80	2.70	0.10
nP ₆	5.13	5.07	0.06
nP ₅	2.63	2.53	0.10
total	12.30	12.06	0.24
i-paraffins			
i-P ₁₀	0.00	0.00	0.00
i-P ₉	1.76	1.68	0.08
i-P ₈	3.75	3.37	0.15
i-P ₇	8.40	8.62	0.22
i-P ₆	9.95	10.10	0.15
i-P ₅	2.20	2.84	0.11
total	26.06	26.61	0.55
naphthenes			
N ₁₁	0.00	0.00	0.00
N ₁₀	0.02	0.02	0.00
N ₉	0.14	0.15	0.01
N ₈	0.59	0.56	0.03
N ₇	0.38	0.35	0.03
N ₆	0.19	0.07	0.04
MCP	1.25	1.22	0.11
total	2.57	2.35	0.22
aromatics			
A ₁₁	1.58	1.51	0.07
A ₁₀	4.72	4.56	0.16
A ₉	13.68	13.07	0.61
A ₈	18.63	19.22	0.61
A ₇	15.03	14.96	0.07
A ₆	5.43	5.68	0.25
total	59.07	58.98	0.10

stream and catalyst along the bed, therefore, a corresponding decrease in rate of reaction is produced. For this reason, commercial catalytic reformers are designed with multiple reactors and with heaters between the reactors to maintain reaction temperature at operable levels. As the feedstock passes through the sequence of heating and reacting, the reactions become less endothermic and the temperature differential across the reactors decreases.

In the first reactor, the major reactions are endothermic and very fast, such as dehydrogenation of naphthenes to aromatics. These reactions cause a very sharp temperature drop in the first reactor from 495 to 443 °C, as can be seen in Figure 7. This remarkable decrease in temperature in the first reactor ($\Delta T_1 = 52$ °C), almost quenches all reactions and more catalyst in the first reactor would not provide additional conversion.

The outlet of the first reactor is reheated to 495 °C and fed to the second reactor. In this second reactor, mostly the isomerization takes place, the remaining naphthenes are dehydrogenated and a moderate temperature drop is observed ($\Delta T_2 = 30$ °C). From the second reactor the effluent is again reheated to 495 °C before entering the third reactor, and finally, the same sequence is followed in the fourth reactor. The temperature drops across the third and fourth reactors are very low (17 and 14 °C, respectively), which is due to the exothermic hydrocracking of paraffins reaction. Dehydrogenation and cracking reactions take place in the last two reactors. The average temperature and the amount of catalyst in the last reactors are higher than the first ones. This allows the transformation of paraffins into

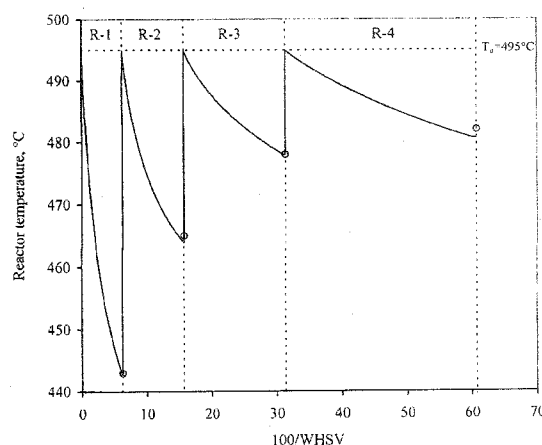


Figure 7. Predicted (—) and actual (○) temperature drop profiles in the four reactors.

Table 5. Temperature Drops along the Reactors

reactor	actual ΔT °C	simulated ΔT °C	absolute difference °C
1	52	52.3	0.3
2	30	31.1	1.1
3	17	17.2	0.2
4	13	14.3	1.3
total	112	114.9	2.9

aromatics by dehydrocyclization and into light paraffins by hydrocracking.

The comparison of temperature drops presented in Table 5 for each reactor shows that the present model predictions match very well with the information reported in the commercial reforming unit. The accumulated absolute difference between predicted and actual reactor temperatures is smaller than 3 °C.

Evaluation of the Effect of Pressure and Temperature on Kinetic Constants. The Krane et al.⁶ kinetic model has two serious limitations: (1) it does not include the influence of temperature on kinetic constants, and (2) the model is valid only at pressure of 300 psig, and variations in reaction pressure are not taken into account. In other words, the Krane et al. model⁶ considers the values of the kinetic constants to be independent of operating pressure and temperature. However, it is well-known that these two process variables considerably affect reforming reactions. To overcome these limitations, the proposed process model includes an Arrhenius-type variation and a factor that accounts for the pressure effect on the rate constants (eq 1).

To evaluate if correction of kinetic constant by temperature and pressure is effective, we validated our model with experimental data obtained in an isothermal pilot plant.²⁷ The process model was run with different options in the kinetic model: (1) considering only the effect of pressure on the rate constants, (2) considering only the effect of temperature on rate constants, and (3) considering the effects of both temperature and pressure on rate constants.

A comparison of experimental data and simulated results obtained with the three different options is presented in Figure 8. It is clearly seen that the correction of the kinetic constant by both temperature and pressure effects improves substantially the reformate composition.

Although there are more realistic kinetic models reported in the literature that describe the reforming reactions using more detailed schemes, lump models are frequently used for modeling and simulation purposes because they are still capable of illustrating the interactions between the process variables and the reactions rate.

Conclusions

A process model for naphtha catalytic reforming reactions has been developed. This model was used for simulating a commercial semiregenerative unit consisting of a series of four catalytic reforming reactors.

The process model includes a kinetic model which takes into account the most important reactions of the catalytic reforming process in terms of isomers of the same nature.

Reformate composition and temperature profiles have been obtained to provide information about the extent of conversion in each of the four reactors. The simulation results have been found to be in very close agreement with plant data.

Nomenclature

C_p = Molar specific heat
 E_a = Activation energy
 F = Molar flow
 k_i = Kinetic constant at T
 k_o = Kinetic constant at T_o
 MW = Molecular weight
 m = Number of components
 P = Reaction pressure
 P_o = Base reaction pressure
 R = Universal constant of gases
 r = Rate of reaction
 S = Cross sectional area
 T = Reaction temperature
 T_o = Base reaction temperature
 $WHSV$ = Weight Hourly Space Velocity
 y = Molar composition
 z = Reactor length
 ΔH = Heat of reaction

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