Coke Deposition in the Thermal Cracking of Ethane

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A novel experimental setup allowed both the kinetics of the thermal cracking of ethane and of the coke formation to be studied over a temperature range extending from 750 to 870°C. The overall kinetics of ethane disappearance are in excellent agreement with previously reported pilot results. Coking rates are initially high but rapidly decrease to reach an asymptotic value. The initial product distribution also differs from the asymptotic product distribution. A kinetic model for the coking is derived from the experiments and used in conjunction with a set of conservation equations for the simulation of industrial ethane cracking. The predicted run length, thickness of the coke layer and evolution of the tubeskin temperatures are in agreement with industrial observations.

SCOPE

Thermal cracking of hydrocarbons around 800°C is the most important process for the production of feedstocks for the petrochemical industry. Side reactions always lead to carbonaceous material that deposits on the wall of the cracking coil thus reducing heat transfer, requiring critical tubeskin temperatures, increasing the pressure drop so that after 20-60 days, depending upon the severity of operation, the production cycle has to be interrupted for decoking by burning off the coke. Little is known about the rate of formation of coke. Yet, this is required for a better planning of the production and for more optimal operation. This paper presents a kinetic study of the coking during ethane cracking in a novel experimental set up and makes use of this information to simulate industrial operation and predict the evolution of the process parameters and the coke layer with time.

CONCLUSIONS AND SIGNIFICANCE

Specially designed equipment consisting of a completely mixed reactor in which a hollow cylinder is suspended at the arm of an electrobalance allows the kinetics of the main reaction(s) and of the coking to be determined. The reactor, with a volume of some 5 mL yields kinetic parameters for the main reactions in agreement with those obtained in a pilot plant. Accurate rates of coking are obtained which are used in the simulation of an existing industrial cracking unit. In this way, it becomes possible to predict the evolution of conversion, product distribution, pressures, and coke layer in the cracking coil. The predicted results are in line with industrial observations.

INTRODUCTION

Coke deposition in the coil of a hydrocarbon cracking furnace is a troublesome phenomenon that requires frequent interruption of the production to burn off carbonaceous material. For an ethane cracker normal run lengths are of the order of 20-60 days, depending upon the operating conditions. Although the kinetics of ethane cracking have been studied by many workers (Froment et al., 1976; Dunkleman and Albright, 1976; Pacey and Purnell, 1972; Lin and Back, 1966) no kinetic information has been reported on the coke deposition.

Only crude measuring techniques have been used so far, like weighing the reactor. Coke is not uniformly deposited, however. Depending upon the mechanism of formation a certain profile is observed, even under isothermal conditions. Weighing integral tubular reactors only leads to an average amount of coke. This is insufficient information to get an insight into the mechanism of formation and to relate the coke content to the composition of the reacting gases, which also is not uniform in an integral tubular reactor, anyway (Froment, 1979).

In a recent paper, Sundaram and Froment (1979) introduced a completely mixed reactor, specifically designed for coking studies in thermal cracking, reported on its use during the pyrolysis of propane and illustrated the application of the results in the simulation of an industrial reactor. In the present paper this approach is extended to the thermal cracking of ethane.

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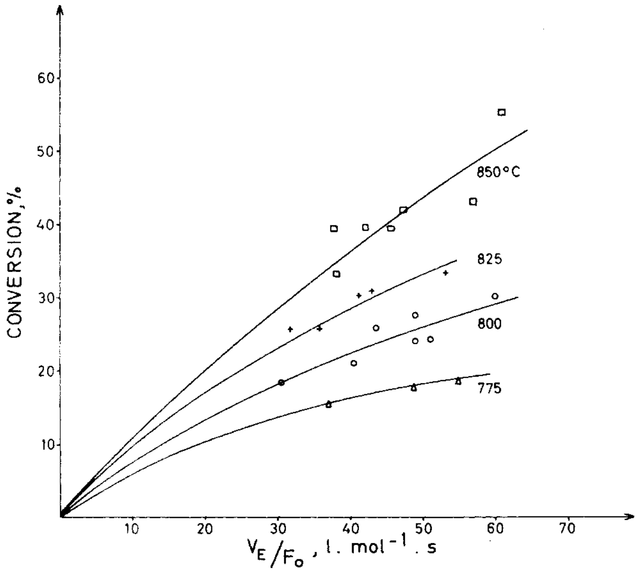

Figure 1. Ethane conversion vs. space time.

EXPERIMENTAL EQUIPMENT

The equipment used is the one described in detail in a previous paper (Sundaram and Froment, 1979) and allows determining the kinetics of both the main reaction(s) and of coking. It consists of a small reactor in which complete mixing is achieved by injecting the ethane and the diluent, nitrogen, through 24 holes drilled in the lid and which contains a small hollow cylinder suspended at the arm of an electrobalance, thus allowing the coke formation to be followed continuously as a function of time. The reactor and cylinder are made of Inconel 600. Weight changes of 40 μg can be detected. Carbon dioxide is flowing through the balance chamber to protect the mechanism from the reacting gases. The reactor effluent is analyzed on line for nitrogen, methane, ethylene, ethane, acetylene, carbon dioxide, propylene, propane, 1-butene, butadiene, butane, benzene and other C_5^+ components by means of three gas chromatographs. Nitrogen is used as an internal standard.

Two columns are the same as those used by Sundaram and Froment (1979). Three meters of porapack N in one chromatograph and two meters of n-octane along with three meters of phenyl isocyanate are used in the other chromatograph. A fifty meters capillary column coated with polypropylene glycol is used in the third chromatograph equipped with FID.

The equipment allows point values of coke to be determined as a function of time and to relate these to the uniform composition of the reacting mixture, a prerequisite for kinetic analysis.

EXPERIMENTAL RESULTS

The temperature range covered by the experiments extended from 750 to 870°C. The pressure was atmospheric. The dilution ratio was approximately 1 mole nitrogen/mole of ethane. The purity of the ethane exceeded 99.8%. There was no addition of sulfur.

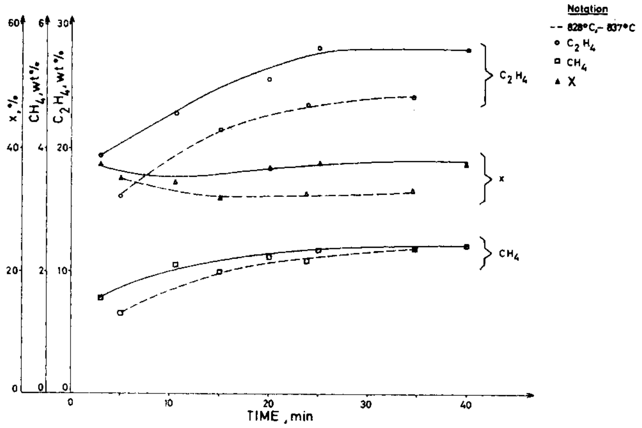

Figure 3. Yields of methane, ethylene and ethane conversion as a function of time.

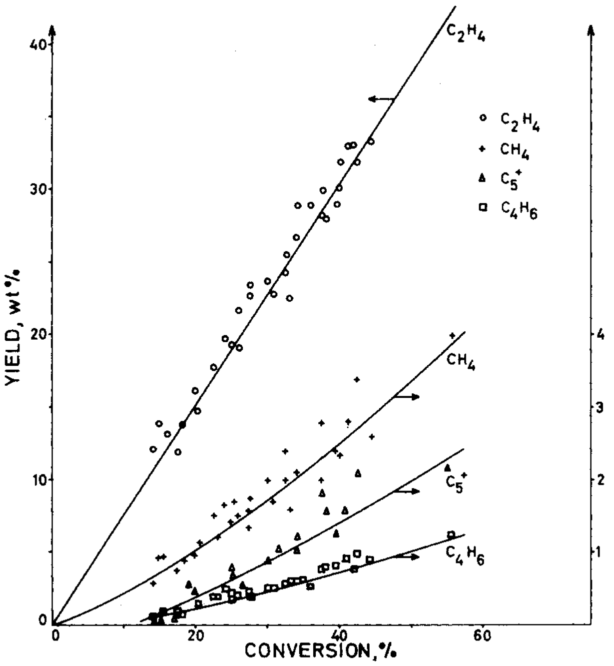

Figure 2. Product distribution of major components for ethane cracking in a completely mixed reactor.

Typical conversion vs. V_E/F_o-curves are shown in Figure 1. The reactor was isothermal, but each individual experimental temperature was corrected to a certain reference temperature to allow a number of curves to be drawn in Figure 1. The equivalent reactor volume concept was discussed in detail by Van Damme et al. (1975). In the calculation of the kinetic parameters the actual temperature and space time were used, however. Figure 2 shows the distribution of major products as a

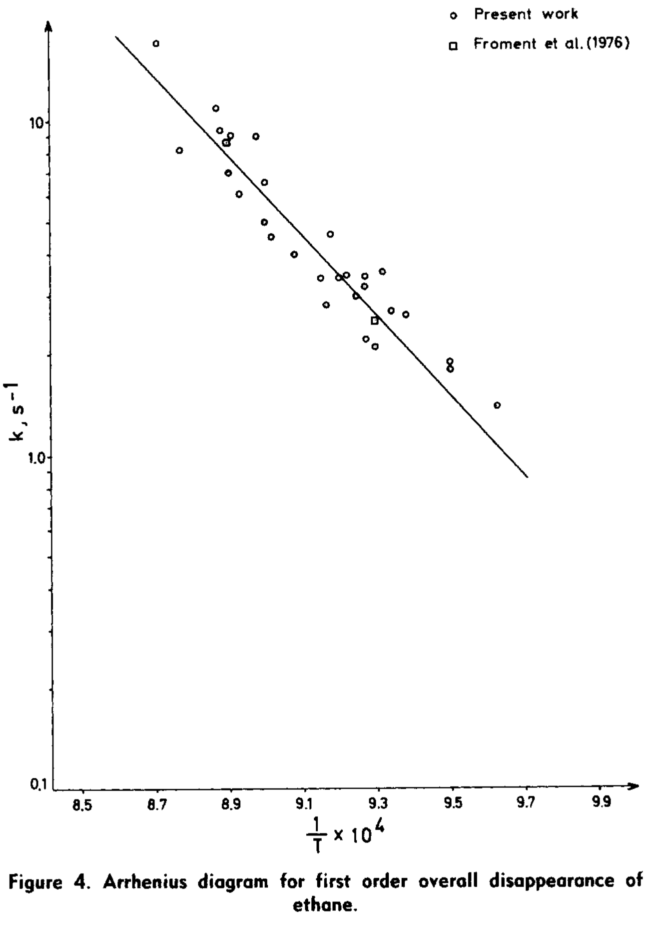

Figure 4. Arrhenius diagram for first order overall disappearance of ethane.

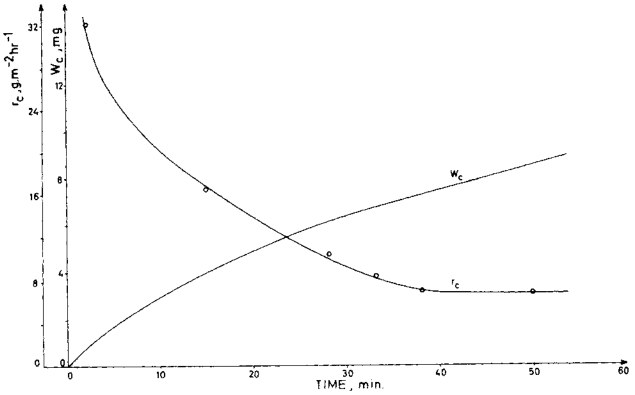

Figure 5. Rate of coke formation and coke content on cylinder as a function of time.

TABLE 1. COKING MECHANISMS

Parallel mechanism
Model I

1. $C_2H_6 \xrightarrow{k_1}$ products
2. $C_2H_6 \xrightarrow{k_2}$ coke

Consecutive mechanisms
Model II

1. $C_2H_6 \xrightarrow{k_1}$ products
3. $C_2H_4 \xrightarrow{k_3}$ coke

Model III

1. $C_2H_6 \xrightarrow{k_1}$ products
2. $C_4^+ \xrightarrow{k_4}$ coke

function of conversion. In such a plot the curves for the different products are independent of temperature.

Of course, the product distribution does not completely agree with that obtained in a plug flow tubular reactor (Froment et al., 1976). A series of experiments was performed with the purpose of finding out whether there is any change with time in the product distribution or not. Such a variation could reflect surface effects. Figure 3 shows typical experimental results. There is no clear cut trend in the overall conversion, but the ethylene and methane yields clearly increase with time to reach asymptotic values after some twenty minutes or specific throughputs ($\Sigma F/V_E$) of the order of 30 moles of hydrocarbon per liter reactor. A similar trend has been reported by Dunkleman and Albright (1976).

KINETICS OF ETHANE CRACKING

The rate equation for the global disappearance of ethane can be written:

$$r = k\left[\frac{C_o(1-x)}{1+x+\delta}\right]^n \tag{1}$$

where r is obtained from the continuity equation for ethane in a completely mixed reactor. The expansion factor, defined as moles produced per mole of ethane cracked, is thereby taken to be two (Froment et al., 1976). The parameters in Eq. 1 were estimated by minimizing the residual sum of squares of the conversion using a Marquardt routine. The order was found to be one, the activation energy 225.8 kJ/mol (54.01 kcal/mol) and the pre-exponential factor $2.51.10^{11}s^{-1}$. These values lead to a k of $2.50s^{-1}$ at 800 and $7.75s^{-1}$ at 850°C as compared with 2.47 and 8.77 obtained by Froment et al. (1976) from experimentation in a tubular pilot reactor. The agreement is remarkable. The Arrhenius-plot for the first order k is given in Figure 4.

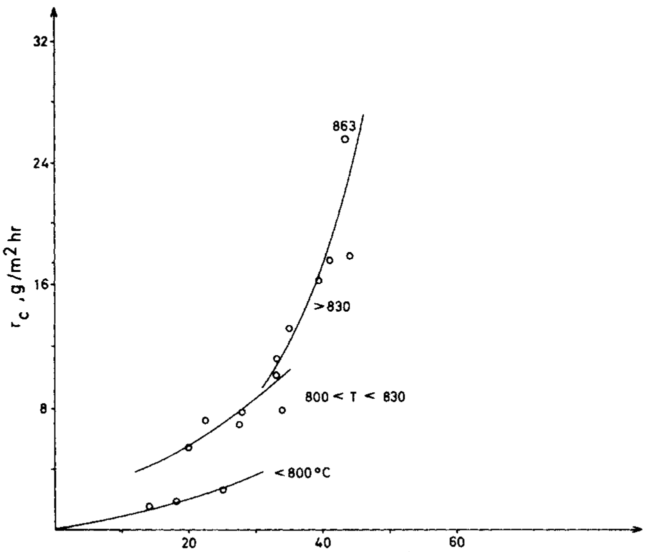

Figure 6. Asymptotic coking rate vs. ethane conversion.

KINETICS OF COKING

Representative curves of coke deposited on the cylinder and of coking rate vs time are shown in Figure 5. The coking rate is high in the beginning, but rapidly decreases to an asymptotic value. The coking rates plotted vs the ethane conversion for various temperatures in Figure 6 are asymptotic values. The high initial values of the coking rate which coincide with the unusual initial values of the yields in the ethylene and methane represented in Figure 3 probably result from wall effects. Once the active sites of the wall are covered by coke a constant rate is observed. It is not clear yet if at this stage only gas phase coking occurs or if gas phase components and already deposited coke precursors are involved. A similar phenomenon has been observed recently by Shah in n.octane cracking (Shah et al., 1976), by Lobo and Trimm (1973), and by Dunkleman and Albright (1976). Its importance should not be over-emphasized. The addition of sulfur components drastically reduces the initial coking rates, as observed also by Shah et al. (1976).

Due to the complexity and still speculative character of coking mechanisms only overall and simplified models, listed in Table 1 were investigated. For the parallel coking mechanism of Model I the coking rate equation would be:

$$r_c = k_2 \frac{1-x}{1+\delta+x}\,\frac{p_t}{RT} \tag{2}$$

where r_c is the coking rate per unit area, derived from the weight change and area of the cylinder suspended at the arm of the electrobalance.

The estimates of the model parameters are given in Table 2. Discrimination between the models by statistical tests was not possible. The activation energy for the parallel coking of Model I is not plausible, however. Preference was given to Model III (coking from C_4^+) since the corresponding residual sum of squares on the rates was lower than that of Model II, but also than Model I. The major components in the C_4^+ fraction are butadiene and benzene. Both are known to be coke precursors (Kinney and Delbel, 1954; Sakai et al., 1970).

SIMULATION OF INDUSTRIAL OPERATION

The set of continuity equations, the energy and pressure drop equation and the coking rate equation required for this simulation are as follows:

TABLE 2. PARAMETER ESTIMATES FOR VARIOUS COKING MODELS

Rate Coefficient	Pre-Exponential Factor (g.coke/(m^{2}s)/(kmol i/m^3)	't' Value	Activation Energy kJ/mol	Activation Energy kcal/mol	't' Value
k_1	$2.51 \times 10^{11*}$	26.9	225.8	54.01	14.8
k_2	1.81×10^{15}	10.7	321.6	76.93	8.8
k_3	1.93×10^{10}	12.0	208.6	49.91	6.3
k_4	$8.55 \times 10^{5**}$	13.4	118.1	28.25	3.9

* Homogeneous, units, s^{-1}.

** Units, g.coke/(m^{2}s)/(kg i/m^3).

$$\frac{dF_j}{dz} = -\Sigma(s_{ij}r_i)\frac{\pi d_t^2}{4} \tag{3}$$

$$\frac{dT}{dz} = \frac{1}{\Sigma F_j C_{p_j}}\left[Q(z)\pi d_t + \frac{\pi d_t^2}{4} r_i(-\Delta H)_i\right] \tag{4}$$

$$\frac{dp_t}{dz} = \frac{\dfrac{d}{dz}\left(\dfrac{1}{M_m}\right) + \dfrac{1}{M_m}\left(\dfrac{1}{T}\dfrac{dT}{dz} + Fr\right)}{\dfrac{1}{M_m p_t} - \dfrac{p_t}{\alpha G^2 RT}} \tag{5}$$

$$\frac{\partial c}{\partial t} = r_c \tag{6}$$

where $Fr = \dfrac{2f}{d_t}$ in the straight portions of the coil and

$$= \left(\frac{2f}{d_t}\right) + \left(0.051 + 0.19\frac{d_t}{R_b}\right)\frac{1.4}{R_b} \text{ in the bends.}$$

Since the coking is slow, quasi steady state conditions may be assumed so that the continuity, energy and pressure drop equations reduce to ordinary differential equations.

The reaction scheme used for the main reactions is that derived by Sundaram and Froment (1977) from the pilot plant results of Froment et al. (1976) by means of a regression-approach. Two reactions accounting for the decomposition of the propane present in the feed were added: $C_3H_8 \rightarrow C_2H_4 + CH_4$, with $A = 0.469.10^{11} s^{-1}$ and $E = 212.5$ kJ/mol (50.60 kcal/mol) and $C_3H_8 \rightleftarrows C_3H_6 + H_2$ with $A = 0.589.10^{11} s^{-1}$ and $E = 214.4$ kJ/mol (51.29 kcal/mol).

Consecutive coking based on Model III was adopted. The total number of continuity equations amounted to 8. The details of the reactor are given in Table 3. Further details concerning the simulation can be found in the paper on coking in propane cracking (Sundaram and Froment, 1979). Initial conversion, heat flux, gas temperature and pressure profiles are shown in Figure 7. The heat flux profile based on internal area corresponding to the clean external tube wall temperature given in Figure 10 was calculated from the correlation proposed by Sundaram and Froment (1980) and derived from two dimen-

TABLE 3. CHARACTERISTICS OF AN INDUSTRIAL REACTOR FOR ETHANE CRACKING

Length	= 88.252 m
Diameter	= 0.108 m
Length of the bend	= 0.479 m
Radius of the bend	= 0.153 m
Wall thickness	= 0.008 m
Inlet temperature	= 652°C
Outlet temperature	= 830°C
Inlet pressure (clean)	= 2.9 bar
Outlet pressure (clean)	= 1.53 bar
Ethane flow rate	= 66.474 kmol/h
Dilution factor	= 0.51 kg/kg

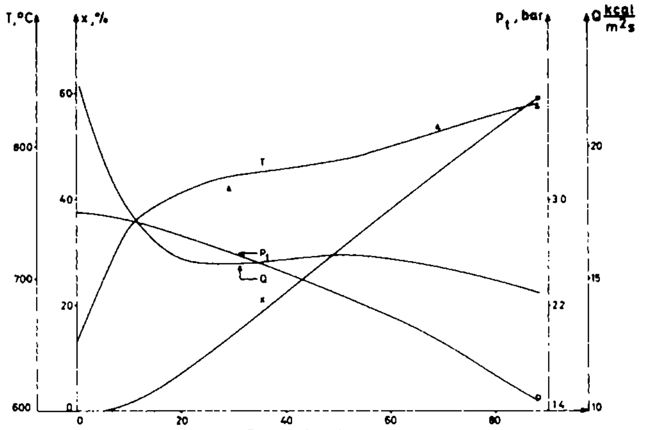

Figure 7. Conversion, heat flux, gas temperature and pressure profiles for industrial cracking of ethane under clean tube conditions (base run). Lines, simulated; points, industrial values.

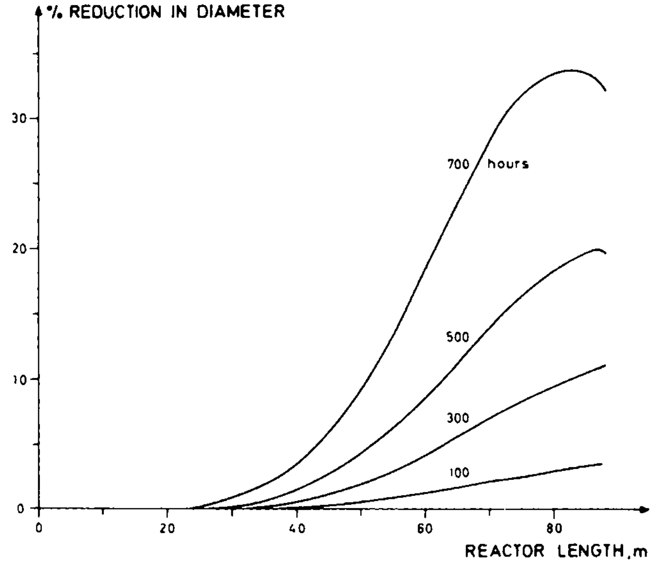

Figure 8. Coke profiles in an industrial reactor, Model III for coking (base run).

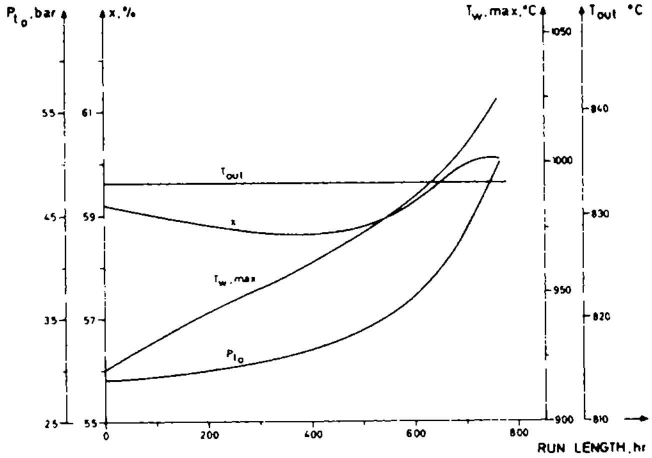

Figure 9. Maximum external tube wall temperature, outlet gas temperature, conversion and inlet pressure as a function of run length.

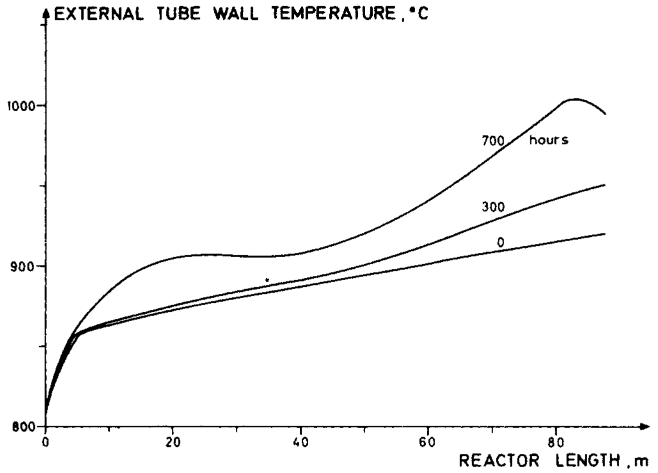

Figure 10. Evolution of external tube wall temperature as a function of run length (base run).

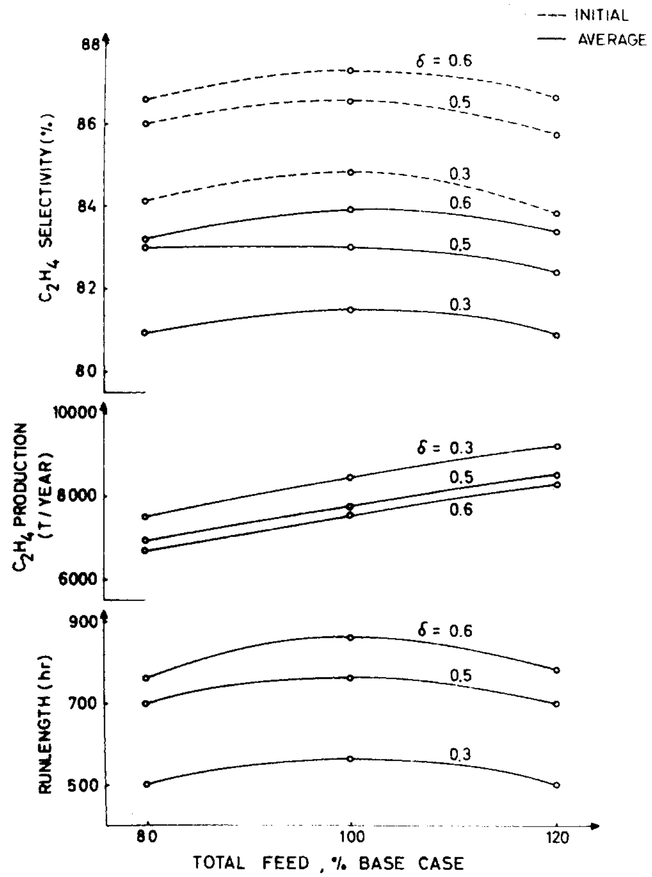

Figure 11. Simulation of industrial operation. Ethylene selectivity, ethylene production and run length as a function of the total feed rate.

sional simulations of this reactor, i.e., accounting for both radial and axial temperature (and concentration) gradients.

To account for the effect of averaging the reaction rate over a cross section the heat transfer coefficient is further multiplied by a factor 1.02 (Sundaram and Froment, 1980). The profiles of Figure 7 are therefore very close to the cross sectional averages that could be derived from the more detailed two dimensional model. When coking is accounted for, a policy for the operation of the reactor has to be adopted. The initial gas temperature profile was maintained for the complete run length, so that the heat flux had to be continuously adapted. Further, the outlet pressure was kept constant, to satisfy downstream requirements, so that the inlet pressure varied with time. The rate determining step of the coke formation was considered to occur at the gas phase temperature, although this does not necessarily imply true gas phase coking.

The asymptotic coking rate Eq. 2 was used, since the initial period is very short when compared to the total run length. Decoking was considered necessary as soon as one of the following criteria was satisfied:

1) External tube skin temperatures exceeding 1030°C
2) Inlet pressures exceeding 7 bar

In the case simulated here, the tube skin temperature of 1030°C was exceeded after 760 hours or 32 days.

Figure 8 shows the reduction in tube diameter resulting from the coke deposition. Figure 9 shows the evolution of the maximum external tube wall temperature, the conversion and the inlet pressure and Figure 10 the evolution of the tube skin temperature with time. Up to some 320 hours the coke layer is maximum at the exit of the reactor for the consecutive coking model and with the heat flux profiles selected here. For run lengths exceeding 320 hours the maximum slightly shifts upstream, however. This is caused by the effect of the decreasing total pressure: the concentration of C_4^+ strongly drops near the exit of the coil although the yield of C_4^+ still increases. The thickness of the coke layer at the exit would be of the order of 1.8 cm after 760 hours. Such layers have been observed in practice.

Up to a length of 20 m there is practically no coke lay down. Nevertheless beyond 450 hours the external tube skin temperature has to be raised in that zone too, mainly to compensate for the relatively high reaction rate resulting from the rapidly increasing inlet pressure.

The initial heat flux at the inlet is 87.9 kJ/m²s (21kcal/m²s), and at the outlet: 58.6 kJ/m²s (14 kcal/m²s). Initially, the difference in tube skin and gas temperature at the coil outlet amounts

TABLE 4. SIMULATION RESULTS FOR AN ETHANE CRACKER FOR VARIOUS FEED CONDITIONS. INLET TEMP.: 652°C.

Nr.	Total flow rate of base run %	Dilution kg/kg	$(p_{t_0})_i$ bar	T_e °C	p_{t_e} bar	Initial conv. %	p_{t_0} shut down bar	Run length hours	Total H.C.feed tons/cycle	C_2H_4 tons/ cycle	C_2H_6 out tons/ cycle	Nr. of cycles/ year	C_2H_4 tons/ year	av. C_2H_4 yield wt %	av.molar C_2H_4 select. %	init. molar C_2H_4 select. %
1	100	0.5	2.9	833	1.48	59.2	5.0	760	1520	695.1	622.3	11.173	7766	45.73	82.96	86.51
2	120	0.5	3.4	827	1.72	54.3	5.37	700	1680	701.7	767.3	12.099	8490	41.77	82.37	85.74
3	80	0.5	2.48	842	1.41	67.1	4.58	700	1120	573.7	379.7	12.099	6941	51.22	83.0	85.99
4	100	0.6	2.9	835	1.45	59.9	5.52	860	1627	763.2	652.3	9.910	7563	46.90	83.88	87.27
5	120	0.6	3.4	828	1.68	55.0	5.35	780	1770	759.3	795.0	10.896	8273	42.89	83.41	86.57
6	80	0.6	2.49	844	1.41	68.1	5.07	760	1150	600.2	377.4	11.173	6706	52.18	83.20	86.58
7	100	0.3	2.85	830	1.48	56.8	4.46	560	1304	561.5	565.9	15.0	8422	43.06	81.51	84.77
8	120	0.3	3.35	823	1.73	52.2	4.7	500	1397	548.7	669.8	16.718	9173	39.28	80.84	83.80
9	80	0.3	2.45	838	1.42	64.6	4.02	500	931	447.8	338.8	16.718	7486	48.08	80.96	84.10

to 88°C but after 760 hours, when the maximum tube skin temperature is 1030°C, the difference is some 180°C. Seen over the run length of 760 hours the tube skin temperature in the maximum rises by some 3.3°C/day. Again, a tube skin temperature rise averaging 3.3°C/day is of the order of magnitude of that experienced in industrial operation. Initially the temperature rise amounts to some 2.1°C/day but close to shut down to 6°C/day. The latter value reflects the rapid rise of the coke layer thickness close to the end of the run.

Another interesting observation is the variation in exit conversion with time. The decline in conversion observed up to 350 hours is caused by the reduction in tube diameter. Beyond 350 hours, however, the effect of the reduction in volume is more than compensated for by the increase in residence time caused by the rise in pressure in early sections of the coil. The yield pattern at the exit will, of course, also vary with time, but not only because of the variation of conversion, but in addition because of the effect of pressure and residence time.

OPTIMIZATION OF OPERATING CONDITIONS

Very little has been done on optimizing the operating conditions of a cracker accounting for the constraints imposed by the coking. Jackman and Aris (1968) applied a systematic approach based upon Pontryagin's maximum principle but the model was too simple and incomplete to be realistic. Yet, the calculations were extremely laborious and lengthy. Robertson and Hanesian (1975) assumed a number of gas temperature profiles, selected an optimum one, maintained it during the whole cycle and took the inlet pressure as the controlling variable for the run length. In the present paper a few simulations were carried out to determine the influence of the feed rate and steam dilution on the run length. The conditions are shown in Table 4. Run nr. 1 is the base run.

For all cases the inlet temperature was kept constant at 652°C. The choice of this temperature is not very critical for the purpose of this study. The temperature profiles for the runs with 120 and 80% of the feed rate of the base run were adapted to achieve an initial ethylene yield that differed by less than 10% of the base run. The exit pressure was kept constant to satisfy the requirements of the downstream equipment. The inlet pressure was raised accordingly. The criterion used to determine the run length was the external tube wall temperature which was not allowed to exceed 1030°C.

The coke deposition and the run length are seen to depend strongly on the steam dilution.

In calculating the number of cycles the time required for decoking was taken to be 24 hours. It can be seen from Figure 11 that the yearly ethylene production is highest with the highest flow rate. This is not necessarily the optimum way of operating the furnace: the selectivity is an important factor in the optimization. Evidently, high dilution favors the ethylene selectivity. A choice between high production and high selectivity strongly depends upon feedstock prices. Fig. 11 and table 4 provide the basic information for such a choice.

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NOTATION

C = concentration of ethane, kmol/m^3
C_c = coke content, g/m^2
C_o = initial concentration of ethane, kmol/m^3
C_{pj} = specific heat of j-th component, kJ/kmolK
d_t = tube diameter, m
f = friction factor
F_o = initial molar flow rate of hydrocarbons, kmol/s
F_j = molar flow rate of j-th component, kmol/s
G = total mass flow rate, kg/m^{2}s
ΔH = heat of reaction, kJ/kmol
k = specific reaction rate coefficient, s^{-1} or g.coke/(m^{2}s)(kmol/m^3)
M_m = mean molecular weight, kg/kmol
n = reaction order
p_t = total pressure, bar
p_{t_o} = inlet pressure, bar
Q = heat flux, kJ/m^{2}s or kcal/m^{2}s
r = reaction rate, kmol/m^{3}s
r_c = rate of coking, g/m^{2}h or g/m^{2}s
R = gas constant, bar m^3/kmolK or kJ/kmolK
R_b = radius of the bend, m
Re = Reynolds number
s_{ij} = stoichiometric coefficient of j-th component in i-th reaction
T = temperature of the fluid, °C or K
T_e = exit gas temperature, °C
T_w = external tube wall temperature, °C
V_E = equivalent reactor volume, L or m^3
x = ethane conversion, %
W_c = weight of coke deposited on cylinder, mg
z = reactor length coordinate, m
α = conversion factor kg$_f$/m^2 to bar
δ = dilution factor mol/mol

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