

Catalytic reforming : the reaction network

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CATALYTIC REFORMING
THE REACTION NETWORK

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Just as shown for catalytic cracking a reaction network can be presented for catalytic reforming, that reduces the actual complexity of the reaction network to a rather simple model. Such a simplified model is shown in figure 1.

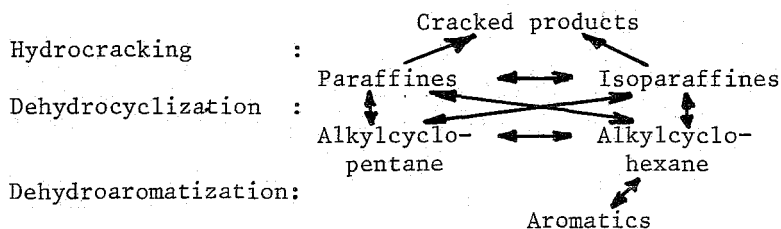


Fig. 1. Simplified reaction network for catalytic reforming.

Reaction	Apprioximate reaction enthalpy kJ/mol
Isomerization	0
Hydrocracking	- 50
Dehydrocyclization	+ 50
Dehydroaromatization (from cyclohexanes)	+ 200

Table 1. Reaction enthalpies for catalytic reforming reactions.

Of these reactions the hydrocracking is the slowest and the dehydroaromatization the fastest.

The reaction enthalpies for a number of these reactions are given in table 1.

These reaction enthalpies are averages. Especially the enthalpies of the dehydrocyclization reaction vary considerable, being only 30 kJ/mol for the conversion of *n* C₉ into C₃-cyclohexane, but 70 kJ/mol for the conversion of *i* C₉ into methylcyclopentane. As the same is valid for the Gibbs free energies of these reactions it is clear that the equilibrium composition of hydrocarbon/hydrogen mixtures not only depends on the hydrocarbon/hydrogen ratio but also on the composition of the hydrocarbon fraction of that mixture. When discussing equilibrium compositions, one has to exclude hydrocracking reactions because the hydrocracking products are thermodynamically the most favoured ones, and the final equilibrium compositions will be a mixture of methane and hydrogen only. As however the rate of the hydrocracking reaction is low, exclusion of these reactions still gives useful information. We will also leave out of consideration the numerous isomerization reactions between the paraffines and isoparaffines and assume that the paraffin fractions will in their isomer composition approach equilibrium, of which table two gives an example.

number of branchings	0	1	2	3
carbon number				
C ₄	65	35		
C ₅	30	60	10	
C ₆	25	45	30	
C ₇	15	45	40	
C ₈	15	45	35	5

Table 2. Equilibrium composition of alkane isomers at 750 K.

From the equilibrium calculations it follows that for temperatures above 600 K and hydrogen pressures between 1 and 3 MPa the cycloparaffin content is always below 5 percent and often negligible. At 600 K the mixture consists almost exclusively of paraffins whereas at 800 K aromatics are the only components, except for C₆ under 3 MPa hydrogen. There the temperature has to be above 900 K before the C₆ paraffins are converted into benzene, as has been shown by Kugelmann (1976).

Radosz and Kramarz (1975) have calculated the equilibrium aromatics content for a number of feed mixtures (different fractions of C₆, C₇, C₈ and C₉) under the assumption that no cycloparaffins would be present. A number of their results have been reproduced in figure 2.

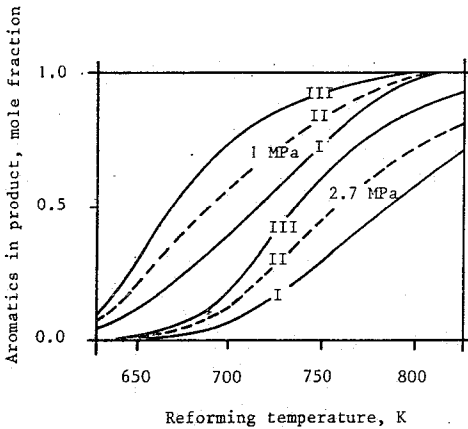


Fig. 2. Effect of feed composition, temperature and pressure on the equilibrium aromatic constant of reformate.

	Feed composition (fraction)			
	C ₆	C ₇	C ₈	C ₉
I	.4	.3	.2	.1
II	.25	.25	.25	.25
III	.1	.2	.3	.4

One other remark has to be made as far as the hydrocracking is concerned. Hamsel and Donaldson (1951) have already shown that products of hydrocracking in general do not crack any further within the reaction time available in normal plants. They found for the catalytic reforming of n heptane the following product distribution of the cracked fraction:

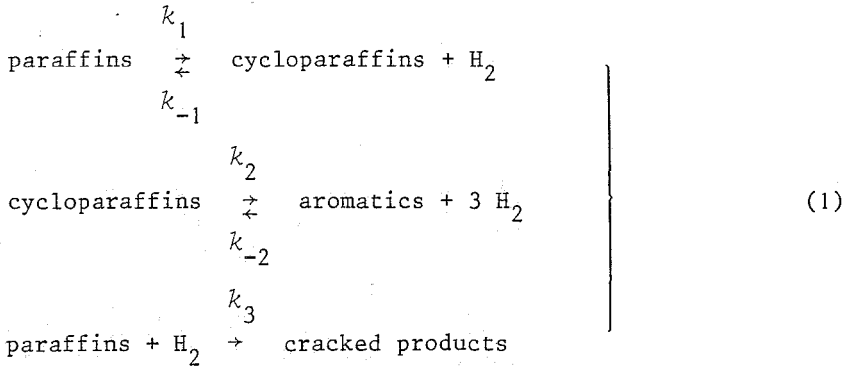
	moles/100 moles feed
methane	3.1
ethane	5.1
propane	25.1
butanes	26.7
pentanes	6.1
hexanes	3.0

Table 3. Distribution of light products from the catalytic reforming of n heptane.

The correspondence in yield of C₁ and C₆, of C₂ and C₅ and of C₃ and C₄ is striking and suggests that these are products from the primary hydrocracking reaction that are not broken down further. In commercial operation there is much less difference in the mole fractions of the cracked products i.a. because of the range of components in the feed. Although generally there is a slight

tendency for the mole fractions to decrease from C_1 to C_5 , equal molar fractions for these compounds can be assumed as a first approximation.

This then means that the reaction scheme of figure 1 can, without much loss of accuracy be substituted by the kinetic scheme:



As discussed above these rate constants are a function of the number of carbon atoms per molecule and must be determined separately.

In order to describe the conversion in a commercial platformer we can approximate the reactors, generally fixed bed axial flow reactors, by adiabatic pseudo homogeneous plug flow reactors for which we have to develop the massbalances for the various components, the enthalpy (heat) balance and the mechanical energy balance.

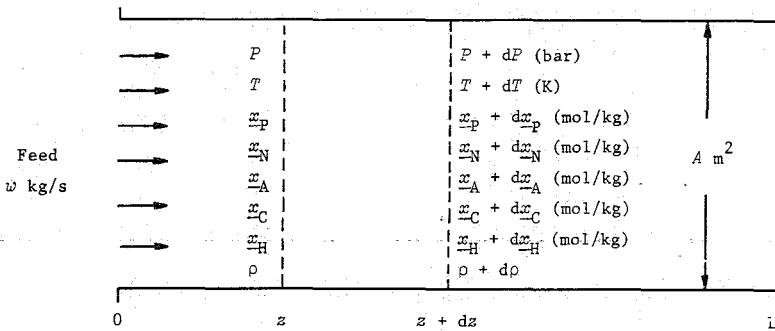


Fig 3. Model of catalytic reforming reactor.

We then have as the mass balances for the differential reactor volume of $A \, dz \, m^3$ for the steady state:

$$\begin{array}{ll}
 \text{for paraffins} & w \, d \underline{x}_P = r_P \, A \, dz \, \rho_{\text{cat}} \\
 \text{for cycloparaffins} & \\
 \text{ (naphthenes)} & w \, d \underline{x}_N = r_N \, A \, dz \, \rho_{\text{cat}} \\
 \text{for aromatics} & w \, d \underline{x}_A = r_A \, A \, dz \, \rho_{\text{cat}} \\
 \text{for cracked prod} & \\
 \text{and} & w \, d \underline{x}_C = r_C \, A \, dz \, \rho_{\text{cat}} \\
 \text{for hydrogen} & w \, d \underline{x}_H = r_H \, A \, dz \, \rho_{\text{cat}}
 \end{array} \quad (2)$$

with r_i the rate constant for the formation of i , per kg catalyst and ρ_{cat} the mass of catalyst per m^3 reactor volume.

We further have: (refer to equation (1))

$$\begin{array}{l}
 r_P = k_{-1} C_N C_{H_2} - k_1 C_P - k_3 C_P C_{H_2} \\
 r_N = k_1 C_P - k_{-1} C_N C_{H_2} - k_2 C_N + k_{-2} C_A C_{H_2}^3 \\
 r_A = k_2 C_N - k_{-2} C_A C_{H_2}^3 \\
 r_C = k_3 C_P C_{H_2} \\
 r_{H_2} = k_1 C_P - k_{-1} C_N C_{H_2} + 3 k_2 C_B - k_2 C_A C_{H_2}^3
 \end{array} \quad (3)$$

We eliminate the concentrations with

$$C_i = \underline{x}_i \, \rho \quad (4)$$

and (from the ideal gas law)

$$\rho = \frac{P}{\underline{x}_{\text{tot}} \, RT} \quad (5)$$

The enthalpy balance for the differential reactor volume $A \, dz \, m^3$ reads for the steady state:

$$- w \sum_i \Delta H_{r_i} \frac{d \underline{x}_i}{dz} = c_p \, dT \quad (6)$$

The summation of the right hand side must be done for the three reactions of equation (1) where \underline{x}_i and ΔH_{r_i} are

for the first reaction:

$$d \underline{x}_i = -d \underline{x}_P - d \underline{x}_C \quad \text{and} \quad \Delta H_{r_i} = 50 \text{ kJ/mol}$$

for the second reaction:

$$d \underline{x}_i = d \underline{x}_A \quad \text{and} \quad \Delta H_{r_i} = 200 \text{ kJ/mol}$$

and for the third reaction

$$d \underline{x}_i = d \underline{x}_C \quad \text{and} \quad \Delta H_{r_i} = -50 \text{ kJ/mol}$$

and

$$c_p = \sum C_{p_i} \underline{x}_i \quad (7)$$

c_p being the specific heat per kg of reaction mixture and C_{p_i} the molar heat, both at constant pressure.

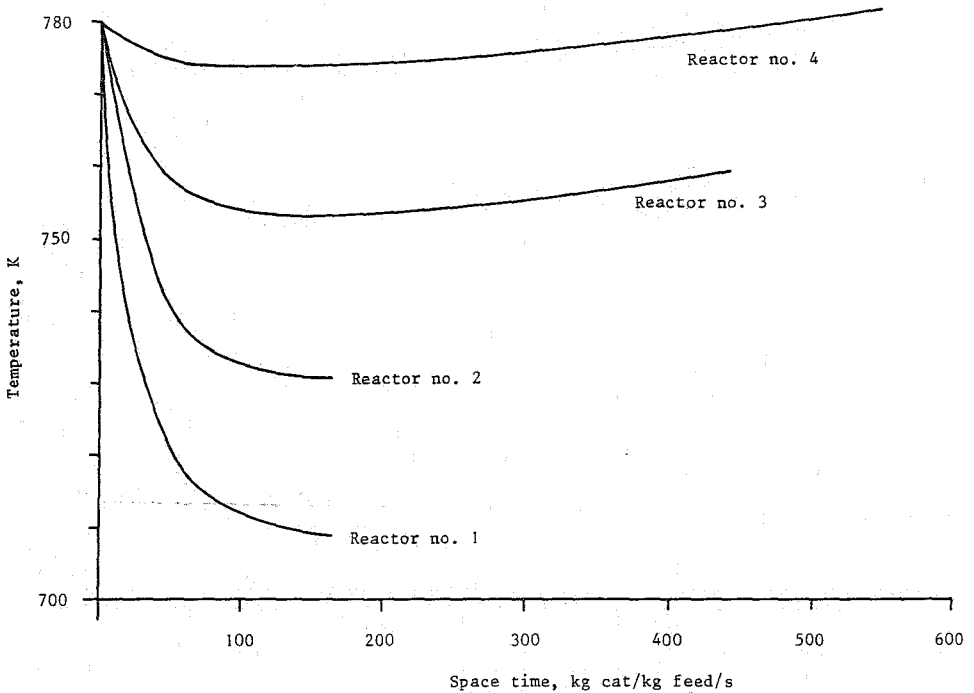


Fig. 4. Calculated temperature profile through a set of four reactors as function of the space time (kg cat/kg feed/s).

Finally we have the mechanical energy balance for a packed bed (Ergun, 1952)

$$dP = 150 \frac{(1-\epsilon)^2}{\epsilon^3} \frac{\mu v_s}{d_p^2} + 1.75 \frac{1-\epsilon}{\epsilon^3} \frac{\mu v_s^2}{d_p} dz \quad (8)$$

with v_s the superficial flow rate $\frac{m^3}{s \cdot m^2}$, ϵ the porosity, μ the absolute viscosity and d_p the particle diameter (m).

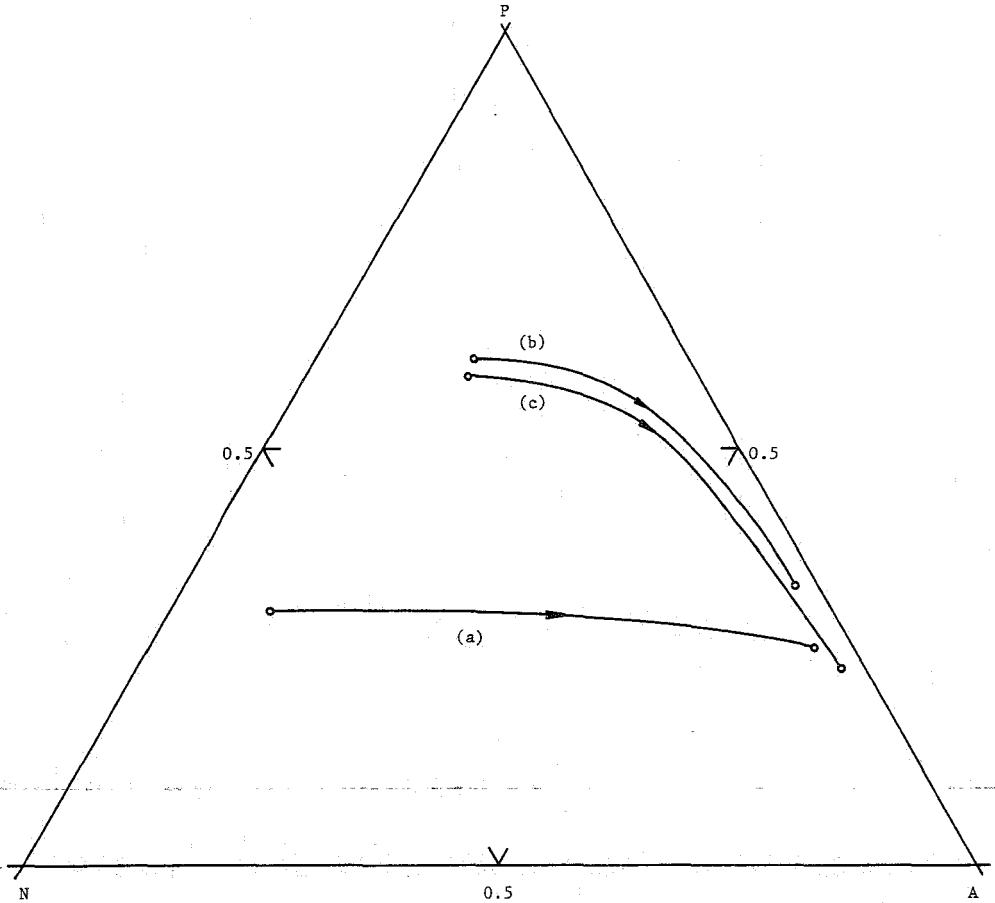


Fig. 5. Reaction paths for catalytic reforming.

- (a) low severity, naphthenic feed. ONF: reformate 95.5
- (b) medium severity, paraffinic feed. ONF: reformate 93.2
- (c) high severity, paraffinic feed. ONF: reformate 99.5

The set of equations obtained in this way can be numerically integrated starting from the given inlet conditions. A numerical example has been given by Smith (1959) for an isobaric case. The temperature profile through the four reactors is given in figure 4.

We see that especially in the third and fourth reactor the exothermic hydrocracking becomes noticeable.

The conversion path is indicated by curve (a) of figure 5, where also are included conversion paths for two more paraffinic feeds. We can see that for the example given by Smith a catalyst has been used with an extremely low conversion rate for paraffins into cycloparaffins. Modern catalytic reformers behave more like indicated by the examples (b) and (c) of figure 5.

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