Catcracker operations: reaction network and kinetics

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CATCRACKER OPERATIONS
REACTION NETWORK AND KINETICS

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1. Product distribution
Depending on the feed composition and the process parameters
the product distribution in catcrackers can vary widely.
In table 1 the product distributions are given for one type of
feedstock but for varying process conditions. The latter have
been chosen in such a way that the yield of respectively
gasoil, gasoline and of butane and lighter have been maximized.

<table>
<thead>
<tr>
<th></th>
<th>max</th>
<th>gasoil</th>
<th>gasoline</th>
<th>C_4</th>
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<tr>
<td>C_2</td>
<td>2.0</td>
<td>3.0</td>
<td>5.0</td>
<td></td>
</tr>
<tr>
<td>propane</td>
<td>0.5</td>
<td>1.5</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>propene</td>
<td>2.0</td>
<td>4.0</td>
<td>6.5</td>
<td></td>
</tr>
<tr>
<td>iso-butane</td>
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<td>5.0</td>
<td>9.0</td>
<td></td>
</tr>
<tr>
<td>n-butane</td>
<td>0.5</td>
<td>1.0</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>butenes</td>
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<td>7.0</td>
<td>10.0</td>
<td></td>
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<tr>
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<td>39.0</td>
<td>60.0</td>
<td>45.5</td>
<td></td>
</tr>
<tr>
<td>light cycle oil</td>
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<td>7.0</td>
<td>7.0</td>
<td></td>
</tr>
<tr>
<td>heavy cycle oil</td>
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<td>3.5</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>coke</td>
<td>7.5</td>
<td>7.5</td>
<td>8.5</td>
<td></td>
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<tr>
<td>loss</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Product distributions in % by wt. for a number of
(rather extreme) operating conditions.

2. Reaction models
In principle the product distribution can be described if all
the components of the feedstock were known and if for each
component the reaction network would be known. How complex such an approach is follows from the work of Greensfelder, Voge and Good (1949) who composed a model for the catalytic cracking of hexadecane.

The model comprises the following rules:

1. Hexadecane forms carbenium ions by hydride abstraction from a secondary position. All secondary positions have the same probability;

2. Carbenium ions crack at the \( \beta \) position (in relation to the carbenium ion). The part with the carbenium ion forms an \( \alpha \) olefine, the other part a new carbenium ion. All components have the same cracking rate constant. Products smaller than \( \text{C}_3 \) are not found;

3. The new carbenium ion isomerises to a secondary carbenium ion and is again subject to \( \beta \) scission. Fragments with 6 or less carbon atoms become either paraffins by hydride-ion abstraction from a hexadecane molecule or olefines by proton donation to a bigger olefin;

4. The olefines with 7 or more carbon atoms are for 50% protonated to carbenium ions.

(1) Thus the first reaction step can be, e.g.

\[
\text{C}_{16}\text{H}_{34} + \text{C}_3^{+}\text{H}_7 \rightarrow \text{C}_4\text{H}_9.\text{C}^+\text{H}^+.\text{C}_{11}\text{H}_{23} + \text{C}_3\text{H}_8
\]

(in total 7 different carbenium ions can be formed).

(2) This carbenium ion splits into

\[
\text{C}_3^{+}\text{H}_7 + \text{C}_{11}\text{H}_{23} \rightarrow \text{C}_1 \text{H}_2 = \text{CH}_2
\]

or into

\[
\text{C}_{10}^{+}\text{H}_{21} + \text{C}_4\text{H}_9\text{CH} = \text{CH}_2
\]

(3) The carbenium ion \( \text{C}_{10}^{+}\text{H}_{21} \) can isomerise into four different products, one of these being

\[
\text{C}_2\text{H}_5^{+}\text{H}_7 \text{C}_7\text{H}_{17} \text{that can split into}
\]

\[
\text{C}_4\text{H}_8 \text{and C}_6^{+}\text{H}_{13}.
\]

The latter becomes hexane or hexene.

(4) The olefin \( \text{C}_1 \text{H}_{23} \text{CH} = \text{CH}_2 \) formed in (2) is for 50% converted into the carbenium ion \( \text{C}_{13}^{+}\text{H}_{27} \) that splits in a way comparable to that indicated for \( \text{C}_{10}^{+}\text{H}_{21} \).

All reactions occurring according to this model are represented in figure 1. This figure is still somewhat simplified as it does not show the differences between olefins and carbenium ions for the \( \text{C}_6 \) and smaller fractions.
Catcracker operations

Fig. 1. Reaction network for the catalytic cracking of hexadecane. The squares in the left column indicate the place in the carbenium ion in the C\textsubscript{16} molecule. The other squares indicate intermediates and end products. Lines indicating reaction emerge from the middle of a side of a square and lead to the corner of an other square.

With the simple assumptions that the rate constant for the formation of C\textsubscript{16} carbenium ions is much smaller than all other rate constants and that the latter are all equal, a product distribution can be calculated that approaches the experimental value very near as shown in figure 2.

As however the feed of a catcracker consists of thousands of different species, and as in reality also other reactions than those assumed by Greensfelder et al take place, it will be clear that the complete reaction network describing all reactions occurring in a commercial installation will be too cumbersome to handle.
A pragmatic solution has been sought in the direction of an experimental approach, based on the assumption that the product distribution of a mixture of reactants can be described as an additive function of the product distribution of the components of the mixture. For instance, White (1969) used 'components' thirty fractions of widely different composition, and determined the product distribution of each fraction for a number of cracking conditions. In this way the product distribution for a catcracker feed, which can be represented as a mixture of a number of the fractions studied by White, can be predicted. The method has not found universal application mainly because the performance of the laboratory reactor used by White performs in quite an other way as a commercial catcracking reactor.

A useful although very simple model is based on the consideration that the process conditions are generally choosen to maximize one of the following products:

1. Gasoline. This is the normal operation, provided an acceptable octane rating can be attained;
2. Butane and lighter. This is for the production of chemical feedstocks and LPG;
3. In the past catcrackers have also been used to lower the viscosity of the feed (visbreaking). See column gasoil in table 1.

Correspondingly Weekman and Nace (1968) developed the following model:
The wide applicability of this model has been proven in practice. The problem now is reduced to find expressions for the rate equations for the reactions of the model.

3. Factors influencing the rate equations of the simplified catcracker model.

Catalytic factors

In general a rate equation has the form:

$$-\frac{dA}{dz} = \nu_x k f \text{(concentrations)}$$  \hspace{1cm} (1)

If (1) applies to a catalytic cracking reaction the rate constant $k$ is proportional to the catalyst concentration and to the activity of the catalyst. In a dense phase reactor the catalyst concentration is more or less a constant; in the more modern riser reactor the catalyst concentration is a function of the cat-oil ratio, C.O.R. and the gasphase density.

Using the ideal gas law and indicating with $\omega_F$, $\omega_G$ and $\omega_L$ the weight fractions feed, gasoline and light products and with $\delta_F$ and $\delta_G$, the number of moles of gasoline respective light products formed from one mole of feed we obtain

$$\rho = \frac{P M_F}{R T} \cdot \frac{1}{\omega_F + \omega_G \delta_G + \omega_L \delta_L}$$  \hspace{1cm} (2)

where $M_F$ = molecular weight of the feed (say 350) and $\delta_G$ and $\delta_L$ are about 3.5 and 9 respectively. Thus we find for the catalyst concentration in a riser reactor:

$$[\text{cat}] = (\text{C.O.R.}) = \frac{(\text{COR}) \cdot P \cdot M_F}{RT \left( \omega_F + \omega_G \delta_G + \omega_L \delta_L \right)}$$  \hspace{1cm} (3)

with the pressure $P$ in pascals the value of $R$ becomes 8.314 J/mol K

The catalyst activity is steadily decreasing by coke deposition, and after one pass through the reactor the catalyst has to be regenerated by just stripping off the volatile material adsorbed on the catalyst and thereafter by burning off the
greater part of the cokelike material on the catalyst. Szépe
and Levenspiel (1968) have shown that most deactivations can
be represented by

$$- \frac{da}{dt} = k \cdot a^m$$  \hspace{1cm} (4)

As follows from data from Blanding (1953) and from Nace (1965)
the equation

$$a(t) = A_c t^{-n}$$  \hspace{1cm} (5)

with $A_c$ the activity after 1 second and $n \approx 0.5$ describes the
experimental results satisfactorily (see figure 3). (Equation (4) follows from (5) by setting $m = \frac{n+1}{n}$).

![Graph showing decrease in activity for cracking catalysts.]

Fig. 3. Decrease in activity for cracking catalysts.
. Blanding (1953)
 x Nace (1965)

For zeolite catalysts Gustafson (1972) has shown that the ac-
tivity is best described by

$$a = a_o e^{-bt}$$  \hspace{1cm} (6)

which might indicate (see Tan and Fuller, 1970) that de deact-
vation is the result of an irreversible Langmuir-Hinshelwood
adsorption.
Kinetic factors
Cracking reactions for a pure component are generally first order in the concentration of that component. When however a complete gasoil fraction is cracked a complication arises. Because the components that crack easiest are converted fastest the 'crackability' of the unconverted fraction decreases, i.e. the overall cracking rate constant decreases with conversion. If the effective cracking rate constant is proportional to the fraction unconverted:

\[ k_{\text{eff}} = k_0 \frac{\omega}{\omega_o} = k_0 (1-x) \]  

in which \( \omega \) represents a weight and \( x \) the fraction converted. The gasoil cracking rate \( r \) then becomes:

\[ r = k_{\text{eff}} \cdot \rho \cdot \frac{C}{C_o} = k_0 (1-x) \cdot \rho \cdot (1-x) \frac{C}{C_o} \]

\[ = k_0 \frac{C}{C_o} \rho (1-x)^2 \]  

For a truly second order reaction in component A we have

\[ r_A = k \frac{C_A^2}{(\rho C_A)^2} \rho = k \frac{C_A^2}{C_{A,0}^2} \rho^2 (1-x)^2 \]  

At constant volume (i.e. constant \( \rho \)), (8) and (9) are indistinguishable, but not at constant pressure. For the gasoline cracking, where we have a smaller number of reactants as in the gasoil fraction, a first order approximation is acceptable. The statement that the orders are approximately 2 and 1 makes a mathematical treatment of the kinetics with e.g. a Langmuir-Hinshelwood model superfluous. Assuming that the catalyst deactivation is the same for the three reactions of the Weekman-Nace model, we can write:

\[ -r_F = (k_1 + k_3) \rho \frac{C_F^2}{C_{F,0}} \text{[cat]} a(t) \]  

\[ r_G = (k_1 \rho \frac{C_F^2}{C_{F,0}} - k_2 \rho \frac{C_G}{C_{F,0}}) \text{[cat]} a(t) \]  

\[ r_L = (k_3 \rho \frac{C_F^2}{C_{F,0}} + k_2 \rho \frac{C_G}{C_{F,0}}) \text{[cat]} a(t) \]
is shown in fig. 4

\[ \text{Fig. 4. Model of a catcracker riser reactor.} \]

4. Application to the riser reactor

a. The massbalance

For a differential volume element \( A \, dz \, m^3 \) (see fig. 5) the massbalance for one second reads:

\[
\frac{w_F}{\rho} \frac{C_F}{z} = \frac{w_F}{\rho} \frac{C_F}{z + dz} - \frac{r_F}{A} A \, dz + \frac{d}{dz} (\rho \frac{C_F}{\rho}) A \, dz \quad (13)
\]

in case of plug flow.

In case axial dispersion has to be taken into account the terms:

\[
- A \, D_{ax} \frac{d}{dz} (\rho \frac{C_F}{z}) \quad \text{and} \quad - A \, D_{ax} \frac{d}{dz} (\rho \frac{C_F}{z + dz})
\]

have to be added respectively to the right and left hand side of equation (13).
Catcracker operations

Fig. 5. Conversion pattern according to equations (10), (11) and (12). $k_1 = 1$, $k_2 = 0.1$, $k_3 = 0.1$.

In the steady state we then obtain

$$\frac{d}{ds} \frac{C_F}{G_F} - D \frac{d^2 (\rho \cdot C_F)}{ds^2} - \frac{\rho}{\bar{F}} = 0$$

(14)

with $\lambda = z/L$, equation (10), $[\text{cat}] = (\text{C.O.R.}) \rho$,

$$\tau_F = \frac{C_F}{G_F}, \quad K_F = (k_1 + k_3) \frac{L}{G_F} \cdot C_F \cdot \rho^2$$

(\text{C.O.R.})

and $G_F = \rho \cdot \bar{u}$ we obtain the dimensionless equation:

$$\frac{d}{d\lambda} \frac{\xi_F}{uL} - \frac{D}{\rho} \frac{1}{uL} \frac{d^2 (\rho \cdot \xi_F)}{d\lambda^2} + K_F \frac{\xi_F^2}{\rho} \frac{a(t)}{\xi_F} = 0$$

(15)

In this equation $\frac{ax}{uL}$ is the mass dispersion number $N_M$ of the reactor.

For $N_M + 0$ we have plug flow, for $N_M$ small ($< 0.1$) the numbers $N$ of ideal mixers in series that show the same behaviour as our reactor is $N = \frac{1}{2N_M}$ and for large $N_M$ we have the equivalent
of one ideal mixer (Kramers and Westerterp, 1963).

For a riser reactor at 780 K with $L = 15 \text{ m}$ $D_t = 1.2 \text{ m}$ and
$w = 40 \text{ kg/s (3500 t/d)}$ the Reynolds number $Re \approx 5 \times 10^5$. Then it
follows for a pure gas (Levenspiel, 1972) that $N_M = 0.016$ and
$N = 30$. The presence of the catalyst will increase the mixing
somewhat but as the catalyst slip velocity is in the order of
some 5 percent of the average linear gas velocity, it can
generally be assumed that the flow in a vertical riser reactor
is a plug flow.

We then have for the gasoil conversion

$$\frac{d \zeta_F}{d\lambda} + K_F \zeta_F^2 \alpha(t) = 0 \quad (16)$$

for the gasoline

$$\frac{d \zeta_G}{d\lambda} - K_F \left( \frac{k_1}{k_1 + k_3} \zeta_F^2 - \frac{k_2}{k_1 + k_3} \zeta_G \right) \alpha(t) = 0 \quad (17)$$

and for the $C_4$ and lighter products

$$\frac{d \zeta_L}{d\lambda} - K_F \left( \frac{k_3}{k_1 + k_3} \zeta_F^2 + \frac{k_2}{k_1 + k_3} \zeta_G \right) \alpha(t) = 0 \quad (18)$$

Fig. 6. The weight fraction of gasoil, gasoline and butane and
lighter according to equations 10, 11 and 12 as a function of
the conversion.

...... logarithmic approximation for fraction $L$. 
Integration of these equations with the starting values:
\[ \lambda = 0 : \zeta = 1 \zeta_G = 0 \zeta_L = 0 \]
yields sets of curves of which fig. 6 is an example.

Further sophistication can be introduced by making a heat balance over the riser reactor, and correcting the rate constants and \( \rho \) for the change in temperature. Generally this type of fundamental approach is used only to develop useful correlations.

b. The practical approach
From fig. 6 we can see (dotted line) that the weight fraction \( C_4 \) and lighter can for a rather wide range of conversions be very well approximated by

\[ \ln \zeta_L = a (1 - \zeta_F) + b \] (19)

This is in agreement by the method described by Ewell and Gadmer (1978), who show that \( \log \zeta \) and \( \log \) (coke make) correlate linearly with conversion. This is shown in fig. 7 where also in \( \zeta_F \) (\( \equiv \ln (1 - \text{conversion}) \)) is plotted as a function of the conversion.

![Fig. 7. Experimental conversion data on logarithmic scale.](image-url)
The advantage of using conversion as the independent variable is that the effects of e.g. feed quality, reactor temperature and catalyst activity can to a large extent be lumped in the conversion parameter. This allows plots of the various yields against conversion to be made with other qualities as secondary parameters. Fig. 8 gives an example of the type of relation used in this approach.

![Diagram](image)

Fig. 8. Yields for gasoline, C₄ and lighter and coke as function of conversion for two reactor temperatures

--- = 783 K

-------- = 811 K

and two feed qualities.

5. The complete unit
A catcracker consists of a heat consuming reactor plus stripper and a heat producing regenerator. To balance the heat production and the heat requirements a number of operating options are available (see fig. 9). In the older fluidized bed catcrackers a feed preheat furnace and catalyst coolers were often provided. Nowadays the feed temperature can generally only be adjusted by allowing more or less 'hot feed' straight from the feed preparator (vacuum destillation) into the feed stream of the catcracker.
More heat can be produced in the regenerator by reducing the stripping efficiency, adding torch oil or by decreasing the CO/CO₂ ratio in the flue gas. The catalyst can be cooled by adding spray water to the regenerator. 

In case the capacity of the regenerator airblower is such that the coke burning capacity is the plant's bottleneck, a high CO/CO₂ ratio (say 0.7) will be chosen. If on the other hand enough air is available and the reactor has high heat requirements maximum CO combustion is advantageous. This results in high regenerator temperatures, which are also useful in reaching low coke on cat levels (say 0.10 % by wt) on the regenerated catalyst. Especially for the zeolitic catalysts this is advantageous, as this results in even greater activity and better selectivity. For the present day reactors this is a must since the residence time in the reactor is some two or three seconds only.
The catalyst circulation is caused by static pressure of the kind shown in figure 10.

![Diagram of catalyst circulation](image)

Fig. 10. Catalyst circulation by static pressure difference \( \Delta p = \Delta h p (p_1 - p_2) g \).

In the catcrackers this means that a positive pressure difference must be maintained over the two slide valves that regulate the catalyst circulation (fig. 9).

This means for slide valve 1 (neglecting the pressure drop from slide valve 1 to the cat level in the regenerator)

\[
P_s + \Delta h_1 \rho_1 > P_r \tag{20}
\]

and for slide valve 2

\[
P_r + \Delta h_2 \rho_1 > P_s + \Delta h_3 \rho_2 \tag{21}
\]

with \( P_s \) and \( P_r \) the stripper and regenerator pressures
\( \Delta h_1 \) the height between the cat levels in stripper and regenerator
\( \Delta h_2 \) the height between regenerator level and slide valve 2
\( \Delta h_3 \) the height of the riser reactor above slide valve 2
\( \rho_1 \) the density of the dense phase
\( \rho_2 \) the density of the dilute phase in the reactor

From this it follows that

\[
P_s + \Delta h_1 \rho_1 > P_r > P_s - \Delta h_2 \rho_1 + \Delta h_3 \rho_2 \tag{22}
\]
Due to the abrasive action of the circulating catalyst (some 700 kg/s \( \approx 60,000 \) t/d) no orifice flow measurement is possible. The cat circulation rate is calculated on basis of the air flow and a carbon hydrogen balance over the regenerator.

The required data are:
- carbon and hydrogen on spent and regenerated catalyst;
- flue gas composition;
- air flow from the airblower.

![Diagram of Catcracker operations]

**Fig. 11.** Catcracker regenerator. Composition of (dry) flue gas (% by vol.): \( N_2 = 85.2 \), \( CO_2 = 8.0 \), \( CO = 6.5 \), \( O_2 = 0.3 \).
Coke on spent cat: 0.90 % by wt.
Coke on spent cat composition: 92 % by wt carbon, 8 % by wt hydrogen.

Example: For data see figure 11.

Air consists of 20.9 % by vol. \( O_2 \) and 79.1 % by vol. \( N_2 \).

Nitrogen balance:

\[
\begin{align*}
\text{In:} & \quad \frac{35.4}{79.1 \times 28 + 20.9 \times 32} \times 79.1 = 0.971 \text{ k mol/s } N_2 \\
\text{Out:} & \quad 0.971 \text{ k mol/s } N_2
\end{align*}
\]

Mass flow of other components in flue gas.

\[
\begin{align*}
\text{Out } CO_2: & \quad \frac{8.0}{85.2} \times 0.971 = 0.091 \text{ k mol/s } CO_2 \\
\text{CO:} & \quad \frac{6.5}{85.2} \times 0.971 = 0.074 \text{ k mol/s } CO \\
\text{O}_2: & \quad \frac{0.3}{85.2} \times 0.971 = 0.003 \text{ k mol/s } O_2
\end{align*}
\]
Oxygen balance:

\[
\begin{align*}
\text{In:} & \quad \frac{79.1 \times 28 + 20.9 \times 32}{35.4} \times 20.9 = 0.257 \text{ k mol/s} \\
\text{Out:} & \quad 0.091 \text{ k mol/s } O_2 \\
& \quad 0.037 \text{ k mol/s } O_2 \\
& \quad 0.003 \text{ k mol/s } O_2 \\
& \quad (\text{balance}) 0.126 \text{ k mol/s } O_2 \\
\end{align*}
\]

C in flue gas: 0.165 k mol/s = 1.98 kg/s
H₂ in flue gas: 0.252 k mol/s = 0.504 kg/s
Say spent catalyst circulation rate = x kg/s

Catalyst balance:

\[
\begin{align*}
\text{In: } & \quad 0.009 \times 0.92 \times x = 0.00828 \times x \text{ kg/s carbon} \\
& \quad 0.009 \times 0.08 \times x = 0.00072 \times x \text{ kg/s hydrogen} \\
& \quad 0.991 \times x \text{ kg/s 'pure' cat} \\
\end{align*}
\]

Out: 0.991 x kg/s pure cat

Coke: \[
\frac{0.55}{99.45} \times 0.991 x = 0.00548 x \text{ kg/s coke}
\]

Say spent coke consists of a fraction α hydrogen and a fraction 1-α carbon.

We then have for the complete regenerator:

Carbon balance
\[
0.00828 x = (1-α) x 0.00548 + 1.98
\]

Hydrogen balance
\[
0.00072 x = α x 0.00548 + 0.504
\]

We find \( x = 705.7 \text{ kg/s (61.000 t/d)} \)

\( α = 0.1 \% \text{ by wt} \)

Such mass balances are calculated on a regular basis during operation in order to obtain the catalyst rate and from that the cat-oil ratio.

The heat transported from the regenerator is calculated from the cat and the dense bed regenerator temperature.

For design purposes this temperature is calculated from a heat balance of the regenerator. This is a rather complicated calculation as it not only requires data for coke on spent and regenerated catalyst, the stripper outlet temperature, the composition of the flue gas and for the external heat losses but, under afterburning conditions, also information on the interaction between the dense and the dilute part of the bed. Under severe afterburning the temperature difference between the dilute and the dense phase can increase to over 60 K and more than 25 percent of the total heat of combustion can be regenerated in the dilute phase.
References

Nace, D.M. (1965), see Weekman (1968), loc. cit., p. 92
White, P.J., Hydrocarbon Processing, 47 (5), 103 (1968)