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 chousen in such a way that the yield of respectively gasoil, gasoline and of butane and lighter have been maximized.

max	gasoil	gasoline	C_4^-
C_2^-	2.0	3.0	5.0
propane	0.5	1.5	3.0
propene	2.0	4.0	6.5
iso-butane	3.0	5.0	9.0
n-butane	0.5	1.0	2.0
butenes	3.0	7.0	10.0
gasoline	39.0	60.0	45.5
light cycle oil	38.0	7.0	7.0
heavy cycle oil	4.0	3.5	3.0
coke	7.5	7.5	8.5
loss	0.5	0.5	0.5

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 β position (in relation to the
   carbenium ion). The part with the carbenium ion forms an α
   olefine, the other part a new carbenium ion. All components
   have the same cracking rate constant. Products smaller than
   C_3 are not found;
3. The new carbenium ion isomerises to a secondary carbenium
   ion and is again subject to β scission. Fragments with 6 or
   less carbon atoms become either paraffins by hydride-ion ab-
   straction 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% pro-
   tonated to carbenium ions.

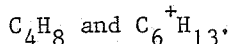(1) Thus the first reaction step can be, e.g.

$$C_{16}H_{34} + C_3\overset{+}{H}_7 \rightarrow C_4H_9 \cdot C\overset{+}{H} \cdot C_{11}H_{23} + C_3H_8$$
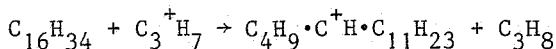
(in total 7 different carbenium ions can be formed).

(2) This carbenium ion splits into

$$C_3\overset{+}{H}_7 + C_{11}H_{23} \cdot CH = CH_2$$
or into
$$C_{10}\overset{+}{H}_{21} + C_4H_9CH = CH_2$$
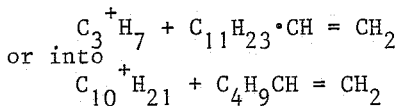
(3) The carbenium ion $C_{10}\overset{+}{H}_{21}$ can isomerise into four different
products, one of these being

$$C_2H_5 \cdot C\overset{+}{H} C_7H_{17} \text{ that can split into}$$

$$C_4H_8 \text{ and } C_6\overset{+}{H}_{13}.$$
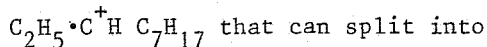
The latter becomes hexane or hexene.

(4) The olefin $C_{11}H_{23}CH = CH_2$ formed in (2) is for 50% con-
verted into the carbenium ion $C_{13}\overset{+}{H}_{27}$, that splits in a
way comparable to that indicated for $C_{10}\overset{+}{H}_{21}$.

All reactions occuring 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 C_6 and smaller fractions.

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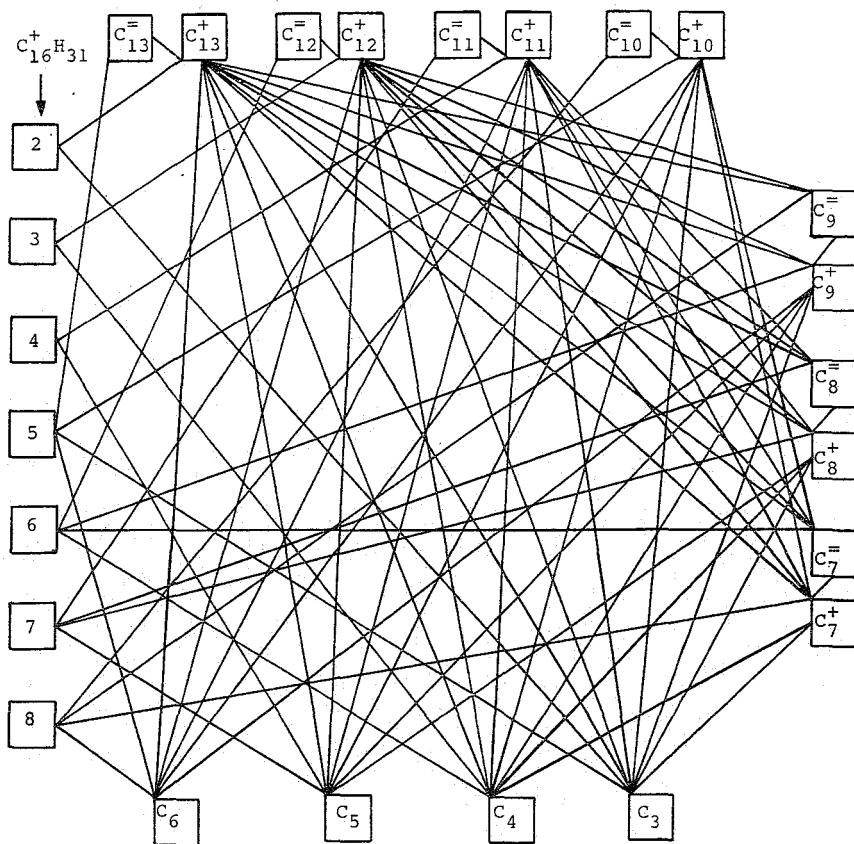decane. The squares in the left column indicate the place in
the carbenium ion in the C_{16} molecule. The other squares indi-
cate intermediates and end products. Lines indicating reaction
emerge from the middle of a side of a square and lead to the
corner of an other square.

With the simple assumptions that the rate constant for the for-
mation of C_{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 reac-
tions occurring in a commercial installation will be too cumber-
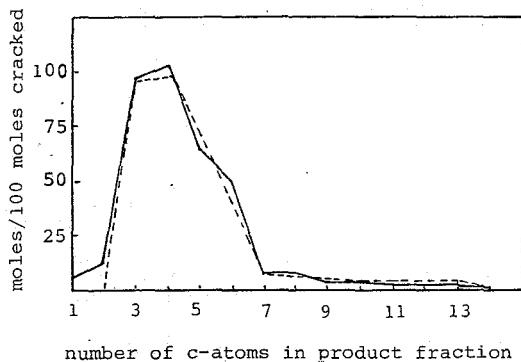some to handle.

number of c-atoms in product fraction

Fig. 2. Catalytic cracking of n hexadecane.
————— experimental data for 24% conversion Al_2O_3-ZrO-SiO_2
catalyst at 773 K
------- calculated according to the carbonium ion model
(Greensfelder et al, 1949)

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 as 'components'
thirty fractions of widely different composition, and deter-
mined 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 per-
forms in quite an other way as a commercial catcracking reactor.

A useful although very simple model is based on the considera-
tion that the process conditions are generally choosen to
maximize one of the following products:
1. Gasoline. This is the normal operation, provided an accept-
   able 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 follow-
ing model:

$$F \xrightarrow{\;k_1\;} G$$

with k_3 and k_2 reactions to L.
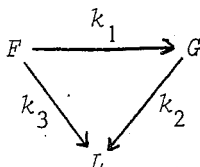
F = feedstock (gasoil)
G = gasoline
L = light products

Simplified reaction model for catcracking.

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:

$$-\frac{dA}{dt} = V_r \; k \; f \text{ (concentrations)} \qquad (1)$$

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 w_F, w_G and w_L the weight fractions feed, gasoline and light products and with δ_G and δ_F the number of moles of gasoline respective light products formed from one mole of feed we obtain

$$\rho = \frac{P \, M_F}{R \, T} \cdot \frac{1}{w_F + w_G \, \delta_G + w_L \, \delta_L} \qquad (2)$$

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

$$[\text{cat}] = (\text{C.O.R.}) = \frac{(COR) \cdot P \cdot M_F}{RT \, (w_F + w_G \, \delta_G + w_L \, \delta_L)} \qquad (3)$$

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

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

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

$$a\ (t) = A_c\ t^{-n} \qquad (5)$$

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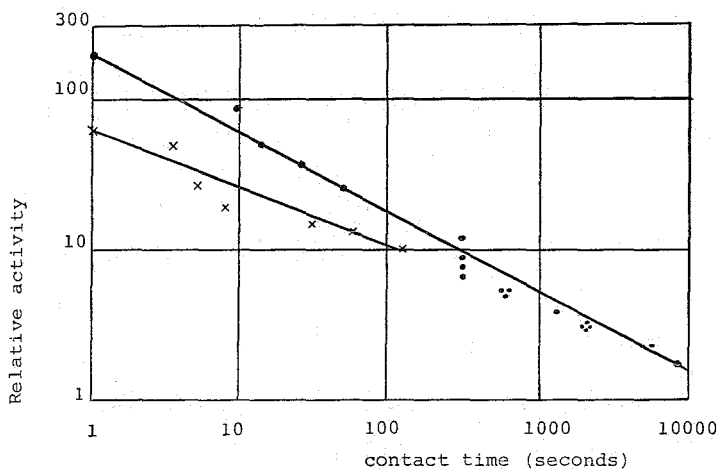(Equation (4) follows from (5) by setting $m = \frac{n+1}{n}$).

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

$$a = a_o\ e^{-bt} \qquad (6)$$

which might indicate (see Tan and Fuller, 1970) that de deacti-
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:

$$k_{eff} = k_o \frac{w}{w_o} = k_o \ (1-x) \tag{7}$$

in which w represents a weight and x the fraction converted. The gasoil cracking rate r then becomes:

$$r = k_{eff} \cdot \rho \cdot \underline{C} = k_o \ (1-x) \cdot \rho \cdot (1-x) \ \underline{C}_o$$

$$= k_o \ \underline{C}_o \ \rho \ (1-x)^2 \tag{8}$$

For a truly second order reaction in component A we have

$$r_A = k \ C_A^2 = k \ (\rho \ \underline{C}_A)^2 = k \ \underline{C}_{A,o}^2 \ \rho^2 \ (1-x)^2 \tag{9}$$

At constant volume (i.e. constant ρ), (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:

$$- r_F = (k_1 + k_3) \ \rho \ \frac{C_F^2}{C_{F,o}} \ [\text{cat}] \ a(t) \tag{10}$$

$$r_G = (k_1 \ \rho \ \frac{C_F^2}{C_{F,o}} - k_2 \ \rho \ \underline{C}_G) \ [\text{cat}] \ a(t) \tag{11}$$

$$r_L = (k_3 \ \rho \ \frac{C_F^2}{C_{F,o}} + k_2 \ \rho \ \underline{C}_G) \ [\text{cat}] \ a(t) \tag{12}$$
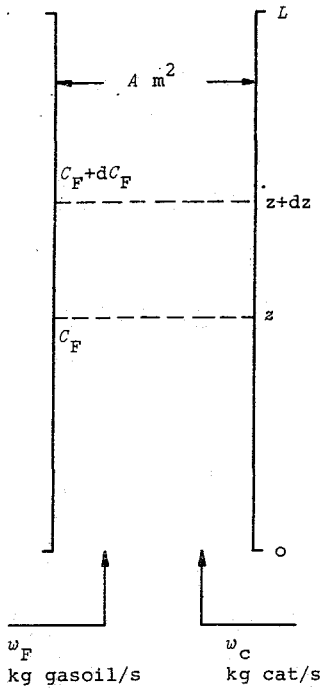
is shown in fig. 4

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:

$$w_F \left. \underline{C}_F \right|_z = w_F \left. \underline{C}_F \right|_{z+dz} - r_F \, A \, dz + \frac{d}{dt} (\rho \, \underline{C}_F) A \, dz \qquad (13)$$

in case of plug flow.
In case axial dispersion has to be taken into account the
terms:

$$- A \, D_{ax} \left. \frac{d \, (\rho \, \underline{C}_F)}{dz} \right|_z \quad \text{and} \quad - A \, D_{ax} \left. \frac{d \, \rho \, \underline{C}_F}{dz} \right|_{z+dz}$$

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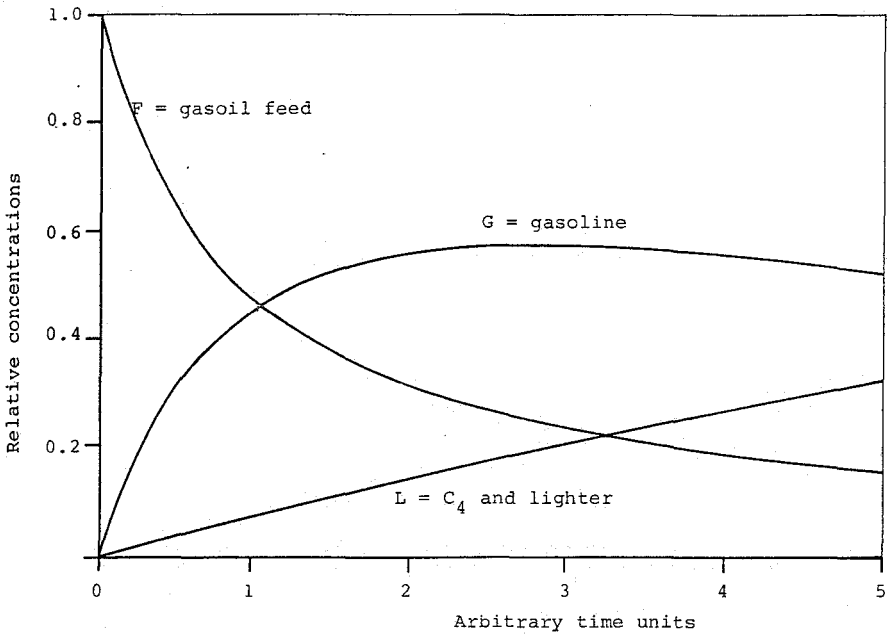of equation (13).

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

$$G_F \frac{d \, C_F}{dz} - D_{ax} \frac{d^2 \, (\rho \, C_F)}{dz^2} - r_F = 0 \tag{14}$$

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

$$\zeta_F = C_F / C_{F,o}, \quad K_F = (k_1 + k_3) \frac{L}{G_F} C_{F_o} \, \rho^2 \, (C.O.R.)$$

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

$$\frac{d \, \zeta_F}{d\lambda} - \frac{D_{ax}}{uL} \frac{1}{\rho} \frac{d^2 \, (\rho \, \zeta_F)}{d\lambda^2} + K_F \, \zeta_F^2 \, a(t) = 0 \tag{15}$$

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

For $N_M \rightarrow 0$ 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 m D_t = 1.2 m and
w = 40 kg/s (3500 t/d) the Reynolds number $R_e \sim 5.10^6$. 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 slipvelocity 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

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

for the gasoline

$$\frac{d\ \zeta_G}{d\lambda} - K_F\ (\frac{k_1}{k_1+k_3}\ \zeta_F^{\ 2} - \frac{k_2}{k_1+k_3}\ \zeta_G)\ a(t) = 0 \tag{17}$$

and for the C_4 and lighter products

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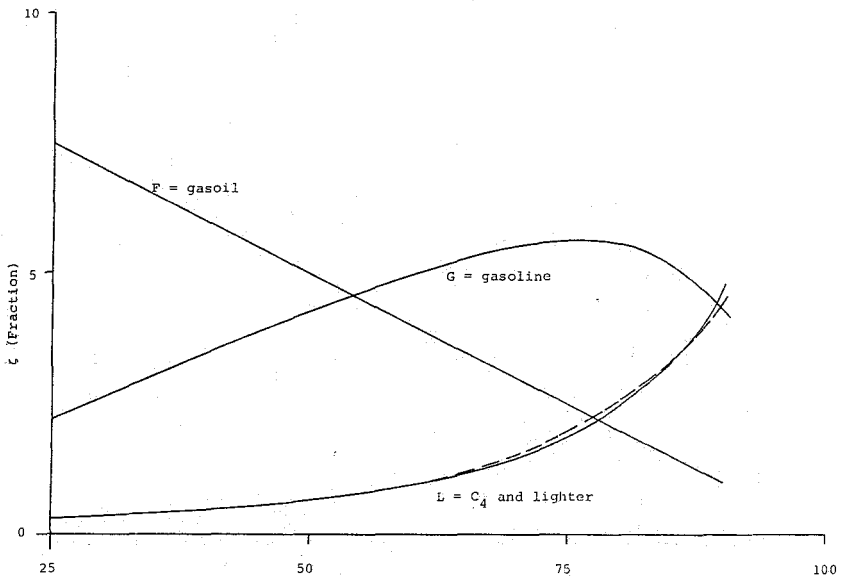

Fig. 6. The weight fraction of gasoil, gasoline and butane and
lighter according to equations 10, 11 and 12 as a function of
the conversion.
..... logarithmic approximation for fraction L.

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 con-
stants and ρ for the change in temperature. Generally this type
of fundamental approach is used only to develop useful corre-
lations.

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

$$\ln \zeta_L = a \, (1 - \zeta_F) + b \qquad\qquad (19)$$

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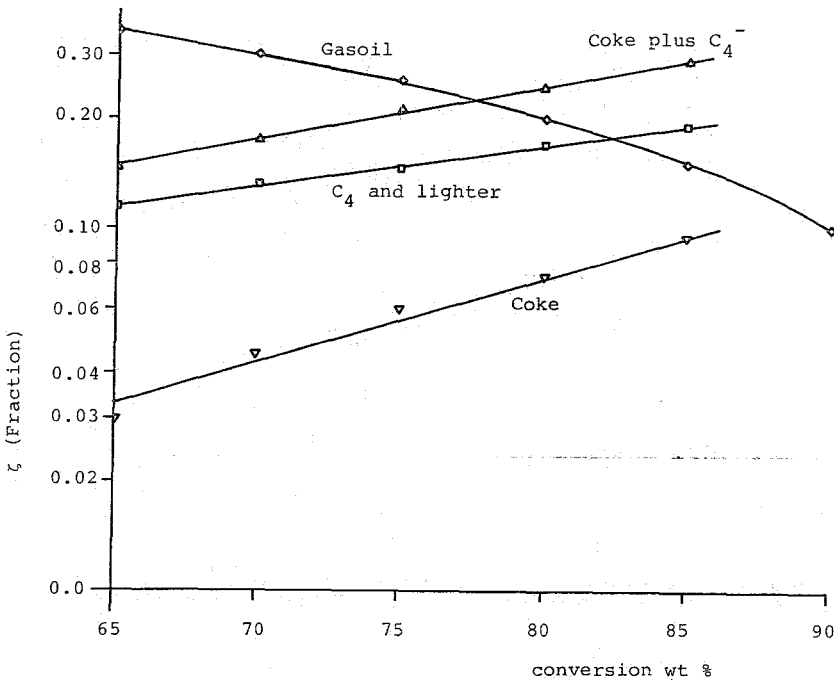the conversion.

Fig. 7. Experimental conversion data on logarithmic scale.

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 secun-
dary parameters.
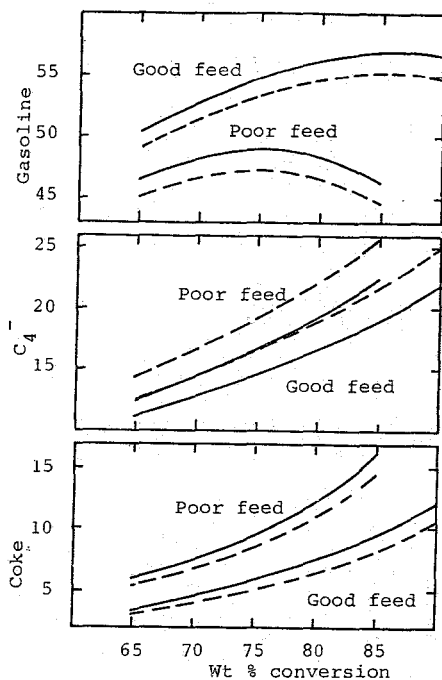Fig. 8 gives an example of the type of relation used in this
approach.

Fig. 8. Yields for gasoline, C_4 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 produc-
tion and the heat requirements a number of operating options
are available (see fig. 9). In the older fluidized bed cat-
crackers 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
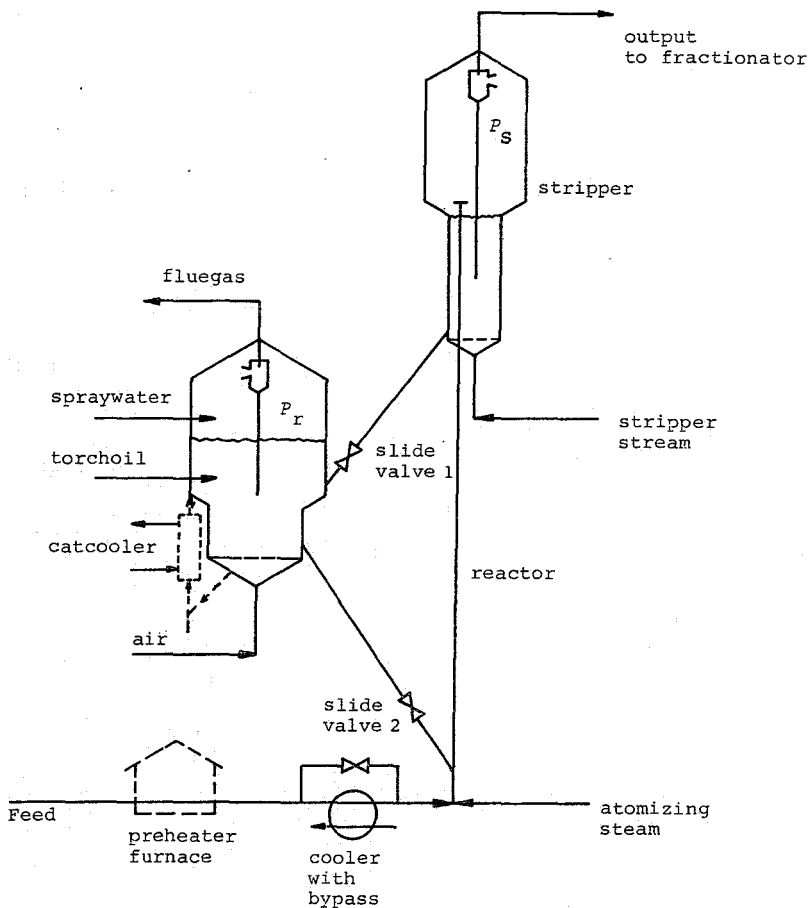the catcracker.

Fig. 9. Catcracker: heat balancing options.

More heat can be produced in the regenerator by reducing the stripping efficiency, adding torch oil or by decreasing the CO/CO_2 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/CO_2 ratio (say 0.7) will be choosen. 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.

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The catalyst circulation is caused by static pressure of the
kind shown in figure 10.

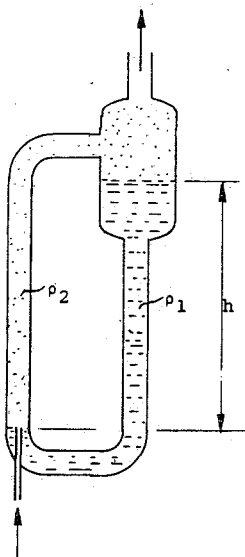Fig. 10. Catalyst circulation by static pressure difference
$\Delta p = h(p_1 - p_2)g$.

In the catcrackers this means that a positive pressure differ-
ence must be maintained over the two slide valves that regu-
late 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)

$$P_s + h_1\, \rho_1 > P_r \tag{20}$$

and for slide valve 2

$$P_r + h_2\, \rho_1 > P_s + h\ s\ \rho_2 \tag{21}$$

with P_s and P_r the stripper and regenerator pressures
h_1 the height between the cat levels in stripper and regenerator
h_2 the height between regenerator level and slide valve 2
h_3 the height of the riser reactor above slide valve 2
ρ_1 the density of the dense phase
ρ_2 the density of the dilute phase in the reactor
From this it follows that

$$P_s + h_1\, \rho_1 > P_r > P_s - h_2\, \rho_1 + h_3\, \rho_2 \tag{22}$$

Due to the abrasive action of the circulating catalyst (some
700 kg/s ∿ 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;
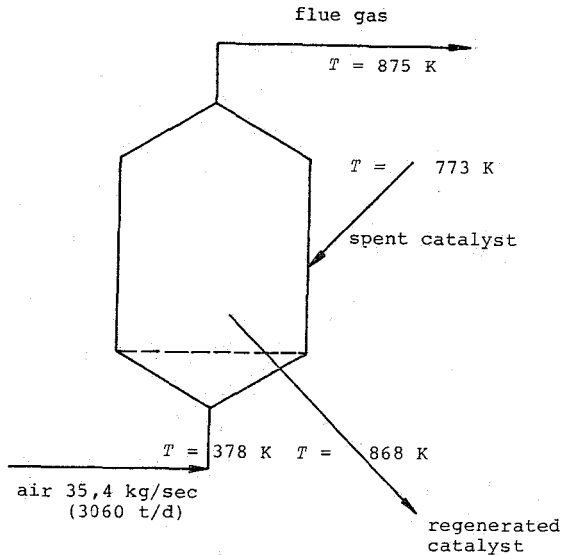- flue gas composition;
- air flow from the airblower.

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:

In: $\dfrac{35.4}{79.1 \times 28 + 20.9 \times 32}$ x 79.1 = 0.971 k mol/s N_2

Out: 0.971 k mol/s N_2
  ← Mass flow of other components in flue gas.

Out CO_2: $\dfrac{8.0}{85.2}$ x 0.971 = 0.091 k mol/s CO_2

   CO : $\dfrac{6.5}{85.2}$ x 0.971 = 0.074 k mol/s CO

   O_2 : $\dfrac{0.3}{85.2}$ x 0.971 = 0.003 k mol/s O_2

Oxygen balance:

In: $\dfrac{35.4}{79.1 \times 28 + 20.9 \times 32} \times 20.9 = 0.257$ k mol/s

Out: in CO_2 0.091 k mol/s O_2
      in CO   0.037 k mol/s O_2
      in O_2 0.003 k mol/s O_2
      in H_2O (balance) 0.126 k mol/s O_2

C in flue gas : 0.165 k mol/s = 1.98 kg/s
H_2 in flue gas: 0.252 k mol/s = 0.504 kg/s
Say spent catalyst circulation rate = x kg/s

Catalyst balance:

In: $0.009 \times 0.92 \times x = 0.00828\ x$ kg/s carbon
    $0.009 \times 0.08 \times x = 0.00072\ x$ kg/s hydrogen
                          0.991 x kg/s 'pure' cat

Out: 0.991 x kg/s pure cat

Coke: $\dfrac{0.55}{99.45} \times 0.991\ x = 0.00548\ x$ kg/s coke

Say spent coke consists of a fraction α hydrogen and a fraction $1-\alpha$ carbon.
We then have for the complete regenerator:
Carbon balance
$0.00828\ x = (1-\alpha)\ x\ 0.00548 + 1.98$
Hydrogen balance
$0.00072\ x = \alpha \cdot x \cdot 0.00548 + 0.504$
We find x = 705.7 kg/s (61.000 t/d)
    and α = 0.1 % 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.

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